# Alkylation of 1-Butene with Isobutane using EMT and Y Zeolites

by

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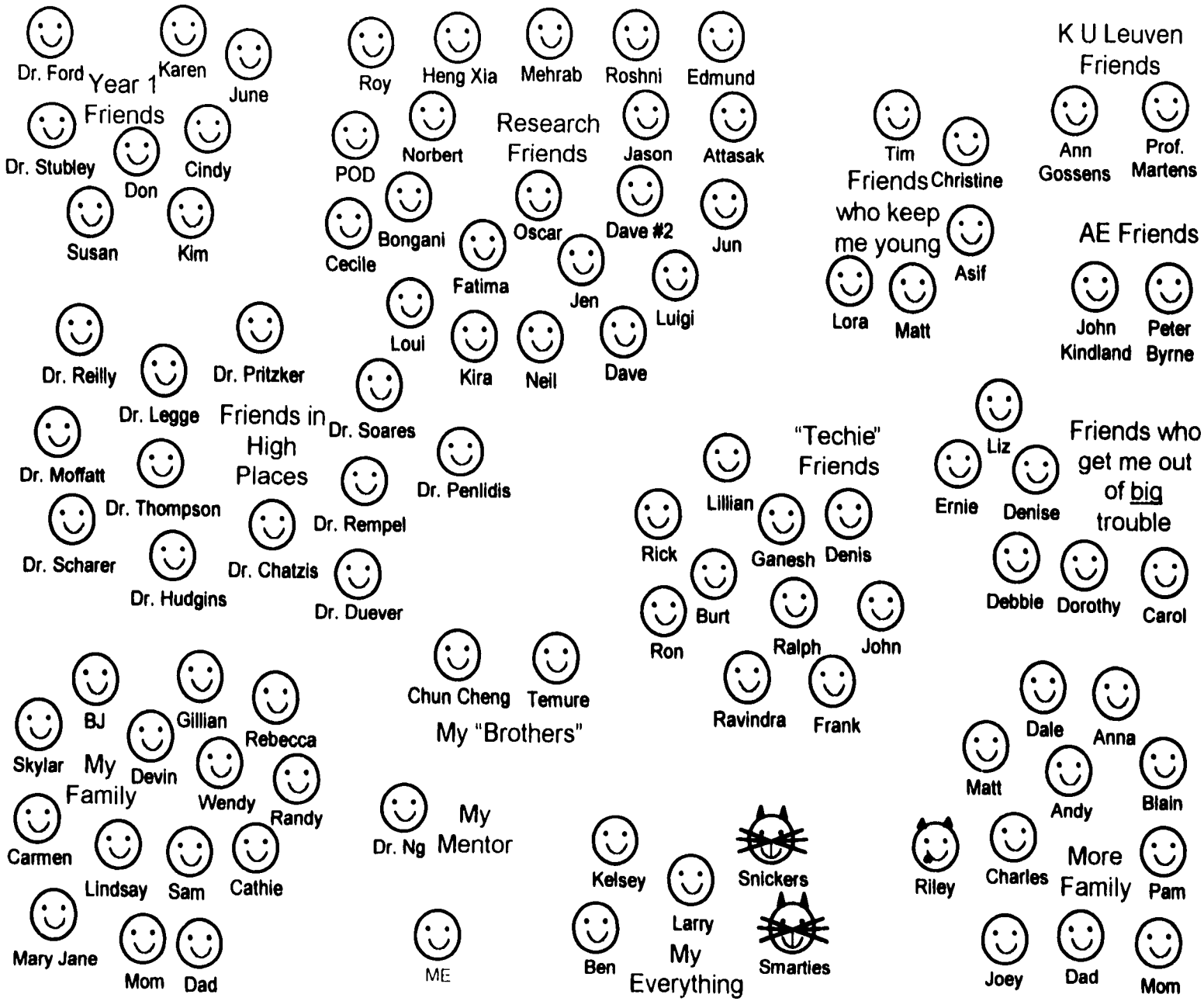
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My Everything
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More Family
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Dad
Mom

## Dedication

I dedicate this thesis to working mothers.

## Abstract

### Alkylation of 1-Butene with Isobutane using EMT and Y Zeolites

Alkylate is the preferred blending stock of reformulated gasoline as it is clean burning, producing less emissions, and possesses high energy and octane. Commercial liquid catalysts employed for the alkylation of butene with isobutane pose significant environmental hazards. Many solid acids have been investigated towards this reaction, but none have reached commercial success. Although high initial activity is demonstrated, rapid deactivation ensues, primarily due to a loss in hydride transfer functioning.

The preferential adsorption of the olefin relative to the isoparaffin makes deactivation an inevitable outcome. The catalyst surface selectively adsorbs butene from the feed, regardless of the feed composition. Eventually the surface acid sites become saturated with oligomers of butene. Pulse feed delivery, with interim isobutane flush periods, can restore deactivated catalysts to fresh state levels. It is possible that catalytic distillation may hold some promise for this challenging reaction, if a suitable solid acid catalyst can be found.

The zeolite, EMT, is a hexagonal phase faujasite synthesized in the presence of a crown-ether template. Literature measurements for pyridine desorption conclude that this zeolite possesses primarily Bronsted acidity, with significant amounts of strong acid sites. These properties are ideally suited to promote efficient hydride transfer in the alkylation of butene with isobutane.

The catalyst, EMT, demonstrated superior performance relative to Y zeolite, improving the Useful Catalyst Lifetime period (butene conversion maintained above 80%) by 41%. Approximately half of the alkyate produced was composed of $C_8$ compounds, of which roughly 60 to 80 % were trimethylpentanes (TMPs). The most valuable octane isomer, 2,2,4-TMP, was present in the largest quantities in the

alkylate, accounting for 30 to 60 % of the TMP fraction. It is believed that the uneven distribution of acid sites on EMT discourages deactivation processes. Alternatively, it is also possible that isobutane adsorption capacity on EMT is improved relative to Y.

The impregnation of 0.5 % Pt onto EMT (0.5%Pt/EMT) produced a minor improvement in the Useful Catalyst Lifetime period and alkylate quality (as measured by TMP content). The levels of TMP were notably higher on 0.5%Pt/EMT, accounting for 80% of the $C_8$ fraction. These improvements are attributed to an increase in the concentration of reactive hydrogen, possibly hydrogen spillover, in the vicinity of the acid site, which enhances the desorption rate of TMP isomers.

The same loading of Pt impregnated on Y zeolite (0.5%Pt/Y) did not exhibit a notable change on catalyst performance. It is suggested that the reactive hydrogen population was overdeveloped, causing the *tert*-$C_4^+$ carbenium ion population to diminish. This behaviour promoted DMH formation and expedited the onset of deactivation. A fine balance between reactive hydrogen participation and active hydride transfer from isobutane is necessary to favour TMP formation and prolong catalyst lifetime.

The efficacy of regeneration was improved on EMT in the presence of Pt. A significant loss in catalyst activity was noted for regenerated EMT whereas recovery of catalyst activity was almost complete on Pt/EMT systems. The same benefits were not observed on 0.5%Pt/Y. Although alkylate quality was similar for fresh and regenerated Pt/Y systems, the amount of liquid produced per gram of catalyst was reduced. It is possible that excessive involvement of reactive oxygen during recalcination caused the noble metal to sinter on the catalyst surface, reducing Pt dispersion. Regenerated Pt/Y behaved in a similar manner to regenerated Y, with no beneficial effect being demonstrated by Pt.

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# Nomenclature

| | |
|---|---|
| AA | atomic absorption |
| AE | Autoclave Engineers |
| A/H | acid to hydrocarbon ratio |
| ANOVA | analysis of variance method |
| alkylate | $C_5^+$ liquid produced from butene/isobutane alkylation |
| BET | Brunauer-Emmett-Teller method |
| BPR | back pressure regulator |
| CAA | Clean Air Act |
| Ce-Y | Cerium exchanged Y zeolite |
| CE | 18-crown-6 ether template used in EMT synthesis |
| DMH | dimethylhexanes |
| DTA/TGA | differential temperature analysis used in conjunction with thermogravimetric analysis |
| EFAL | extraframework aluminum in zeolite structure |
| EMT | acidic form of hexagonal phase faujasite prepared using 18-crown-6 ether template |
| ESR | electron spin resonance |
| FAU | acidic form of cubic phase faujasite prepared using a 15-crown-5 ether template |
| FCC | fluid catalytic cracking |
| FID | flame ionization detector |
| FTIR | Fourier Transform Infrared Spectroscopy |
| GC | gas chromatography |
| GC-MS | gas chromatography used in conjunction with mass spectroscopy |

| | |
|---|---|
| $H_o$ | Hammett acidity |
| $H_{so}$ | spillover hydrogen |
| H-EMT | acidic form of EMT zeolite |
| HPLC | high pressure liquid pump |
| HTL | heated transfer line |
| H-Y | acidic form of Y zeolite |
| ID | inner diameter |
| i-NNN | i next-nearest alumina neighbours in a zeolite framework where i = 0 to 4 |
| I/O | isoparaffin (isobutane) to olefin (butene) molar ratio in feed stream |
| IR | Infrared spectroscopy |
| LaxEMT | x % of Na are exchanged for La in EMT |
| MFC | mass flow controller |
| MON | motor octane number |
| MSA | mesoporous silica alumina |
| MTBE | methyl tertiary butyl ether |
| Na-EMT | sodium form of EMT zeolite |
| Na-Y | sodium form of Y zeolite |
| NMR | nuclear magnetic reasonance |
| NMRPG | nuclear magnetic reasonance pulse field gradient method |
| PC | personal computer |
| PE | Perkin Elmer |
| PLC | programmable logic controller |
| RE | rare earth metal |
| RE-Y | rare earth metal exchanged Y zeolite |
| RE-USY | rare earth metal exchanged Ultra Stable Y zeolite |
| RFG | reformulated gasoline to meet CAA requirements |
| RON | research octane number |
| RVP | Reid vapour pressure |
| SA | surface area |

| | |
|---|---|
| Si/Al | Silicon to aluminum mole ratio |
| surf | surface |
| TEOS | tetraethylortho silicate |
| TGA | thermogravimetric analysis |
| TMOS | tetramethylortho silicate |
| TMP | trimethylpentane |
| TMP/DMH | trimethylpentane to dimethylhexane mole ratio |
| TOS | time on stream |
| TPD | temperature programmed desorption |
| UCS | unit cell size |
| UHP | ultra high purity |
| USHY | ultrastable HY |
| WHSV | weight hourly space velocity |
| XRD | powder X-ray diffraction |
| Y | acidic form of Y |
| $C_5$+ | hydrocarbons with greater than or equal to 5 carbons in their structure |
| $C_5$-$C_7$ | hydrocarbons with between 5 to 7 carbons in their structure |
| $C_8^=$ | olefins containing 8 carbons in the structure |
| $C_8$ | hydrocarbon with 8 carbons in the structure |
| $C_9$+ | hydrocarbons with greater than or equal to 9 carbons in their structure |
| 0.1 % Pt/EMT | 0.1 % Pt impregnated on H-EMT |
| 0.5 % Pt/EMT | 0.5 % Pt impregnated on H-EMT |
| 0.5 % Pt/Y | 0.5 % Pt impregnated on H-Y |

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# Chapter 1

# Introduction

## 1.1 MERIT OF ALKYLATION RESEARCH

Ground-level ozone, formed by photochemical reactions involving nitrogen oxides and hydrocarbons, is a serious air pollution problem. Automobiles contribute roughly one-third of the total hydrocarbon emissions feeding this problem. The U.S. Clean Air Act (CAA) of 1990, has favoured strict upper limits on the Reid vapour pressure (RVP), as well as the oxygenate, benzene, aromatic and olefin content in

the gasoline pool (Gonzalez, 1992; Rhodes, 1994; Khan & Reynolds, 1996). This has directed a dramatic review of current gasoline composition, in an effort to combat this problem (see Table 1.1). Refineries are being forced to reformulate gasoline composition, to satisfy environmental regulations while still maintaining high efficiency and performance.

**Table 1.1:** CAA Formulation Requirements for RFG

| Gasoline Property | RFG Specification |
|---|---|
| RVP | 7.2 psi max. |
| Oxygen | 2 wt. % min. |
| Benzene | 1 vol. % max. |
| Aromatics | 25 vol. % max. |
| Olefins | 9.9 vol. % max. |
| Sulfur | 500 ppm max. |
| Metals | none |

Aromatics represent a high energy, high octane value fraction of gasoline. Therefore, restrictions in the amounts of aromatics, implies an overall reduction in the octane rating and energy content of the gasoline pool. Oxygenates are a viable blending stock to elevate octane rating; however, they possess the lowest energy content of all components in gasoline (Rhodes, 1994a). In addition, they have not demonstrated a positive effect on ozone formation (Bell et al, 1995). Clearly, they are not the sole answer.

Alkylate, the product of alkylation reactions, is an ideal candidate to resolve this issue. The term "alkylation", encompasses any reaction involving the addition of alkyl groups to an organic molecule, to yield a branched organic product. Highly branched alkanes possess both a high Motor Octane Number (MON) and Research Octane Number (RON). For this reason, alkylate has become the preferred blending stock in reformulated gasoline. Aside from enhancing octane levels, it is clean burning producing less emissions, possesses low volatility and density and contains

no sulfur or aromatics. There are projections that alkylate will eventually comprise 36 % of the reformulated gasoline in the U.S to meet the stringent criteria (Corma & Martinez, 1993). This would require between 10 to 35 % expansion of existing capacity to meet this demand.

Alkylation of butene with isobutane, offers several advantages over other alkylation reactions. Firstly, isooctane, the product of this reaction, has a very high octane rating. Another advantage of alkylation of butene with isobutane, is that the $C_4$ reactants necessary for this reaction, are readily available as a low value Raffinate I (by-product of fluid catalytic cracking (FCC) and steam cracking units) as well as Raffinate II (raffinate from MTBE process).

## 1.2 BUTENE/ISOBUTANE ALKYLATION WITH LIQUID ACIDS

### 1.2.1 Commercial Liquid Acid Catalysts

The two catalysts, which are used commercially for the alkylation of isobutane with $C_3$ to $C_5$ olefins, are sulfuric acid and hydrofluoric acid. In 1994, approximately 212,000 $m^3/d$ of alkylate were produced worldwide from these feedstocks, with roughly 60 % made from HF alkylation units (Sheckler et al, 1994; Rao & Vatcha, 1996).

The mechanisms using each liquid acid are different, with HF demonstrating superior activity for the production of high octane alkylate. Although Hammett acidity measurements indicate that $H_2SO_4$ possesses a higher acid strength than HF (Misono & Okuhara, 1993), the solubility of isobutane in HF is superior. Hydrofluoric acid is better able to facilitate hydride transfer reactions between dissolved isobutane and octyl carbenium ions, resulting in superior alkylate quality. Overall, HF demonstrates higher activity for isoparaffin/olefin alkylation relative to $H_2SO_4$ and is the preferred liquid acid (Corma & Martinez, 1993). In addition, catalyst costs are much lower for

HF processes relative to those involving $H_2SO_4$.

Unfortunately, both catalyst systems pose significant corrosion hazards during transportation, storage and handling. The formation of acidic, sludge-containing spent acid and high molecular weight hydrocarbons, is an unavoidable by-product of the $H_2SO_4$ process. The sludge must be separated and regenerated off site to recycle the acid, incurring additional risk and expense. The residual acidic sludge must be disposed, presenting further environmental concern and cost to the operation.

The high volatility of HF makes it prone to forming mists upon release to the atmosphere, endangering public safety. The modification of HF through the use of less volatile pyridinium-polyhydrogen fluoride (PPHF) has repressed this tendency making HF operation somewhat safer.

Since 1990, there has been substantial pressure to develop a more environmentally friendly catalyst for alkylation of isobutane with normal $C_3$ to $C_4$ olefins. Economic advantages also exist in replacing liquid acid technology. Liquid acid costs account for approximately 30 % of the total catalyst cost in petroleum refining (Corma & Martinez, 1993). In addition, the rate of catalyst consumption for $H_2SO_4$ alkylation processing is two orders of magnitude (by weight) greater than that for catalytic cracking catalysed by zeolites (Corma & Martinez, 1993). Clearly, the potential for economic benefits in replacing liquid acid technology, and the more benign nature of solid acids, encourage further research in this area.

### 1.2.2 Product Distribution from Liquid Acid Catalysed Butene/Isobutane Alkylation

The reaction temperature for $H_2SO_4$ catalysed butene/isobutane alkylation is in the range of 0 to 10°C and employs an I/O ratio (molar ratio of isoparaffin/olefin in feed stream) between 5 to 8. Hydrofluoric acid systems can operate at higher temperatures, in the vicinity of 10 to 40°C, but require higher I/O ratios in the range of

10 to 15.

The principle of partial molal quantities can be used to estimate the octane values of the alkylate produced from both processes (Hutson & Logan, 1975) (see Equation 1-1):

$$\text{Octane Number}_{\text{Alkylate}} = \sum_{i=1}^{n} (\text{Octane Number}_{\text{Pure Cmpt } i}) (\text{Mole Fraction}_{\text{Cmpt } i}) \quad (1\text{-}1)$$

Using pure component octane numbers (see Table 1.2), the octane number of the alkylate can be calculated.

Octane values of alkylate from processes using $H_2SO_4$ or HF, range from 95 to 98 (Corma & Martinez, 1993). In general, butene/isobutane alkylate using $H_2SO_4$, is lower in octane value relative to the product from the HF process. A typical alkylate product distribution from butene/isobutane alkylation using $H_2SO_4$ is shown in Table 1.3.

Trimethylpentanes (TMPs) are the preferred products of alkylation, as they possess a RON $\geq 100$ (see Table 1.2). The isomer, 2,2,4-TMP, is the preferred isomer since it has the highest MON with zero sensitivity (difference between MON and RON). Although other TMP isomers exhibit higher RON values, they also show significantly greater sensitivity levels. Dimethylhexanes (DMH) are secondary products and possess an octane number between 55 and 82. Clearly, maximizing the TMP/DMH ratio is the goal of any alkylation process.

Conjunct polymers are acid-soluble polymers, or red oil, with a molecular weight in the general range of 300 to 500. This high molecular weight material is formed as a minor by-product during the alkylation of isobutane with butene, particularly when $H_2SO_4$ is employed and less so with HF (Albright et al, 1988). Conjuct polymers contain $C_5$ and possibly $C_6$ ring groups and are highly unsaturated, with a hydrogen to carbon ratio of 1.52 to 1.75 (Albright et al, 1993). A small amount of conjunct polymers is desirable in liquid acid catalysed alkylation as they are excellent sources of hydride ions and improve alkylate quality. Excessive levels of

the polymers dilute the strength of the liquid acid reducing its effectiveness. Feed acids typically contain 98 to 99 % acid, with the balance being water. For $H_2SO_4$, spent acids consist of 90 to 92 % acid, 4 to 6 % conjunct polymers and the remainder is water (Albright et al, 1988).

**Table 1.2:** Pure Component Octane Numbers[1]

| Component | | RON[2] | MON[3] | Sensitivity = RON - MON[4] |
|---|---|---|---|---|
| $C_4$ | *i*-$C_4$ | 102.1 | 97.0 | 5.1 |
| | *n*-$C_4$ | 94.0 | 89.1 | 4.9 |
| $C_5$ | *i*-$C_5$ | 93.0 | 89.7 | 3.3 |
| | *n*-$C_5$ | 61.8 | 63.2 | -1.4 |
| $C_6$ | 2,2-DMB | 91.8 | 93.4 | -1.6 |
| | 2,3-DMB | 104.3 | 94.2 | 10.1 |
| | 2-MP | 73.4 | 73.5 | -0.1 |
| | 3-MP | 74.5 | 73.3 | 1.2 |
| | *n*-$C_6$ | 24.8 | 26.0 | -1.2 |
| $C_7$ | 2-MH | 42.4 | 46.4 | -4.0 |
| | 3-MH | 52.0 | 55.0 | -3.0 |
| | 2,2-DMP | 92.8 | 95.6 | -2.8 |
| | 2,3-DMP | 91.1 | 88.5 | 2.6 |
| | 2,4-DMP | 83.1 | 83.8 | -0.7 |
| | 3,3-DMP | 80.8 | 86.6 | -5.8 |
| | 2,2,3-TMB | 112.1 | 101.3 | 10.8 |
| $C_8$ | 2-MHp | 21.7 | 23.8 | -2.1 |
| | 3-MHp | 26.8 | 35.0 | -8.2 |
| | 2,2-DMH | 72.0 | 77.0 | -5.0 |
| | 2,3-DMH | 71.3 | 78.9 | -7.6 |
| | 2,4-DMH | 65.2 | 69.9 | -4.7 |
| | 2,5-DMH | 55.5 | 55.7 | -0.2 |
| | 3,4-DMH | 76.3 | 81.7 | -5.4 |
| | 2,2,3-TMP | 109.6 | 99.9 | 9.7 |
| | 2,2,4-TMP | 100.0 | 100.0 | 0.0 |
| | 2,3,3-TMP | 106.1 | 99.4 | 6.7 |
| | 2,3,4-TMP | 102.7 | 95.9 | 6.8 |
| $C_9$ | 2,2,5-TMH | 91.0 | 88.0 | 3.0 |

1 Hutson & Logan, 1975; Chauvin et al, 1994; Olah et al, 1996
2 RON is a measure of highway performance of fuel
3 MON is a measure of city performance of fuel
4 Sensitivity is difference between highway and city performance of fuel

**Table 1.3:** Typical Product Distribution from *n*-Butene/Isobutane Alkylation using $H_2SO_4$ Catalyst[1]

| | |
|---|---|
| *$C_5^+$ Liquid (mol %)* | |
| $C_5$ - $C_7$ | 7.5 |
| $C_8$ | 88.1 |
| $C_9^+$ | 4.4 |
| *$C_8$ Fraction (mol %)* | |
| TMP | 90.8 |
| DMH | 9.2 |
| *Indicators* | |
| TMP / DMH | 9.9 |
| RON | 97.8 |
| MON | 93.9 |
| (RON + MON) / 2 | 95.9 |

1 Albright et al. 1992; Corma & Martinez, 1993

## 1.3 MAJOR PROCESS LICENSORS ENGAGED IN SOLID ACID CATALYSED BUTENE/ISOBUTANE ALKYLATION RESEARCH

Many companies are actively engaged in the development of an alternative catalyst for alkylation of isobutane with butene. The success of zeolites in catalytic cracking, created interest in applying them for isoparaffin-olefin alkylation reactions. Zeolites display high initial activity but deactivate rapidly. To date, no technology has reached commercial success (Rotman, 1996).

The Exxon / Haldor Topsoe A/S /Kellog process uses fixed-bed technology (Rhodes, 1994b), and a catalyst consisting of liquid trifluoromethane sulfonic acid supported on a solid silica medium (Crossland, 1993). The paraffin-olefin mixture is passed through the catalyst bed and the flow reversed when acid is detected in the product stream. The process has been tested at a 0.5 b/d pilot plant starting in 1991 (Rhodes, 1994a; Rotman, 1996). Existing reactor systems would have to be replaced

to employ this technology.

The catalyst technology used in the Kerr-McGee (HAT Process) system is a very low concentration of hydrocarbon-soluble alkylaluminum chloride (Crossland, 1993; Rhodes, 1994b). The catalyst is first mixed with the isobutane and then mixed with the olefin stream. As the reaction nears completion, the catalyst degrades to a less active form and precipitates out of solution. The spent catalyst is gravity-separated and regenerated. The HAT process has lower operating costs than those using $H_2SO_4$ and offers the advantage of retrofit capabilities with existing HF units.

The catalyst technology for the Catalytica / Neste / Conoco process involves a solid and inexpensive catalyst incorporating $BF_3$ on an ETA/Gamma alumina or zirconium carrier (Crossland, 1993; Rhodes, 1994b). The 7 b/d pilot plant unit has experienced difficulties in keeping the acid on the carrier. Although a slight financial advantage over $H_2SO_4$ technology has been demonstrated, the margin is not sufficient to justify implementation of the new technology. This group is currently looking for additional partners to continue the program (Rotman, 1996).

Chemical Research & Licensing Co. (CR & L) / Chevron / Sheridan have developed technology which uses a slurry catalyst, involving an organometallic "salt" of $SbF_5$ supported on a $SiO_2$ carrier (Rhodes, 1994a; Rotman, 1996). A refinery pilot plant running at 10 b/d, has been in operation since 1993, using temperatures in the range of $H_2SO_4$ systems.

Several other groups are pursuing research in alkylation, but details are not as readily available (Crossland, 1993). Mobil Oil is exploring catalysts of the type $BF_3 \cdot H_3PO_4$, $BF_3 \cdot SiO_2$ or $BF_3$ supported on β-zeolite. Institute Français du Pétrole (IFP) is applying fluorine modified zeolite. UOP is examining carbon supported HF and several zeolites.

## 1.4 PROPOSED BUTENE/ISOBUTANE ALKYLATION REACTION MECHANISM ON SOLID ACIDS

### 1.4.1. Traditional Mechanism via Carbenium Ions

It is generally accepted that isoparaffin-olefin alkylation proceeds via a carbenium ion mechanism, in the presence of a liquid acid catalyst. Although it is assumed that the same type of mechanism proceeds on a heterogeneous catalyst, no direct evidence has been show to support this theory.

The mechanism for the alkylation of 1-$C_4^=$ with *i*-$C_4$ will be described (Corma et al, 1993). Isomerization of 1-$C_4^=$ is rapidly facilitated on fresh and aged Y zeolites (see Table 1.4), with 2-$C_4^=$ being the preferred isomer (Chu & Chester, 1986).

**Table 1.4**: Comparison of 1-Butene Isomerization on REHY[1] with Thermal Equilibrium Composition
(semi-batch reactor; $T_{calc}$=538°C; $T_{rxn}$=91°C; P=320psig; $C_4^=$ WHSV=7.2$h^{-1}$; I/O=9)

| Butene Isomer | REHY @ 90°C (Experimentally Determined) | | Thermal Equilibrium @ 90°C |
|---|---|---|---|
| | Fresh | Aged | |
| 1-$C_4^=$ | 22 | 15 | 1.9 |
| *trans*-2-$C_4^=$ | 48 | 58 | 10.7 |
| *cis*-2-$C_4^=$ | 30 | 27 | 10.3 |
| *i*-$C_4^=$ | N.D. | N.D. | 77.1 |

1 Chu & Chester, 1986
N.D. = not detected

Although the formation of *i*-$C_4^=$ is highly favoured thermodynamically, based on calculations using $\Delta H_f°$ and $\Delta S_f°$ data (Reid, Prausnitz & Sherwood, 1977), it is rarely detected in alkylation reactor effluents. This is believed to be a consequence of its highly reactive nature.

### *1.4.1.1 Protonation of the olefin to form sec-$C_4^+$ ion*

The first step of the mechanism is the protonation of the olefin ($C_nH_{2n}$), by a Bronsted acid site ($H^+_{(surf)}$), to form a secondary butyl carbenium ion (note that *sec*-$C_nH_{(2n+1)}^+{}_{(surf)}$ = *sec*-$C_4^+{}_{(surf)}$) (see Equation 1-2).

$$C{=}C-C-C \quad + \quad H^+_{(surf)} \longrightarrow \quad C-C^+-C-C_{(surf)} \qquad (1\text{-}2)$$

This initiation step is highly important in the early stages of the reaction, in order to generate high surface concentration of ions.

### *1.4.1.2 Formation of tert-$C_4^+$ ion*

Isomerization of primary and secondary-butyl carbenium ions, via hydride and methyl shifts, are not highly favoured, as they are short chain carbocations. Rather, a more likely event is hydride transfer from an adsorbed molecule of isobutane, to form a more stable, tertiary butyl carbenium ion (*tert*-$C_4^+$) and *n*-butane (see Equation 1-3).

$$C-C^+-C-C_{(surf)} + C-\underset{\displaystyle C}{\overset{\displaystyle |}{C}}-C \longrightarrow C-C-C-C + C-\underset{\displaystyle C}{\overset{\displaystyle |}{C^+}}-C_{(surf)} \qquad (1\text{-}3)$$

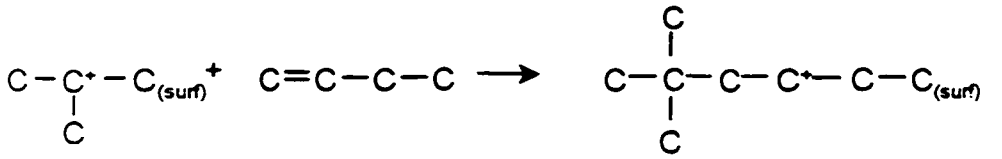
Hydride transfer to secondary carbenium ions (*sec*-$R^+$) is very slow and therefore, an induction period is often observed until a high concentration of *tert*-$C_4^+$ has been generated (Corma & Martinez, 1993). At longer reaction times, regeneration of the *tert*-$C_4^+$ is facilitated in the last stage of the chain sequence.

Another possible route of *tert*-$C_4^+$ formation, involves hydride transfer from isobutane to an adsorbed tertiary carbenium ion (*tert*-$R^+$) since hydride transfer to *tert*-$R^+$ is faster than to *sec*-$R^+$ (Cardona et al, 1995) (see Equation 1-4):

$$tert\text{-}R^+_{(surf)} + i\text{-}C_4 \longrightarrow R + tert\text{-}C_4^+{}_{(surf)} \qquad (1\text{-}4)$$

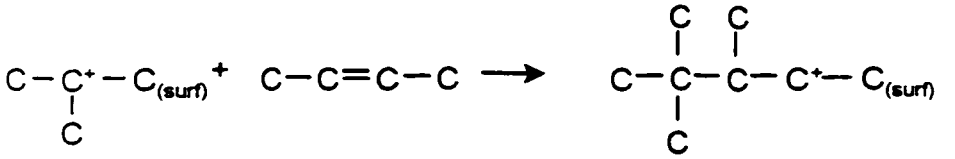
### *1.4.1.3 Addition of tert-$C_4^+$ ion to second olefin*

The *tert*-$C_4^+$ combines with a second butene molecule to form the corresponding $C_8$ carbenium ion (see Equation 1-5).

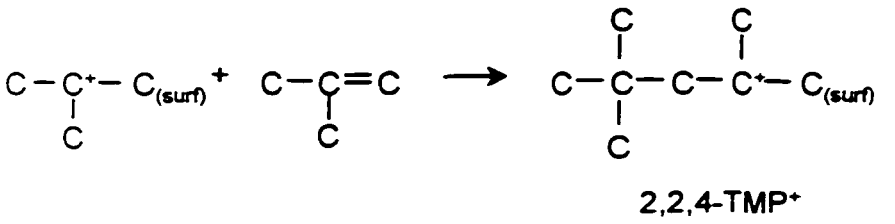


2,2-DMH$^+$ (1-5)

The addition of *tert*-$C_4^+$ to other isomers of butene (see Equations 1-6 and 1-7) are also illustrated, as they will be present due to the rapid isomerization of 1-$C_4^=$ to 2-$C_4^=$ and *i*-$C_4^=$ on solid acid catalysts (Chu & Chester, 1986).



2,2,3-TMP$^+$ (1-6)




(1-7)

### *1.4.1.4 Isomerization of $C_8^+$ ion to more stable forms*

The octyl carbenium ion may undergo rapid isomerization, via hydride and methyl shifts, to form more stable carbenium ions (note that hydride shifts are much faster than methyl shifts). The rearrangements, which are possible for 2,2,3-TMP$^+$, are illustrated in Figure 1.1.

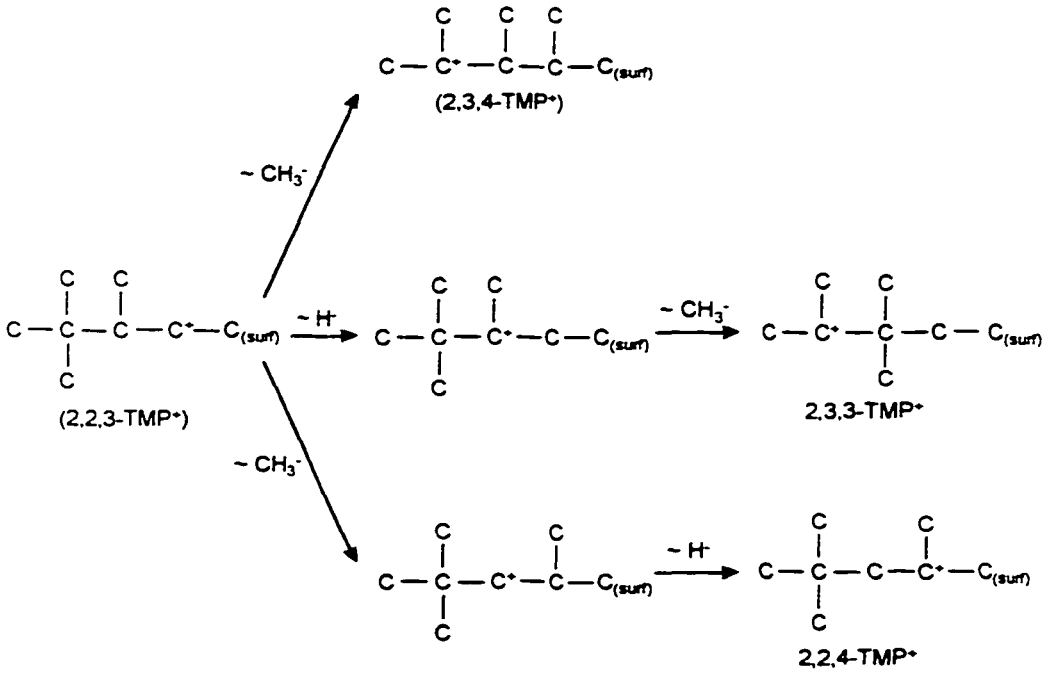
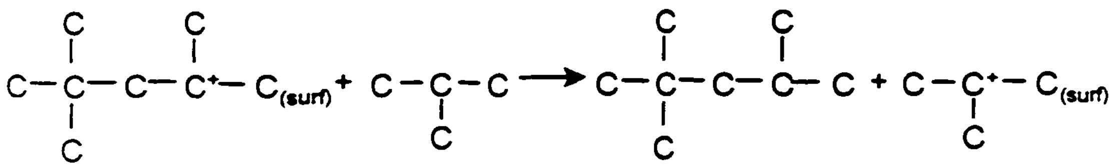



**Figure 1.1**: Isomerization of 2,2,3-TMP$^+$ via Methyl and Hydride Shifts

*1.4.1.5 Hydride transfer to $C_8^+$ ion*

The octyl carbenium ion can undergo hydride transfer from isobutane, yielding the corresponding isoparaffin. In addition, the *tert*-butyl cation is regenerated in this last step thus perpetuating the chain sequence. The reaction involving 2,2,4-TMP$^+$ is shown in Equation 1-8. Relative amounts of *n*-butane and TMPs in the product distribution during the initial stages of the reaction, suggest that the formation of *tert*-butyl cation, via Equation 1-3, is approximately 15 times slower than that produced via Equation 1-8, on Ultrastable HY (USY) (Cardona et al, 1995).


(1-8)

2,2,4-TMP

It is also possible for hydride transfer to be facilitated by a molecule other than isobutane (see Equation 1-9):

$$C_8^+{}_{(surf)} \quad + \quad R \quad \longrightarrow \quad C_8 \quad + \quad R^+{}_{(surf)} \qquad (1\text{-}9)$$

## 1.4.2 Mechanism via Covalent Surface Esters

Recently, it has been suggested that acidic heterogeneous conversion of hydrocarbons is facilitated by the bifunctional character of zeolite catalysts of high Si content, complementing the traditional carbenium ion mechanism. It is proposed that

a Bronsted site transfers a proton to the adsorbed molecule, while simultaneously, a proton is abstracted from the "protonated" species by a surface basic site (Pine et al, 1984; van Santen, 1991).

The driving force of this concerted mechanism is the compensation effect of energy gained from broken bonds, with energy required for those which are newly formed, thus eliminating excessive activation barriers. The adsorbed species can be regarded as a covalently bonded surface ester rather than a carbenium ion (see Figure 1.2). These results were substantiated using quantum mechanical calculations, to determine the geometry and electronic structure of the surface alkoxides in their ground state (Kazansky & Senchenya, 1989).

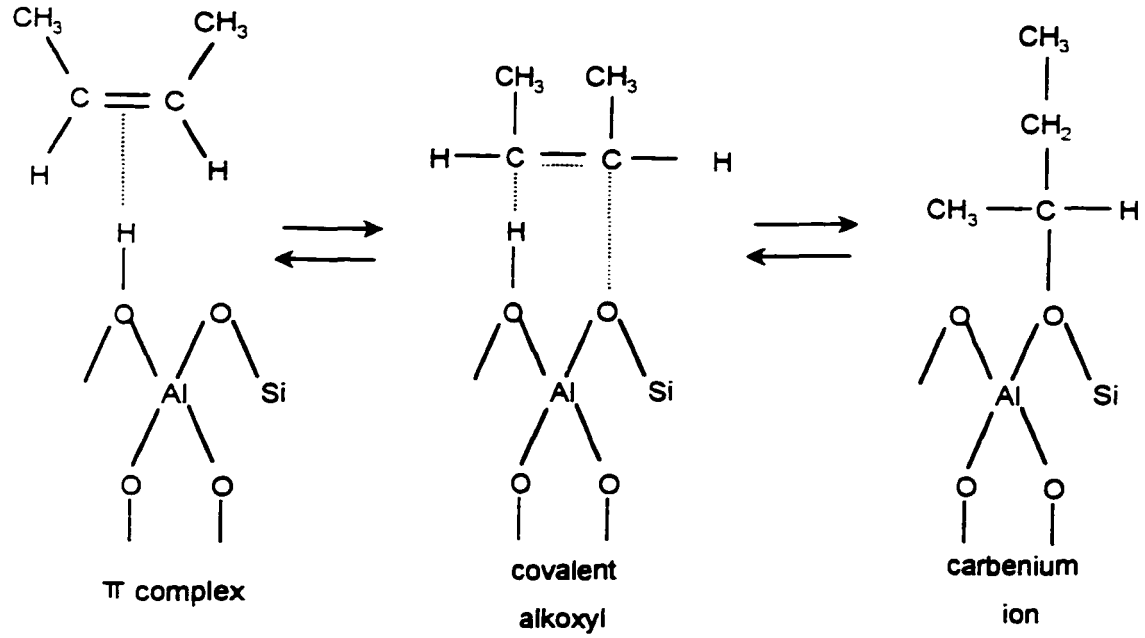



**Figure 1.2**: Proposed States of Butene Adsorption on Heterogeneous Acid Sites, based on Quantum Mechanical Calculations (van Santen, 1991)

Vibrational excitation of the covalent ester causes the C-O bond to stretch. As this bond elongates, the surface alkoxyl groups become structurally more like a carbenium ion (see Figure 1.2). Predicted activation energies for lengthening of the C-O bond, are relatively low. In this way, the covalent alkoxides can behave as a transition state to the formation of a carbenium ion, through elongation of the C-O bond.

In addition to these two adsorption modes, $\pi$ complexes of the olefin to surface OH groups can also result in the formation of a carbenium ion (see Figure 1.2). In this sense, equilibria should exist between the three complex forms, during catalytic reactions of olefins.

The $\pi$ complexes are less stable than covalent alkoxyls (Kazansky & Senchenya, 1989). In contrast, low activation energies are required for proton transfer to an olefin. Hence, chemisorption is highly favourable at low temperatures and acts as the principal source of carbenium ion formation.

At higher temperatures, the $\pi$ complexes decompose more rapidly than surface esters, and therefore, act as the major source for carbenium ion formation. In this fashion, quasicarbenium ion transition states result from two different rate-limiting steps:

- protonation of $\pi$-bonded olefins which dominates at low temperatures
- vibrational excitation of covalent surface esters which becomes the main route of carbenium ion formation at high temperatures

## 1.5 SIDE REACTIONS OF BUTENE/ISOBUTANE ALKYLATION

Unfortunately, alkylation of butene with isobutane is not the only reaction, which occurs under alkylation conditions. Side reactions occur simultaneously, including:

- oligomerization
- polymerization
- disproportionation
- cracking
- self-alkylation

### 1.5.1 Oligomerization

Oligomerization results from desorption of the octyl carbenium ion to form the corresponding $C_8$ olefin, and regenerating the surface acid site (see Equation 1-10).

$$C_8^{+}{}_{(surf)} \longrightarrow C_8^{=} + H^{+}{}_{(surf)} \qquad (1\text{-}10)$$

The preferential adsorption of olefins over paraffins in zeolites with low Si/Al ratio (Corma, Faraldos, et al., 1990), as well as the concentration effect in the small zeolite cavity, favours oligomerization over alkylation for catalysts with high Bronsted acidity.

Oligomerization is also promoted by nickel compounds (sulfates and chlorides are best) supported on oxides (silica, alumina, silica-alumina or zeolites) (Chauvin et al., 1988, Chauvin et al, 1997). In this case, the active site is generally assumed to be a hydride complex of $Ni^{+}$. This reaction, as well as polymerization of butene, are the major side reactions, which proceed under alkylation conditions.

### 1.5.2 Polymerization

Polymerization reactions result from the addition of a second olefin to the octyl carbenium ion (see Equation 1-11).

$$C_8^{+}{}_{(surf)} + C_4^{=} \longrightarrow C_{12}^{+}{}_{(surf)} \xrightarrow{R} C_{12} + R^{+}{}_{(surf)} \qquad (1\text{-}11)$$

Polymerization reactions are promoted by sites of medium acidity which are not sufficiently strong to facilitate the hydride transfer step from an isobutane molecule. Similar to the case of oligomerization, the preferential adsorption of olefins over paraffins, in conjunction with the concentration effect inherent in zeolites, favour polymerization reactions.

### 1.5.3 Disproportionation

Disproportionation is the combination of two molecules of the same type to form two molecules of differing type, one of higher molar mass and the other of lower molar mass (see Equation 1-12).

$$2\ C_8H_{18} \longrightarrow C_7H_{16} + C_9H_{20} \qquad (1\text{-}12)$$

### 1.5.4 Cracking

Larger isoalkyl cations can undergo cracking, yielding smaller isoalkyl cations and olefins (see Equations 1-13 and 1-14)).

$$C_{12}^{+}{}_{(surf)} \longrightarrow C_5, C_6, C_7 \text{ compounds} \qquad (1\text{-}13)$$

$$C_{16}^{+}{}_{(surf)} \longrightarrow C_8 \text{ isomers} \qquad (1\text{-}14)$$

This can lead to the formation of the desired product, isooctane, and is claimed to occur extensively on zeolites (Chu & Chester, 1986). Cracking reactions are favoured by strong acid catalysts and elevated temperatures (Corma et al, 1994b; Corma et Wojciechowski, 1982, Corma et al, 1994a, O'Young et al, 1994; Corma et al, 1996a).

### 1.5.5 Self-Alkylation

Self-alkylation of isobutane involves the alkylation of isobutane with isobutene, which is produced through hydride abstraction from another isobutane molecule. The primary product of the reaction is 2,2,4-TMP (see Equations 1-15, 1-16 and 1-7).

$$i\text{-}C_4 + R^{+}{}_{(surf)} \longrightarrow \text{tert-}C_4^{+}{}_{(surf)} \qquad (1\text{-}15)$$

$$\text{tert-}C_4^{+}{}_{(surf)} \longrightarrow i\text{-}C_4^{=} + H^{+}{}_{(surf)} \qquad (1\text{-}16)$$

$$\text{tert-}C_4^{+}{}_{(surf)} + i\text{-}C_4^{=} \longrightarrow \text{2,2,4-TMP}^{+}{}_{(surf)} \qquad (1\text{-}7)$$

Isobutane self-alkylation has been demonstrated to be of considerable importance in the formation of the preferred isomer 2,2,4 –TMP, using HF and zeolite catalysts (Corma & Martinez, 1993; Kazansky & Senchenya, 1989; Cardona et al, 1995).

## 1.6 MEASURES OF CATALYST PERFORMANCE

It is very difficult to assess catalyst performance when several competing side reactions are occurring simultaneously. A general guideline for comparing catalyst performance will be provided in this section.

### 1.6.1 Butene Conversion (Butene Disappearance)

An excess of isobutane is used in alkylation due to the preferential adsorption of olefins over paraffins in zeolites and other solid acids. For this reason, the progression of the reaction is monitored by the conversion of butene, as it is the limiting reactant.

It is important to realize that butene conversion is not a true indication of the amount of product formed. Accumulation of products in the catalyst pores occurs, even in the absence of catalyst deactivation, due to the strong adsorption of butene to the acid sites. It can be said that product retention will be small in the initial stages of the reaction, but will increase with longer time-on-stream (TOS), eventually reaching some asymptotic value.

In spite of this complication, butene disappearance is a reliable indicator of catalyst activity. An active catalyst will adsorb butene readily whereas a deactivated catalyst will demonstrate limited ability for this function.

### 1.6.2 Alkylate Yield

The alkylate yield can be expressed on several different bases. The expressions used in the literature are listed below:

$$\text{Alkylate Yield} = \frac{\text{g } C_5+}{\text{g } C_4^= \text{ fed}} \quad , \quad \frac{\text{g } C_5+}{\text{g } C_4^= \text{ fed} \cdot \text{g cat}}$$

Ideally, the alkylate yield should be 2 g $C_5^+$/g $C_4^=$ fed. This estimate is based on a 1:1 stoichiometric ratio of reaction between butene:isobutane and assumes that the molar mass of butene and isobutane are approximately the same.

### 1.6.3 Classification of $C_5^+$ Product Distribution

The product distribution is classified into three basic fractions, which are used to denote relative catalyst activity for those particular reactions. The fractions and their classifications are:

| | |
|---|---|
| $C_5$ - $C_7$ | Cracking |
| $C_8$ | Alkylation, Oligomerization, Cracking |
| $C_9^+$ | Polymerization |

### 1.6.4 Classification of $C_8$ Fraction

The $C_8$ fraction is divided into three basic classes with each class used as a measure of a particular reaction:

| | |
|---|---|
| TMP | Alkylate with High Octane Value |
| DMH | Alkylate with Low Octane Value |
| $C_8^=$ | Oligomerization Products |

The TMPs are the most desirable class, as they possess the highest octane value (see Table 1.2). The isomer, 2,2,3-$TMP^+$, is the primary product of the alkylation of 2-$C_4^=$ with *i*-$C_4$ (see Equation 1-6), whereas self-alkylation of *i*-$C_4$ results in the primary product 2,2,4-$TMP^+$ (see Equation 1-7). Other TMP isomers are formed through isomerization of these $TMP^+$ isomers through methyl and hydride shifts (see Figure 1.1).

The DMHs are less preferable than the TMPs, as their octane values are significantly less. They are believed to primarily result via two mechanisms (Simpson et al, 1996), which are shown in Figure 1.3. The group, $C_8^=$s, are the least desirable class in the $C_8$ fraction, as their amounts are limited in the gasoline pool according to CAA formulation requirements for RFG (see Table 1.1).

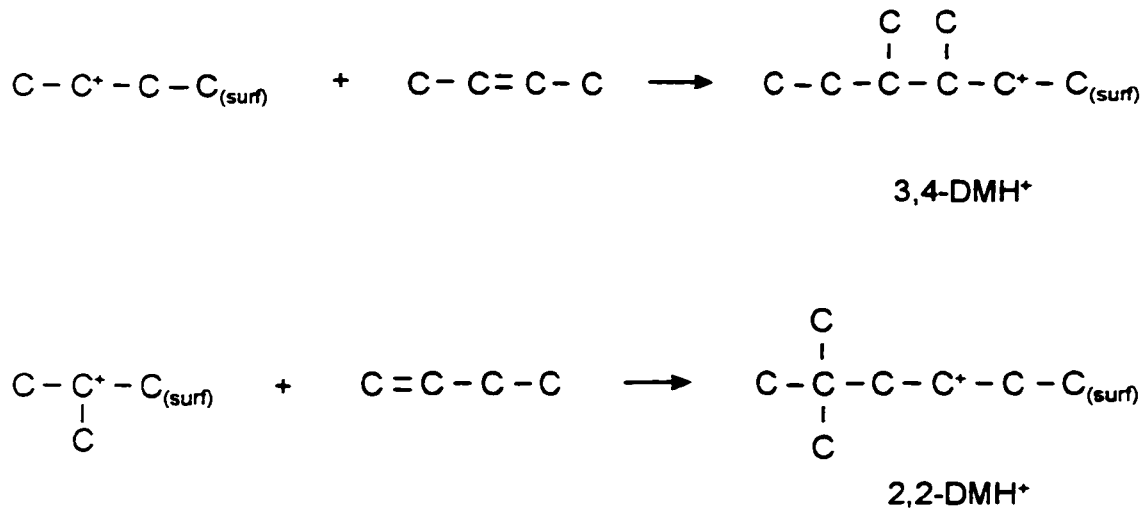



**Figure 1.3:** Routes for DMH Formation

### 1.6.5 Measures of Selectivity in $C_8$ Fraction

Several expressions (molar ratios) are used to measure the efficiency of the reaction to the most valued octane product. The objective is to maximize these measures of $C_8$ selectivity.

$$\frac{\text{TMP}}{\text{DMH}} = \frac{\text{High Octane Products}}{\text{Low Octane Products}}$$

$$\frac{\text{2,2,4-TMP}}{\text{TMP}} = \text{fraction of most valued (octane) TMP isomer}$$

### 1.6.6 Indicator of Steric Effects on Reaction

From a structural viewpoint, 2,3,4-TMP and 2,3,3-TMP have the least steric hindrance of the TMP isomers, on the basis of Lennard-Jones diameter calculations (see Appendix A3.2.5). In addition, these isomers possess the highest diffusivity values, relative to the other TMP isomers (Chu & Chester, 1986). From a structural point of view, 2,2,3-TMP and 2,2,4-TMP are the only TMP isomers which can be formed by $C_4$ fragments, and are also thermodynamically more favourable (see Section 1.7). Therefore, the ratio of thermodynamically favoured isomers divided by least sterically hindered isomers, provides a measure of the importance of steric factors on the reaction.

$$\frac{\text{2,2,4-TMP + 2,2,3-TMP}}{\text{2,3,4-TMP + 2,3,3-TMP}} = \frac{\text{thermodynamically favoured isomers}}{\text{isomers with least steric restrictions}}$$

### 1.6.7 Indicator of Effective Hydride Transfer

Effective hydride transfer results in saturated products such as TMPs and DMHs. Unsaturated and high molecular weight compounds are formed in an environment with poor hydride transfer functioning. The mass ratio of saturated to unsaturated products in the $C_8$ fraction, provides a measure of the effectiveness of the hydride transfer functioning.

$$\frac{\text{TMP} + \text{DMH}}{C_8^{=} + C_9^{+}} = \frac{\text{saturated products in } C_8 \text{ fraction}}{\text{oligomerization and polymerization products}}$$

## 1.7 COMPARISON OF BUTENE/ISOBUTANE ALKYLATE COMPOSITION WITH THERMAL EQUILIBRIUM MEASUREMENTS

Product distributions, obtained experimentally from liquid and solid acids, deviate considerably from those measured at thermal equilibrium (see Table 1.5). The deviation noted for liquid acid systems, is most likely a consequence of changes in solubility of reactants, particularly isobutane, in the acid. On solid acids, three factors can explain the departure from equilibrium predictions. Firstly, strong adsorption of hydrocarbons, particularly at low temperatures, creates a concentration effect such that the actual amounts of reactants in the vicinity of the acid site are quite high. This strongly favours consecutive bimolecular reactions. Secondly, olefins are preferentially adsorbed over paraffins onto solid acid sites, particularly on zeolites with low Si/Al ratio. This promotes oligomerization and polymerization reactions over alkylation reactions (see Chapter 2). Finally, the pore sizes of solid acids will introduce steric effects during product formation, as well as imposing

restrictions on the diffusional rates of products out of the pore network.

**Table 1.5**: Comparison of TMP and DMH Selectivity on Liquid and Solid Acid Catalysts, with Thermal Equilibrium Composition

| Catalyst | HF[1] | $H_2SO_4$[1] | REHY[1] | Thermal Equilibrium Composition | | | |
|---|---|---|---|---|---|---|---|
| Temperature [°C] | n.a. | ~10 | 90 | ~20[1] | 50[2] | 90[3] | 127[1] |
| *TMP Dist. [%]* | | | | | | | |
| 2,2,4-TMP | 65.5 | 47.0 | 29.8 | 67.1 | 63.5 | 61.4 | 59.2 |
| 2,2,3-TMP | 2.5 | 3.1 | 5.6 | 16.8 | 17.5 | 16.5 | 16.6 |
| 2,3,4-TMP | 17.0 | 26.5 | 25.8 | 8.0 | 9.0 | 10.8 | 11.2 |
| 2,3,3-TMP | 14.9 | 23.4 | 38.8 | 8.1 | 10.0 | 11.3 | 13.0 |
| *DMH Dist. [%]* | | | | | | | |
| 2,5-DMH | 21.4 | 64.7 | 23.9 | | 55.0 | | 30.4 |
| 2,4-DMH | 34.8 | | 49.2 | | 36.2 | | 25.5 |
| 2,3-DMH | 38.4 | 29.4 | 6.0 | | 4.0 | | 4.0 |
| 2,2-DMH | | 2.0 | | | | | 22.2 |
| 3,3-DMH | | | | | | | 12.7 |
| 3,4-DMH | 5.4 | 4.0 | 20.9 | | 4.8 | | 5.1 |

1 Chu & Chester, 1986
2 Cardona et al, 1995
3 Corma & Martinez, 1993

## 1.8 RESEARCH METHODOLOGY

### 1.8.1 Problem Statement and Objectives

A catalyst is a material which increases the rate of reaction towards equilibrium without being substantially consumed in the process (Gates, 1995). The **activity** of a catalyst is a measure of how quickly it catalyses a reaction. The effectiveness of the catalyst at promoting the reaction to the desired products is called the **selectivity**. The **stability** of the catalyst is an indication of how quickly it loses its activity or selectivity while in operation. The measure of how effectively a deactivated catalyst can be brought back to a state of high activity and selectivity is called the

**regenerability** of a catalyst.

No solid acid has achieved commercial success in the production of alkylate due to short catalyst lifetime. The failure of solid acids is primarily a loss in hydride transfer function after a short time on stream.

The present study examined the alkylation reaction in detail, to isolate the essential catalyst properties required to activate alkylation and identify weaknesses or limitations of solid acids. Particular attention was focused on the ability of the catalyst to promote hydride transfer, as the loss of this function expedites the onset of deactivation. This provided the foundation for the catalyst design. A reaction mechanism was proposed incorporating the routes where hydride transfer ability can be improved, using the newly designed catalyst system.

The catalyst should maintain high activity and stability for isobutane alkylation with 1-butene. The catalyst should also maximize the selectivity to the TMP isomers, particularly 2,2,4-TMP, as these possess the highest octane values of all $C_8$ products. The performance of the proposed catalyst was compared to that of Y zeolite, in a flow reactor. The catalyst design was critically evaluated to assess the effectiveness of hydride transfer ability in the new design.

Deactivation appears inevitable on any solid acid catalyst system. Therefore, the catalyst must be able to withstand the rigors of regeneration. The performance of the regenerated catalyst systems, was compared to their fresh catalyst performance levels.

### 1.8.2 Catalyst Requirements

The primary reason for rapid catalyst deactivation is the loss of the hydride transfer function, which ultimately favours oligomerization and polymerization reactions and leads to coke formation. For this reason, the main focus in the catalyst development was the promotion and maintenance of the hydride function, for extended reaction times.

Certain properties have been identified as necessary to achieve a high alkylation yield and selectivity. These can be categorized into two types: chemical properties and physical properties.

### *1.8.2.1 Chemical Properties*

The catalytic properties should facilitate the desired alkylation reaction and promote the desorption of the isooctane product. Simultaneously, these chemical properties should minimize the occurrence of undesirable side reactions. The salient chemical properties are listed below:

1. Bronsted acid sites of medium to strong strength are preferred (Corma & Martinez, 1993).

2. An isomerization function, primarily for sec-$C_4^+$ to tert-$C_4^+$ and for $C_8^+$ to TMPs is required. This demands large catalyst pores to eliminate steric restrictions.

3. The catalyst must facilitate hydride transfer selectively from isobutane to ensure rapid desorption of the octyl carbenium ion. This is necessary to minimize consecutive reactions leading to high molecular weight products which ultimately result in coke formation.

4. The catalyst should not promote undesirable side reactions, such as oligomerization, polymerization or cracking of $C_8$ product. This may be difficult, as many of the catalyst requirements for alkylation are similar, to those required by oligomerization, polymerization and cracking reactions. Cracking reactions demand strong acid sites, whereas oligomerization and polymerization reactions require medium strength acid sites. This suggests that a narrow distribution of acid strength is best suited to alkylation, a requirement that is very difficult to achieve on solid acid

catalysts.

### *1.8.2.2 Physical Properties*

Certain physical properties are necessary to facilitate the diffusion of the reactants to the active sites as well as effectively promote diffusion of the products out of the catalyst pores. In addition, certain physical properties are essential for application in an industrial setting, to ensure that the catalyst can withstand the rigours of transport and regeneration conditions. A list of the important attributes are:

1. Large internal pore sizes to facilitate the diffusion of reactants to the active site, isomerization of the octyl carbenium ion and, most importantly, diffusion of the desired TMP products out of the pore network.

2. A tri-directional pore network is essential to efficiently facilitate diffusion of reactants and products.

3. Good thermal and hydrothermal stability are critical to favour effective regenerability.

4. The catalyst must demonstrate robustness and be able to withstand handling stresses during transport.

5. The catalyst must possess sufficient crush strength to endure the weight of catalyst particles above them in the bed.

### 1.8.3 Approach to Evaluating Catalyst Performance

The performance of the newly designed catalyst was evaluated using a computer controlled flow reactor, equipped with on-line sampling and gas chromatographic (GC) analysis. The influence of reactor operating conditions, as well as catalyst pretreatment parameters, was evaluated and compared to a reference catalyst, Y zeolite.

### 1.8.4 Chronological Phases of Research Plan

The research plan can be divided into six chronological phases. A brief description is provided outlining the scope of each phase involved in the project.

#### *1.8.4.1 Phase I: Catalyst Development*

The literature was reviewed to identify potential candidates for catalytic components suited for alkylation. A methodical approach was taken to catalyst development, identifying the shortcomings of existing catalytic systems. With this knowledge, as well as theoretical considerations, a catalyst design was proposed.

#### *1.8.4.2 Phase II: Equipment Set-up for Flow Experiments*

The computer controlled flow reactor to be used for assessing catalyst performance, was installed, tested and brought to a fully operational state. On-line GC analysis was implemented, including establishing communication lines between the BTRS reactor software and GC software, as well as designing and installing a manual splitting valve to act as a GC split injector. Once complete functioning of the on-line GC component was established, chromatographic component identification was performed using injections of known standards as well as GC-MS.

#### *1.8.4.3 Phase III: Preparation and Characterization of Catalyst Systems*

The catalyst was synthesized using methods established in the literature. Phase identification was confirmed by comparison to published X-ray diffraction (XRD) spectra. The reproducibility of the synthesized material was carefully examined in this phase, as this has been reported to be a source of variability in catalyst performance.

#### *1.8.4.4 Phase IV: Effect of Operating Conditions*

Factors, which have been identified as influential on alkylation (i.e. reaction temperature, calcination temperature, olefin weight-hourly-space-velocity (WHSV) and cyclical feed addition, catalyst type), were examined. The effects of these variables on alkylate yield and selectivity were evaluated, and the preferred operating conditions identified.

#### *1.8.4.5 Phase V: Effect of Pt on Catalyst Performance*

The effect of catalyst properties, on alkylate yield and selectivity, was explored in Phase V. These include the nature of catalyst support and Pt loading. Spent catalysts from previous experiments, were regenerated *in situ*, and their performance was assessed in the reconditioned state. The influence of Pt, on the efficacy of regeneration, was a primary focus in this phase.

# Chapter 2

# Catalyst Design

The viability of solid acid catalysts employed for alkylation, has been studied intensively for the last three decades. Solid acid systems typically demonstrate a high initial activity but rapidly undergo deactivation with longer times on stream. A review of the solid acid systems investigated as potential alkylation catalysts, is provided in this section.

# 2.1 REVIEW OF LARGE PORE ZEOLITES FOR BUTENE / ISOBUTANE ALKYLATION

## 2.1.1 Properties of Zeolites

The successful application of Y zeolites as the active ingredient in cracking catalysts during the 1960's, prompted research into the usage of zeolites for alkylation reactions. The preferential adsorption of olefins over paraffins on zeolites, implies that the actual isoparaffin/olefin (I/O) ratio on the catalyst surface, is much less than the I/O ratio in the bulk liquid phase surrounding the catalyst (Corma et al, 1990). To enhance the adsorption of isobutane over butene, reactions are performed at bulk I/O ratios in excess of the stoichiometric amounts required.

It has been nearly a quarter of a century since zeolites were first demonstrated to catalyse isobutane/olefin alkylation (Garwood & Venuto, 1968). To date, zeolites have still not achieved commercial success in the production of alkylate, primarily due to rapid catalyst deactivation (Rotman, 1996). In spite of the lack of success, alkylation research involving zeolites continues.

### *2.1.1.1 Nature of Acidity in Zeolites*

The zeolite lattice consists of a three dimensional network of cations with valences of 4 or 3 (usually $Si^{4+}$ and $Al^{3+}$ respectively) attached to four neighbouring oxygen atoms. The $SiO_4$ tetrahedra are neutral, whereas, a "-1" charge is associated with the $AlO_4^-$ tetrahedra. Electrical neutrality of the $AlO_4^-$ tetrahedra is achieved by the presence of cations located at various crystallographically defined positions, with a large proportion being in internal locations. When the cations are $H^+$, a Bronsted acid site is created, and the zeolite assumes an acidic form (see Figure 2.1). The "onium" type coordination of the oxygen atom is the basis of the high acidity of the

attached proton.

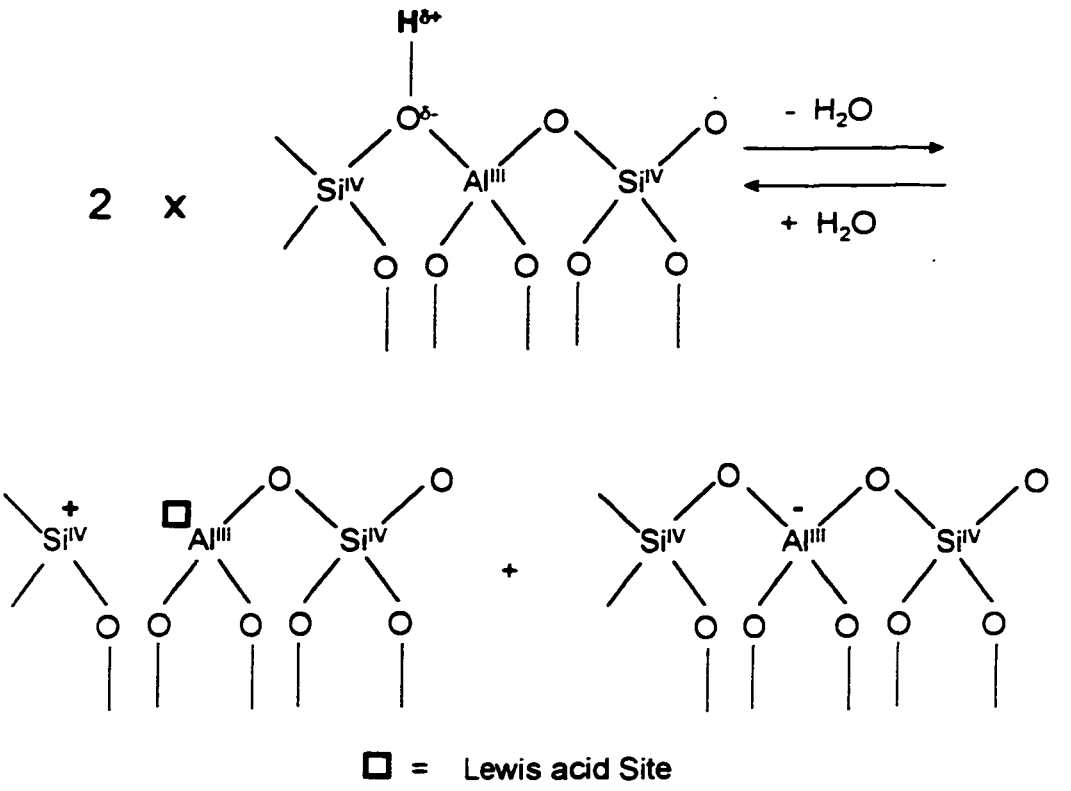



**Figure 2.1**: Interconversion of Bronsted and Lewis Acidity on Zeolites

Two Bronsted acid sites can be converted to one Lewis acid site, through the removal of a water molecule. A simplified, but not complete, depiction of the process is shown in Figure 2.1 (Gates, 1992). Note that Lewis acid sites can be converted back to a Bronsted sites through water addition, provided that the crystal phase has not been altered by severe thermal treatment. Calcination temperatures in excess of approximately 700°C, cause extensive dealumination to occur (Ward, 1967). Extra-framework Al species develop, bearing Lewis acid sites which do not convert to Bronsted acid sites upon water addition. Therefore, provided calcination temperature are sufficiently mild to ensure structure stability, high calcination temperatures support the formation of Lewis acid sites as more and more water is driven off. In

contrast, lower calcination temperatures favour the domination of Bronsted type acidity.

The unit cell size (UCS) is a function of the Si/Al ratio in the zeolite framework and also provides a measure of the total number of tetrahedrally coordinated Al atoms in the framework. Since aluminum atoms are responsible for acidity in zeolites, the UCS provides a direct measure of the number of potential acid sites. It is generally accepted that as the UCS decreases, the acid site density decreases. It is believed that the strength of an acid site is directly related to its degree of isolation from neighbouring acid sites. In this way, the most isolated acid sites, are those which have zero next-nearest alumina neighbours (0-NNN). These sites will exhibit the highest acid strength followed by 1-NNN and so on (Pine et al, 1984).

Adsorption of hydrocarbons onto the Bronsted acid site is dependent upon the stability of the carbenium ion/surface ester intermediates. This in turn, is a function of the deprotonation energy of the proton, as well as the stabilization of the protonated species by the negative charge generated on the lattice oxygen. This emphasizes the complexity of the dynamic behavior of acidity in a solid acid relative to a liquid acid.

### *2.1.1.2 Hydrocarbon Adsorption on Zeolites*

The adsorption properties of zeolites arise from van der Waals and electrostatic forces, due to overlapping adsorption potentials within the small cavities of the pore network. The adsorption behaviour of paraffins and olefins differs, as a result of their interaction with the zeolite surface.

FTIR spectroscopy revealed only weak interaction, or physisorption, between isobutane and zeolitic acid sites, on La-Y zeolite at 25 and 80°C (Flego et al, 1995). The adsorption FTIR spectrum for 1-butene, indicated chemical interaction between zeolite hydroxyl groups and 1-butene molecules, as well as the formation of oligomers. Hydroxyl bands at 3558 (OH in sodalite), 3624 $cm^{-1}$ (OH associated with Al defects) and 3668 $cm^{-1}$ (OH in supercages) disappeared, and chain oligomer

formation was revealed at 1370 $cm^{-1}$. As the loading of 1-butene was increased, the concentration of adsorbed oligomers increased. Similarly, unreacted physisorbed 1-butene (1630 $cm^{-1}$) also increased with 1-butene loading (Flego et al, 1995).

The adsorption characteristics of isobutane/1-butene mixtures (I/O = 9) at 80°C were also examined with FTIR (Flego et al, 1995). The spectrum revealed that isobutane reduced the extent of chemisorbed 1-butene and also suppressed oligomerization activity. It appears that the isobutane exhibited a dilution effect, reducing the probability of oligomerization reactions from occurring.

The Si/Al ratio has a strong influence on the adsorption properties of Y zeolite. The higher the degree of dealumination, the lower the capacity of adsorption (Stach et al, 1986; Corma et al, 1990). Olefins adsorb preferentially over paraffins (Corma et al, 1990) and isoparaffins over straight chain paraffins (Santilli et al, 1993; Denayer et al, 1998), particularly at low Si/Al ratios. Dealumination of the zeolite, reduces the adsorption selectivity towards the olefin. For dealuminated Y zeolite with Si/Al=140, the extent of adsorption of butene and butane are approximately equal at 80°C (Corma et al, 1990).

### 2.1.2 Cubic Phase Faujasites Prepared from Na-rich Hydrogels - Y and USY (Dealuminated Y)

**Table 2.1**: Structural Properties of Y and USY

| Nomenclature | Y | USY |
|---|---|---|
| Si/Al Ratio | 1 - 3 | > 3 |
| Phase | Cubic | |
| Number of O Atoms in Aperture | 12 | |
| Network | 3-dimensional | |
| Mean Pore Diameter | 7.4 Å | |

Higher Si/Al ratios in Y zeolites can be achieved through dealumination, using either steam treatment or chemical means. The dealuminated Y materials, which have Si/Al ratios greater than 3, are called Ultrastable Y (USY). Removal of aluminum from the unit cell causes an overall reduction in the UCS and total number of acid sites (total acidity). The reduced concentration of acid sites suppresses the probability of polymerization reactions from occurring, thus improving catalyst stability. The properties of both Y and USY zeolites are summarized in Table 2.1.

Initially, Y zeolites demonstrated very high activity at temperatures below 100°C yielding product distributions drastically different from thermodynamic predictions. Similar product arrays were achieved when alkylating either 1-butene or 2-butene with isobutane. This suggests that isomerization of 1-butene to 2-butene, the thermodynamically preferred isomer, is faster than alkylation of 1-butene with isobutane (Kirsch et al, 1972).

The influence of steam dealumination on catalyst acidity, as measured by infrared spectroscopy (IR) of adsorbed pyridine, is summarized in Table 2.2 (Corma et al, 1994b). The results indicate that dealumination of USY by steam treatment leads to a reduction in total acidity, particularly Bronsted type.

**Table 2.2**: Acidity of USY Samples, on the Basis of IR Pyridine Adsorption as a Function of Desorption Temperature (Corma et al, 1994b)

| I.D. | Steam Deal. Temp [°C] | USC [nm] | Si/Al Ratio[1] | TGA ANALYSIS Acidity [μmole pyridine retained/g catalyst][2] | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | BRONSTED | | | LEWIS | | |
| DTA Desorption Temp [°C] | | | | 250 | 350 | 400 | 250 | 350 | 400 |
| USY-1 | 500 | 2.450 | 5.4 | 110 | 58 | 28 | 41 | 34 | 27 |
| USY-2 | 712 | 2.435 | 13.6 | 80 | 32 | 13 | 29 | 14 | 14 |
| USY-3 | 740 | 2.428 | 35.3 | 46 | 18 | 4 | 16 | 7 | 7 |
| USY-4 | 760 | 2.426 | 62.2 | 39 | 15 | 2 | 20 | 13 | 13 |

1 framework Si/Al ratio reported

2 pyridine desorption temperature used as a measure of quality (i.e. strength) of acid site and amount of pyridine retained as a measure of quantity of acid sites

Comparison of alkylate yield and selectivity on USY zeolites (steam dealuminated at various temperatures) at short TOS, is maximized for the largest UCS (lowest Si/Al ratio) as shown in Table 2.3. These results suggest that alkylate production is favoured by a high density of strong acid sites having either 0 or 1 Al in the next nearest neighbour (0-NNN or 1-NNN respectively) position (Corma et al, 1994b). Alternatively, it is also possible that the cavity becomes too small as more Al is removed, preventing formation of the bulky TMP isomers.

The extraframework aluminum (EFAL) species generated during the dealumination process, have been found to interact with HF and LF hydroxyls, creating Bronsted sites of superacid strength (will not desorb pyridine at 400°C) (Corma, 1989). The presence of EFAL in mildly dealuminated catalysts has been demonstrated to exert a positive effect on extending catalyst lifetime and enhancing alkylation activity (Corma et al, 1996a).

It is possible that EFAL species are present in the sample dealuminated under mild steaming conditions (500°C). This would explain the large amounts of strong acid sites (as measured by the amount of pyridine retained by Bronsted acid sites after heating to 400°C during Fourier Transform infrared spectroscopy (FTIR) analysis) measured for this sample. This would enhance catalyst performance with respect to alkylation, as well as prolong the catalyst lifetime. Unfortunately, EFAL was not investigated by the authors (Corma et al, 1994b), and therefore, any conclusions are purely speculative.

A decrease in the UCS via dealumination compromises the quality of the alkylate, as indicated by the TMP/DMH ratio. This is most likely a consequence of steric factors, resulting from the reduction in space available, which favours the formation of DMHs over TMPs (see Table 2.3).

The primary product of alkylation of 2-butene with isobutane is 2,2,3-TMP. However, substantial levels of 2,2,4-TMP are observed for the Y-zeolites with UCS $\geq$ 2.435 nm (see Table 2.3). This suggests that either these catalysts have strong isomerization capabilities or they promote self-alkylation of isobutane, which has been reported elsewhere (Kirsch, et al, 1972).

**Table 2.3**: Alkylate Product Distribution on USY, as a Function of UCS (TOS=1min., $T_{rxn}$=50°C, I/O=15) (Corma et al, 1994b)

| Steam Dealumination Temp. [°C] | 500 | 712 | 740 | 760 | • As UCS is reduced<br>• Si/Al ratio increases<br>• Strength of acid site increases<br>• Density of acid site decreases |
|---|---|---|---|---|---|
| Si/Al Ratio | 5.4 | 13.6 | 35.3 | 62.2 | |
| USC [nm] | 2.450 | 2.435 | 2.428 | 2.426 | |
| 2-$C_4^=$ Conv [%] | 99.6 | 100.0 | 90.6 | 92.0 | |
| Alkylate Yield [g $C_5$+/g $C_4^=$ fed] | 0.84 | 0.49 | 0.19 | 0.20 | • ideally should be: 2 g $C_5^+$/g $C_4^=$ fed |
| *$C_5$+ Liquid [mass%]* | | | | | |
| $C_5$-$C_7$ | 34 | 34 | 11 | 13 | • cracking activity |
| $C_8$ | 49 | 42 | 49 | 40 | |
| $C_9$+ | 17 | 24 | 40 | 47 | • polymerization activity |
| *$C_8$ Fraction [mass%]* | | | | | |
| TMP | 78 | 72 | 12 | 18 | • high octane alkylate |
| DMH | 20 | 28 | 55 | 55 | • low octane alkylate |
| $C_8^=$ | 2 | 0.4 | 33 | 27 | • oligomerization products |
| *TMP Fraction [%]* | | | | | |
| 2,2,4-TMP | 39 | 39 | 23 | 27 | • highest octane value |
| 2,2,3-TMP[1] | 7 | 6 | 18 | 15 | • direct product of rxn |
| 2,3,4-TMP | 23 | 27 | 37 | 36 | • least sterically hindered |
| 2,3,3-TMP | 31 | 28 | 22 | 22 | • least sterically hindered |
| *Indicators [mass fr]* | | | | | |
| $\frac{\text{TMP}}{\text{DMH}}$ | 3.8 | 2.6 | 0.2 | 0.3 | • high/low octane alkyiate |
| $\frac{\text{2,2,3- + 2,2,4-TMP}}{\text{2,3,4- + 2,3,3-TMP}}$ | 0.88 | 0.82 | 0.69 | 0.71 | • thermodynam. favoured /least sterically hindered |
| $\frac{\text{TMP+DMH}}{C_8^= + C_9^+}$ | 2.6 | 1.8 | 0.6 | 0.5 | • effective/ineffective hydride transfer |

1 separation of 2,2,3-TMP and 2,4-DMH not achieved; each component assumed to be half of total

The hydride transfer ability of the catalyst is critical to favour the formation of the *tert*-butyl carbenium ions as well as promoting desorption of the octyl carbenium ions. It is well established that reducing the UCS below 2.430 nm severely decreases the hydride transfer activity, resulting in a higher olefinic content in the alkylate (as

measured by alkylate MON) (Pine et al, 1984). Significant levels of isooctenes for Y-zeolites with UCS below 2.430 nm were observed, in agreement with this trend (see Table 2.3).

The levels of *n*-butane produced in the preliminary stages of the reaction in the absence of catalyst deactivation, provide another measure of the hydride transfer ability of the catalyst (Corma et al, 1994b). Successful hydride transfer from isobutane to a *sec*-butyl carbenium ion, yields *n*-butane and a *tert*-butyl carbenium ion (see Equation 1-3):

$$sec\text{-}C_4^{+}{}_{(surf)} + i\text{-}C_4 \longrightarrow n\text{-}C_4 + tert\text{-}C_4^{+}{}_{(surf)} \qquad (1\text{-}3)$$

As expected, low levels of *n*-butane are observed after 1 minute TOS for the catalysts with UCS below 2.430 nm. In contrast, Y-zeolite with UCS > 2.430 nm, produced elevated levels of *n*-butane for the same TOS.

These results, in conjunction with the distribution of the different acid sites on the catalyst, suggest that hydride transfer was best facilitated by a low Si/Al ratio (large UCS). Similarly, the steric requirements of alkylation, demand a catalyst with a large UCS.

As the catalyst ages, high molecular weight carbonaceous type species are retained on the active sites, preferentially the stronger Bronsted acid sites. This reduces the hydride transfer ability of the catalyst as well as inducing pore blockage. The decaying catalyst promotes oligomerization rather than alkylation. Desorption of the octyl and higher carbenium ions from the acid centers, occurs by loss of a proton by the cation, rather than uptake of a hydride ion from an isobutane molecule. This results in a higher olefinic content in the product distribution (Corma et al, 1994b). The behaviour of the deactivating catalyst suggests that the acid site strength needed to promote reactions under alkylation conditions can be ranked as follows: cracking > alkylation > dimerization (oligomerization) (Corma et al, 1994b; Corma &

Wojciechowski, 1982; Corma et al, 1994a; O'Young et al, 1994; Corma et al, 1996a).

Another approach to tempering catalyst acidity and extending catalyst lifetime. is to cation exchange the parent material (Y or USY) with a rare earth metal (RE). La and Ce have been exchanged in Y zeolite (RE-Y), to increase the density of acid sites with suitable strength for isobutane/butene alkylation, according to the Hirschler-Plank mechanism (see Equation 2-1).

$$RE(H_2O)^{3+} + \text{Zeol-}O^- \longrightarrow RE(OH)^{2+} + \text{Zeol-OH} \qquad (2\text{-}1)$$

Upon ion exchange, hydrated complexes of the RE ions occupy the supercages, but later migrate to sites in the sodalite cages during calcination. At higher RE exchange, the RE ions occupy additional sites in the supercages as well.

The performance of RE-Y applied to alkylation of butene with isobutane has been explored. The catalyst Ce-Y demonstrated improved catalyst performance over Y and RE-USY with respect to alkylate yield (g $C_5^+$/g 1-$C_4^=$ fed) (Chu & Chester, 1986). However, rapid catalyst deactivation still ensued, mainly due to the loss of hydride transfer function, resulting in oligomerization activity being facilitated rather than alkylation (Rorvik et al, 1996b).

### 2.1.3 Faujasites Prepared in the Presence of Crown Ether Templates - EMT (Hexagonal Phase) and FAU (Cubic Phase)

**Table 2.4**: Structural Properties of EMT and FAU

| Nomenclature | FAU | EMT | |
|---|---|---|---|
| Phase | cubic | Hexagonal | |
| Si/Al Ratio | 3-5 | 3-5 | |
| Template | 15-crown-5 ether | 18-crown-6 ether | |
| # of O Atoms in smallest Aperture | 12 | 12 | |
| Network | 3-dimensional | 3-dimensional | |
| Cages | supercage | hypercage (50 %) | hypocage (50 %) |
| Void Volume [$nm^3$] | 1.15 | 1.24 | 0.61 |
| Accessibility to Cages | 4 circular channels (0.74 nm) | 2 circular channels (0.74 nm) 3 elliptical channels (0.69 x 0.74 nm) | 3 elliptical channels (0.69 x 0.74 nm) |

A method has been recently proposed for preparation of cubic (FAU) and hexagonal (EMT) faujasite-type zeolites with Si/Al ratios up to 5, by using crown-ether templates (Delprato, et al, 1990). The hexagonal phase can be synthesized from aluminosilicate hydrogels containing 18-crown-6 ether, whereas, the cubic phase is produced when 15-crown-5 is used as the template (see Table 2.4). Up to this time, high yields of well-defined faujasite-type zeolites with a framework Si/Al ratio greater than 3 could not be achieved, without post-synthesis treatment (i.e. chemical dealumination or steam dealumination).

FAU and EMT have similar structure types, and hence, geometrical pore sizes. Both are built from truncated octahedra, called "sodalite cages" or cubo-octehadra, which are linked together through hexagonal prisms to form faujasite sheets.

Different linking of the sodalite cages produces the different microporous structures of FAU and EMT (see Chapter 3).

Although the EMT, FAU and USY have similar physical structures, acidity measured by pyridine FTIR spectra reveal significant differences in the distribution and predominance of the type of acid sites (see Table 2.5). EMT and FAU were both calcined at 540°C for 5 h whereas the conditions for USY were 500°C for 3 h. At these calcination temperatures, all of the faujasites favour the formation of Bronsted acid sites over Lewis acid sites. Spectra of pyridine desorption reveal that Bronsted acid site concentrations are significantly greater those of Lewis acid sites, for all catalysts and all desorption temperatures. The relative ratio of pyridine adsorption at 400°C versus 250°C, used as a measure of strong to weak acid sites (Corma et al, 1994b), indicates that the EMT and FAU have a much greater proportion of strong to weak acid sites (see Table 2.6).

**Table 2.5**: Acidity of EMT, La-exchanged EMT, FAU and USY, on the Basis of IR Pyridine Adsorption as a Function of Desorption Temperature[1]

| | BRONSTED Acidity [mmol pyridine retained/g cat.] | | | LEWIS Acidity [mmol pyridine retained/g cat.] | | |
|---|---|---|---|---|---|---|
| DTA [°C] | 250 | 350 | 400 | 250 | 350 | 400 |
| EMT[2] | 0.50 | 0.43 | 0.42 | 0.08 | 0.07 | 0.07 |
| La40EMT[3] | 0.40 | 0.34 | 0.32 | 0.18 | 0.14 | 0.14 |
| La80EMT[3] | 0.38 | 0.31 | 0.29 | 0.07 | 0.06 | 0.05 |
| FAU[2] | 0.51 | 0.45 | 0.39 | 0.12 | 0.12 | 0.12 |
| USY[4] | 0.20 | 0.11 | 0.05 | 0.07 | 0.04 | 0.04 |

1 pyridine desorption temperature used as a measure of quality (i.e. strength) of acid site and amount of pyridine retained as a measure of quantity (i.e. density) of acid sites

2 data from Stocker et al, 1996; Si/Al =3.5; Extinction coefficients: IMEC(B) = 1.67 cm/μmol, IMEC(L) = 2.22 cm/μmol

3 data from Mostad et al, 1997; LaxEMT represent x % La exchange of parent EMT (Si/Al =3.9); Extinction coefficients: IMEC(B) = 1.67 cm/μmol, IMEC(L) = 2.22 cm/μmol

4 data from Corma, Martinez & Martinez, 1994b; Si/Al = 2.6; re-calculated data such that the extinction coefficients applied by Stocker et al, 1996 were also applied

**Table 2.6**: Analysis of Acid Site Distribution with respect to Site Type and Strength, for EMT, La-exchanged EMT[1], FAU and USY

| | Relative Strength of BRONSTED Acid Sites [400/250][2] | Relative Strength of LEWIS Acid Sites [400/250][2] |
|---|---|---|
| EMT | 0.84 | 0.88 |
| La40EMT | 0.80 | 0.78 |
| La80EMT | 0.76 | 0.71 |
| FAU | 0.76 | 1.00 |
| USY | 0.25 | 0.57 |

1 LaxEMT where *x* indicates % exchange of La
2 Strong (400°C desorption temperature) / Weak (250°C desorption temperature) Acid Sites on the basis of pyridine desorption

A comprehensive review of the Bronsted acidity on USY and EMT, supports these observations (Su et al, 1993). The catalyst EMT demonstrated higher thermal stability of the hydroxyls and pore structure, a greater mean acid strength and larger proportion of very strong protonic sites relative to USY.

Recent efforts modelling the siting patterns of Si and Al in the framework for FAU and EMT synthesized in the presence of crown ethers, have concluded that the Al ordering is not random, as is the case in parent and dealuminated Y zeolites crystallized from a sodium aluminosilicate hydrogel. Rather, the models predict Al-enriched and Al-depleted regions for the crown ether prepared materials, in agreement with experimentally determined Si(nAl) populations (where n = 0, 1, 2, 3 or 4) based on Si NMR spectra (Feijen et al, 1996). It is proposed that the presence of one crown ether in each cage directs the aluminum placement on the basis of charge balance with the Na cation (Feijen et al, 1994b; Feijen et al, 1996). The effect of uneven Al distribution, on acidity, is not known, as it is unique to the crown ether synthesized faujasites. However, pyridine desorption IR spectra suggest that high concentrations of strong acid sites are formed. This type of acid site density may be well suited to alkylation.

Preliminary results confirmed this hypothesis using EMT for alkylation of 2-butene with isobutane (Stocker et al, 1994; Rorvik et al, 1996; Stocker et al, 1996). In

a 300 mL stirred semibatch autoclave, isobutane was added first under nitrogen pressure and heated to the reaction pressure. The reagent, 2-Butene, was charged at a constant WHSV for 2 $h^{-1}$, until an I/O ratio of 5, 10 or 20 is reached. A disadvantage of this approach is that a time-averaged picture of the catalytic events is depicted. Differential samples of gas-phase products were collected and analyzed on-line. Heavier liquid products were collected using an ice trap and evaluated off-line.

Very high I/O ratios were inherent during the initial stages of the reaction. This ratio gradually declined through further butene addition, until the final I/O ratio was reached at 2 h. After this time, butene addition was ceased. Under these circumstances, very high alkylation yields and reduced oligomerization are expected. In addition, self-alkylation is strongly favoured, a condition not mentioned by the authors. A separate study involving isobutane as the only reactant using EMT would reveal its ability for self-alkylation reactions.

Catalyst performance, with respect to alkylate yield, can be ranked as follows: EMT > FAU > Ce-Y (98 % Ce exchanged Y zeolite). The high densities of strong acid sites may explain the superior performance of FAU and EMT over the Y zeolite. Temperature demonstrated little effect on the yield of alkylate in the range of 80 to 100°C. The I/O ratio exerted considerable influence when increased from 5 to 20 (Rorvik et al, 1996).

The high levels of TMP production suggest that self-alkylation of isobutane may be important. This was also supported by the dependence of 2,2,4-TMP production on the stirring speed (Rorvik et al, 1996). At lower stirrer rpm, 2,2,4-TMP wafavoured. As the stirrer speed was increased, the quantity of 2,2,4-TMP formed declined to a steady value. These results suggest that a uniform dispersion of the olefin in the isoparaffin under high stirring speeds, reduced the probability of 2,2,4-TMP formation, through self-alkylation of the isoparaffin. Also, the semi-batch nature for reactant addition favours self-alkylation of the isoparaffin.

The catalyst, EMT, strongly favoured highly branched alkylate, as indicated by the TMP/DMH ratio (see Table 2.7). The least sterically hindered isomers (2,3,3- and

2,3,4-TMP) predominated in the TMP distribution, similar to fixed bed studies for long TOS involving other catalytic systems (Cardona et al, 1995).

**Table 2.7**: Alkylate Product Distribution on Ce-Y, H-FAU and H-EMT[1] (T = 80°C, semi-batch, I/O=20, t = 3h) (Rorvik et al, 1996)

| Catalyst | Ce-Y | FAU | EMT | • FAU and EMT synthesized using crown ether templates |
|---|---|---|---|---|
| 2-$C_4^=$ Conv [%] | 34 | 70 | 89 | |
| Alkylate Yield [g $C_5$+/g $C_4^=$ fed] | 0.30 | 1.30 | 3.65 | • ideally should be: 2 g $C_5^+$/g $C_4^=$ fed |
| *$C_5$+ Liquid [mass%]* | | | | |
| $C_5$-$C_7$ | 12 | 13 | 8 | • cracking activity |
| $C_8$ | 84 | 74 | 82 | |
| $C_9$+ | 4 | 13 | 10 | • polymerization activity |
| *$C_8$ Fraction [mass%]* | | | | |
| TMP | 43 | 56 | 86 | • high octane alkylate |
| DMH | 14 | 14 | 11 | • low octane alkylate |
| $C_8^=$ | 43 | 30 | 3 | • oligomerization products |
| *TMP Fraction [%]* | | | | |
| 2,2,4-TMP | 18 | 20 | 17 | • highest octane value |
| 2,2,3-TMP | 5 | 7 | 9 | • direct product of reaction |
| 2,3,4-TMP | 38 | 36 | 34 | • least sterically hindered |
| 2,3,3-TMP | 40 | 37 | 40 | • least sterically hindered |
| *Indicators [mass fr]* | | | | |
| TMP / DMH | 3.2 | 3.9 | 4.1 | • high/low octane alkylate |
| (2,2,3- + 2,2,4-TMP) / (2,3,4- + 2,3,3-TMP) | 0.29 | 0.37 | 0.35 | • thermod. favoured /least sterically hindered isomers |
| (TMP+DMH) / ($C_8^=$ + $C_9^+$) | 1.2 | 1.5 | 6.4 | • effective/ineffective hydride transfer |

1 Catalyst calcined externally at 540°C for 5 hours in air during catalyst preparation. Prior to reaction, catalyst calcined externally at 400°C for 2 h, then transferred to reactor and pre-treated at 200°C for 2 h.

The most encouraging aspect of EMT is the effectiveness at which it facilitated hydride transfer ((TMP + DMH)/($C_8^=$ + $C_9^+$)). The proportion of $C_8^=$ and $C_9^+$ in the product distribution in substantially less than the $C_8$ paraffin production (see Table

2.7). It appears that the slightly larger hypercage, improved accessibility through additional openings in the larger hypercage, as well as straight channel access to hypercage, strongly favour efficient hydride transfer for this reaction. This has long been a stumbling block in the application of heterogenous catalysts for alkylation, whereby, rapid catalyst deactivation ensues primarily as a consequence of loss of hydride transfer ability.

Similar to Y and USY, EMT and FAU possess a high density of acid sites. These sites promote alkylation; however, the close proximity of acid sites also encourages oligomerization activity. For this reason, dealumination of EMT and FAU zeolites, using either a chemical or physical (steam) method, have been explored to better tailor the acidity level to alkylation.

A recent investigation used $(NH_4)_2SiF_6$ to dealuminate FAU and EMT (Stocker et al, 1996). The performance of the parent and dealuminated materials, with respect to alkylation, were studied (see Table 2.8). The catalyst, EMT, demonstrated superior performance over FAU in all regards. This agrees with the findings of previous investigations for the parent materials (Stocker et al, 1994; Rorvik et al, 1996).

The effect of EFAL was not investigated by the authors. A recent investigation examining *n*-hexane cracking, concluded that dealumination in EMT, FAU and USY proceeded in a similar manner (Zholobenko et al, 1995), whereby, dealuminated catalysts were more active than the parent materials. Enhanced Bronsted acidity, due to the formation of tetrahedrally coordinated EFAL species, was concluded to be responsible for the improved performance. Another interesting finding of this study was that EMT exhibited shape selectivity effects and produced significantly higher yields of iso-products relative to FAU and USY.

**Table 2.8**: Alkylate Product Distribution on Parent and Dealuminated FAU and EMT[1] (t = 3h, T = 80°C, semi-batch reactor) (Stocker et al, 1996)

| Catalyst | Par. EMT | Deal. EMT | Par. FAU | Deal. FAU | • FAU and EMT synthesized using crown ether templates |
|---|---|---|---|---|---|
| 2-$C_4^=$ Conv [%] | 88 | 98 | 66 | 67 | |
| Alkylate Yield [g $C_5$+/g $C_4^=$ fed] | 4.13 | 5.70 | 1.54 | 2.33 | • Ideally should be: 2 g $C_5^+$/g $C_4^=$ fed |
| *$C_5$+ Liquid [mass%]* | | | | | |
| $C_5$-$C_7$ | 10 | 8 | 23 | 18 | • Cracking activity |
| $C_8$ | 82 | 76 | 68 | 72 | |
| $C_9$+ | 8 | 16 | 9 | 10 | • Polymerization activity |
| *$C_8$ Fraction [mass%]* | | | | | |
| TMP | 83 | 85 | 82 | 80 | • high octane alkylate |
| DMH | 16 | 15 | 14 | 16 | • low octane alkylate |
| $C_8^=$ | 1 | 0 | 4 | 4 | • oligomerization products |
| *TMP Fraction [%]* | | | | | |
| 2,2,4-TMP | 29 | 39 | 23 | 27 | • highest octane value |
| 2,2,3-TMP | 9 | 6 | 18 | 15 | • direct product of reaction |
| 2,3,4-TMP | 27 | 27 | 37 | 36 | • least sterically hindered |
| 2,3,3-TMP | 35 | 28 | 22 | 22 | • least sterically hindered |
| *Indicators [mass fr]* | | | | | |
| TMP / DMH | 5.2 | 5.8 | 5.3 | 5.1 | • high/low octane alkylate |
| (2,2,3- + 2,2,4-TMP) / (2,3,4- + 2,3,3-TMP) | 0.62 | 0.36 | 0.57 | 0.49 | • thermodyn. favoured/least sterically hindered isomers |
| (TMP+DMH) / ($C_8^=$ + $C_9^+$) | 9.8 | 4.8 | 5.2 | 5.5 | • effective/ineffective hydride transfer |

1 Catalyst calcined externally at 540°C for 5 hours in air during catalyst preparation. Prior to reaction, catalyst calcined externally at 400°C for 2 h, then transferred to reactor and pre-treated at 200°C for 2 h.

The ratio of pyridine adsorption at 400°C relative to that at 250°C (ratio of strong to weak acid sites) for the parent and dealuminated EMT, are 0.84 and 0.85 respectively (Stocker et al, 1996). For FAU, the respective ratios are 0.76 and 0.72. All samples retained some pyridine at 550°C, indicating the presence of very strong acid sites. These ratios emphasize the distinctive characters of EMT and FAU despite their similar structure, and may explain the differences observed in their

performance with respect to alkylation.

The EMT system favoured the formation of TMPs over DMHs, with 2,3,3-TMP and 2,3-DMH being the dominant isomers in each respective fraction. In contrast, FAU demonstrated a greater tendency to oligomerize, as reflected by the higher $C_8^=$ content in the product distribution. Polymerization proceeded to a greater extent on FAU relative to EMT, which is not surprising in view of its greater preponderance to oligomerize.

Dealumination of EMT enhanced alkylation yield, primarily in favour of greater $C_9^+$ formation at the expense of the preferred $C_8$ fraction. Although 2,3,3-TMP continued to be the dominant TMP isomer, dealumination of EMT resulted in a decline of 2,2,4-TMP formation. Under all conditions, 2,2,3-TMP, the primary product of 2-$C_4^=$ and *i*-$C_4$ alkylation, was the least favoured TMP isomer.

Recall that dealumination of Y zeolites results in the formation of EFAL species, which have been found to exert a pronounced effect on catalytic activity. It is of interest to examine whether FAU or EMT synthesized using crown-ether templates, display the same effect, particularly in view of the unique Al distribution in the catalyst.

A much higher $C_9^+$ content was observed in the product distribution for the dealuminated EMT suggesting enhanced polymerization. In addition, a drop in cracking activity was evidenced by the lower $C_5$ - $C_7$ levels. These results suggest that catalyst deactivation, as a result of coke deposition, proceeded at a more rapid rate on the dealuminated EMT catalyst. This restricted the formation of 2,2,4-TMP and favoured the formation of the least sterically hindered TMP isomers. This hypothesis is supported by the fact that hydride transfer declined as a consequence of dealumination.

Dealumination of FAU produced a similar increase in alkylation yield and selectivity. No significant change in the TMP/DMH ratio was noted, although dealumination of FAU appeared to discourage the formation of 2,2,4-TMP. This agrees with the trend observed for EMT and USY.

Similar to Y and USY zeolites, rare earth metal exchange (i.e. La) in EMT and FAU, have also been explored, to determine if the acidity can be tuned to fit alkylation demands. The exchange of 40 % and 80 % La in EMT (La40EMT and La80EMT respectively) caused an overall reduction Bronsted acidity (Mostad et al, 1997).

The catalyst, La40EMT, demonstrated superior performance over EMT, in terms of alkylate yield (g $C_5$-$C_8$ paraffins/g dry cat) and selectivity (g $C_5$-$C_8$ paraffins/g 2-$C_4^=$ conv.). It appears that the hydride transfer ability was improved with the introduction of La, as indicated by a suppression of oligomerization and polymerization activities and elevated cracking and alkylation activities (see Table 2.9).

Although similar TMP/DMH ratios were observed for both EMT and La40EMT, the latter catalyst improved 2,2,4-TMP selectivity significantly. In general, the introduction of La enhanced the production of the TMP isomers that are more sterically hindered and slower to diffuse out of the catalyst pores.

The effect of calcination temperature, on alkylate yield and selectivity, was also explored. At 45 % La exchange, the optimal calcination temperature was identified as 450°C. This calcination temperature possessed the highest proportion of strong Bronsted acid sites (see Table 2.6) of those exchanged with La, supporting the belief that very strong acid sites are necessary to promote hydride transfer and delay the onset of catalyst deactivation.

At higher exchange levels (80 % La exchange), a decrease in butene conversion, yield and selectivity resulted, with elevated amounts of $C_9^+$ produced. Studies at 51 % La exchange in EMT concluded that the optimum ion exchange level was below 51 % (Rorvik et al, 1997).

The catalyst, La40FAU (40 % La exchange in FAU), demonstrated inferior performance to EMT and La40EMT, and favoured higher levels of cracking, oligomerization and polymerization levels at the expense of alkylation (Mostad et al, 1997). Although La40FAU and La40EMT possess similar geometrical sizes and total acidities, structural differences exist. The catalyst, EMT, possesses larger hypercages and improved accessibility to these cages through five channels, as

opposed to four in FAU. It may be that these structure differences are responsible for the enhanced performance of La40EMT over La40FAU.

**Table 2.9**: Alkylate Product Distribution on EMT and La-Exchanged EMT[1] (t = 3h, T = 80°C, semi-batch reactor; I/O=10) (Rorvik et al, 1997)

| Catalyst | EMT | La40 EMT | La80 EMT | • LaxEMT where x indicates degree of La exchange |
|---|---|---|---|---|
| 2-$C_4^=$ Conv [%] | 88 | 100 | 81 | |
| Alkylate Yield [g $C_5$+/g $C_4^=$ fed] | 1.7 | 2.2 | 1.2 | • ideally should be: 2 g $C_5^+$/g $C_4^=$ fed |
| *$C_5$+ Liquid [mass %]* | | | | |
| $C_5$-$C_7$ | 8 | 10 | 10 | • cracking activity |
| $C_8$ | 82 | 85 | 78 | • alkylation/oligomerization |
| $C_9$+ | 10 | 5 | 12 | • polymerization activity |
| *$C_8$ Fraction [mass%]* | | | | |
| TMP | 82 | 84 | 84 | • high octane alkylate |
| DMH | 15 | 15 | 15 | |
| $C_8^=$ | 3 | 1 | 1 | • oligomerization products |
| *TMP Fraction [%]* | | | | |
| 2,2,4-TMP | 18 | 38 | 20 | • highest octane value |
| 2,2,3-TMP | 5 | 7 | 3 | • direct product of reaction |
| 2,3,4-TMP | 36 | 23 | 41 | • least sterically hindered |
| 2,3,3-TMP | 41 | 32 | 36 | • least sterically hindered |
| *Indicators [mass fr]* | | | | |
| $\frac{\text{TMP}}{\text{DMH}}$ | 5.6 | 5.6 | 5.7 | • high/low octane alkylate |
| $\frac{\text{2,2,3- + 2,2,4-TMP}}{\text{2,3,4- + 2,3,3-TMP}}$ | 0.29 | 0.82 | 0.29 | • thermodyn. favoured /least sterically hindered isomers |
| $\frac{\text{TMP+DMH}}{C_8^= + C_9^+}$ | 6.3 | 15.9 | 6.1 | • effective/ineffective hydride transfer |

1 Catalyst calcined externally at 540°C for 5 hours in air during catalyst preparation. Prior to reaction, catalyst calcined externally at 400°C for 2 h, then transferred to reactor and pre-treated at 200°C for 2 h.

## 2.2 IDENTIFICATION OF PREFERRED ACIDIC SUPPORT

Many solid acids have been explored for application to butene isobutane. These include β-zeolite (Corma et al, 1994a; Corma et al, 1994b; Corma et al. 1994c; Corma et al, 1994d; Nivarthy et al, 1998; Loenders et al, 1998), MCM-22 (Corma et al, 1994a), ZSM-5 (Chu & Chester, 1986; Weitkamp & Jacobs, 1993), SAPO-37 (Mostad et al, 1996), $SO_4^{2-}/ZrO_2$ (Cormaet al, 1994c; Corma et al, 1994d; Corma et al. 1994e; Xiao et al, 1998) and heteropoly acids and their salts (Corma et al, 1996d; Blasco et al, 1998). The catalyst Nafion-H, a solid superacid polymer, has also been applied to butene/isobutane alkylation (Rorvik et al, 1995). Although high activity is frequently demonstrated by several solid acid systems, rapid deactivation ultimately ensues, primarily due to loss of hydride transfer functioning.

The success of any solid acid, lies in its ability to maintain strong hydride transfer. A high density of strong Bronsted acid sites is necessary to facilitate alkylation of butene with isobutane. Unfortunately this arrangement also promotes oligomerization of butene, a more facile reaction. Literature studies on Y, FAU and EMT zeolites, conclude that catalyst performance improves by tempering catalyst acidity through partial dealumination or rare earth metal exchange. It appears that a compromise between enhancing hydride transfer and suppressing oligomerization tendencies is necessary.

This lays the foundation for the catalyst design requirements. The catalyst EMT, was chosen as the acidic support in the present research, for the following reasons. Firstly, EMT has a slightly higher Si/Al ratio (typically between 3 and 5) relative to that of Y zeolite (between 1 and 3), representing a slightly lower acid site density.

Secondly, EMT possesses a high density of strong Bronsted acid sites, which are isolated from other groups of strong sites by dense siliceous regions. The ratio of strong to weak acid sites is very high for EMT relative to USY. This type of acid strength distribution is ideally suited for alkylation, as it offers a high concentration of strong Bronsted acid sites to facilitate hydride transfer. These pockets of acid sites

are surrounded by inert siliceous regions, which may suppress oligomerization tendencies.

Thirdly, pyridine IR spectra suggest that EMT possesses predominantly Bronsted type acidity over the entire acid strength distribution. This is unique to this type of material. This is ideally suited for alkylation, as the carbenium mechanism is facilitated by strong Bronsted acid sites. Also, the low concentrations of Lewis acid sites, imply that undesirable side reactions promoted by Lewis acidity will be minimized.

Fourthly, the hypercages of EMT are slightly larger and have improved accessibility through five channels, relative to the smaller supercages of H-USY providing access through four channels. This is beneficial to the formation of isomerized products, based on alkylation and cracking studies, as well as favouring efficient diffusion of the products out of the catalyst network. Finally, the thermal and hydrothermal stability of EMT, are found to be very high. This is particularly important when considering the severe conditions employed during regeneration processes.

Research on EMT is relatively new. The material was first synthesized in 1990 and has not been studied extensively with respect to alkylation. Preliminary results on cracking and alkylation reactions, conclude that EMT is capable of maintaining high catalytic activity and postponing the onset of catalyst deactivation. For these reasons, EMT was chosen as the acidic component in the catalyst design of the present investigation.

## 2.3 REVIEW OF HYDROGEN SPILLOVER

### 2.3.1 Definition of Hydrogen Spillover

The loss of hydride transfer has been associated with catalyst deactivation in solid acid catalysed reactions. For this reason, a primary consideration in the catalyst design will be the enhancement of the hydride transfer ability of the catalyst, to delay the onset of deactivation. Spillover is a phenomenon, which offers potential to address this issue.

Spillover involves the transport of an active species, formed or sorbed on a surface, onto a second surface, that does not sorb or form active species under the same conditions. The spillover species can either react with other sorbing species on the second surface and/or it can serve to activate the second phase.

The surface, which adsorbs and forms the active species, is called the *donor surface* or *activator*. The surface that gains access to the activated species, by being in contact with the donor surface, is called the *accepting surface*. The donor surface can be mounted on an inert support and physically mixed with the acceptor phase or it can be mounted directly on the acceptor phase (see Figure 2.2).

Movement of the spillover species is achieved by the formation of equivalent bonds with similar neighbouring surface atoms. In essence, it is an effective exchange of bonds between the adsorbed species and the surface, which facilitates movement. Surface diffusion of the spillover species is generally agreed to be the rate limiting step in the overall process of spillover (Conner et al, 1986; Conner et al, 1995). The energetics of hydrogen spillover ($H_{so}$) is illustrated in Figure 2.3.

Reverse spillover occurs when the spillover species diffuses back to the activating center, where it can recombine (if dissociated), react or desorb. At steady state, spillover involves a competitive formation of spillover species and their demise through reverse spillover (Conner et al, 1995).

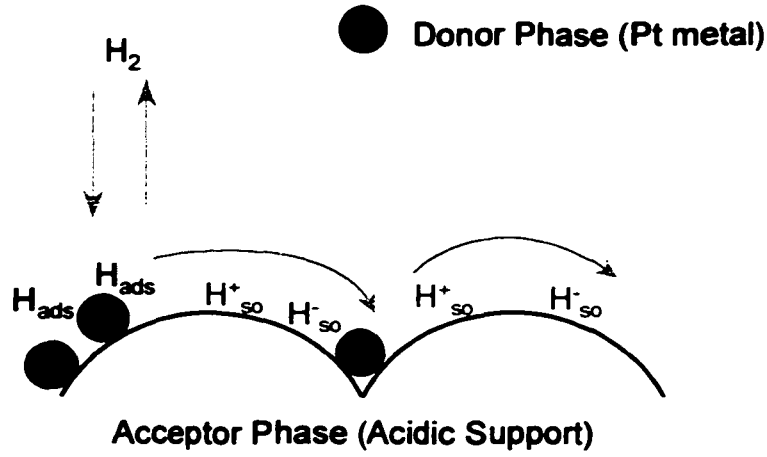



**Figure 2.2**: Schematic of Donor and Acceptor Phases for Spillover Species

The existence of spillover is a highly controversial subject, although recent evidence using electron spin resonance (ESR) in conjunction with a spin trap, provides convincing evidence of the existence of spillover (Spencer, 1994). Three conferences have been devoted entirely to the subject of spillover (Lyon, France (1983), Leipzig, Germany (1989) and Kyoto, Japan (1993)) echoing the support for this subject in the research community.

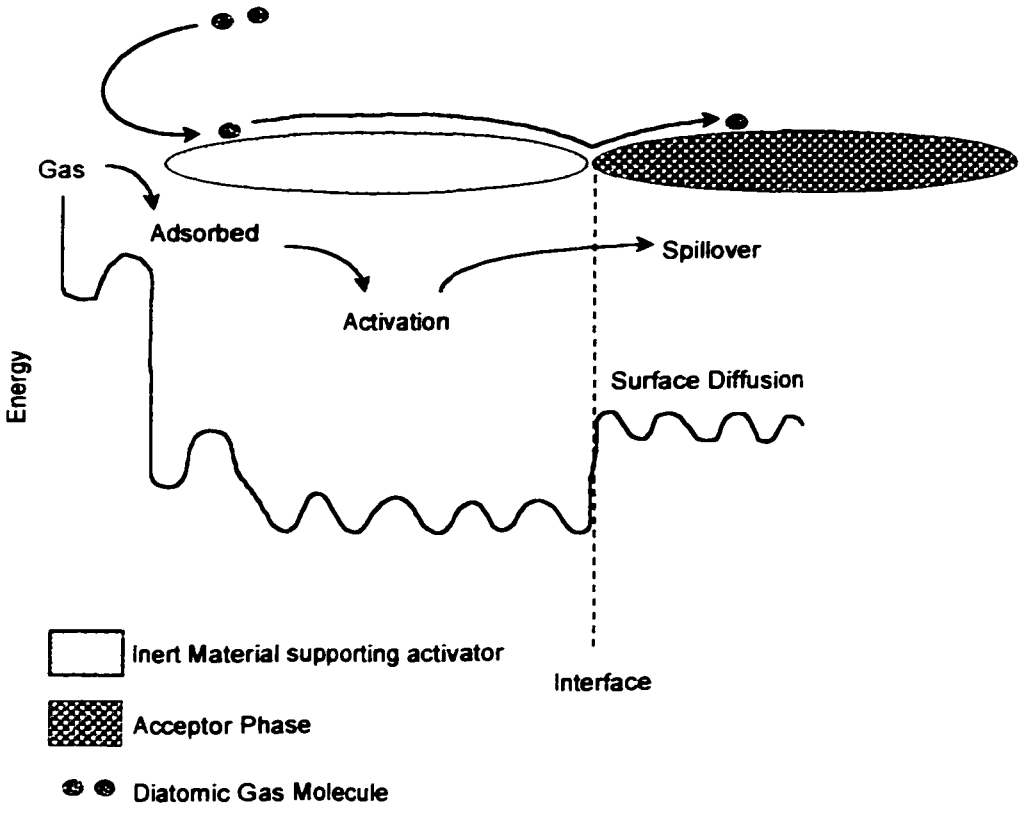



**Figure 2.3**: Energetics for Spillover of Gaseous Diatomic Molecule from the Gas Phase to the Accepting Surface (Conner et al, 1986)

### 2.3.2 Nature of Spillover Species

The most important spillover species are $H_2$ and $O_2$, although others such as CO (Teichner, 1993), $N_2$ (Conner & Falconer, 1995), isocyanate, methoxy ($CH_3O$), formate (CHOO) species as well as hydrocarbons, have been reported. Hydrogen is the fastest spillover process in terms of development of a spillover population, and is believed to be facilitated by surface hydroxyls (Ohgoshi et al, 1993; Dmitriev et al,

1983). A relationship between surface basicity and diffusion of $O_{so}$ (spillover oxygen) has been suggested (Martin & Duprez, 1993).

A noble metal (Group VIII transition metal such as Pt, Pd or Ni, listed in order of preference) supported on an oxide (carbon, $Al_2O_3$, $SiO_2$ but zeolite also possible) is used to generate spillover hydrogen (Bond, 1983). The nature of the hydrogen spillover species is a subject of debate. Some groups claim that molecular hydrogen forms two protonic hydrogen species ($H^+_{so}$), with the electrons reducing the metal of the metal oxide surface (see Equation 2-2):

$$H_2 \longrightarrow 2\ H^+_{so} + 2\ e^-_{so} \qquad (2\text{-}2)$$

There is evidence of this form of spillover species, when the metal is supported on a reducible oxide. However, this mechanism is difficult to envision on non-reducible metal oxides where spillover is active.

Others claim that diatomic spillover hydrogen species are formed which become bound to the surface ($H_{so}$-) (see Equation 2-3):

$$H_2 \longrightarrow 2\ H_{so}- \qquad (2\text{-}3)$$

Still, others suggest the formation of ionic species ($H^+_{so}$ or $H^-_{so}$) upon $H_2$ dissociation (see Equation 2-4):

$$H_2 \longrightarrow H^+_{so} + H^-_{so} \qquad (2\text{-}4)$$

although a $H^-_{so}$ has never been detected.

Finally, a free radical species is proposed by some groups ($H\bullet_{so}$) (see Equation 2-5):

$$H_2 \longrightarrow 2\ H_{so}\bullet \qquad (2\text{-}5)$$

Irrespective of the nature of the spillover species, profound effects on the reaction rate are claimed. It is believed that spillover can proceed by a variety of mechanisms, and may involve any one of the proposed species under certain circumstances. It is generally believed that the nature of the acceptor is influential in determining the form of the spillover species.

## 2.4 INCORPORATION OF HYDRIDE TRANSFER PROMOTER INTO SOLID ACID ALKYLATION CATALYST DESIGN

Solid acid catalysed reactions suffer from the tendency for the acid sites to become deactivated due to coke deposition. It is proposed that the onset of catalyst deactivation can be delayed by incorporating a noble metal into the catalyst design to activate hydrogen spillover.

### 2.4.1 Proposed Alkylation Mechanism Involving Spillover

It is proposed that spillover hydrogen can diffuse to coke retained on the acid sites of the metal oxide surface, and hydrogenate it to form smaller hydrocarbons which can diffuse out of the pore network. The acid site will thus be regenerated and

the accumulation of polymerized materials will be minimized (Conner & Falconer, 1995). Catalyst lifetime will be extended and steric restrictions of transitional species minimized. Hopefully this will exert a positive effect on the production of the bulky isomer 2,2,4-TMP.

It is also possible for spillover hydrogen to enhance the hydride transfer ability of the catalyst (see Figure 2.4). As previously mentioned, the nature of the acceptor phase is influential in determining the form of the spillover species. For zeolites, it is generally believed that spillover species assume the form of $H^+_{so}$ and $H^-_{so}$. The noble metal (Pt shown) will promote the adsorption of molecular hydrogen and form the spillover species ($H^+_{so}$ and $H^-_{so}$) according to Equation 2-4. It has been well documented that exchange with surface -OH groups is promoted by noble metals, with Pt demonstrating superiority over all others (Dmitriev et al, 1983).

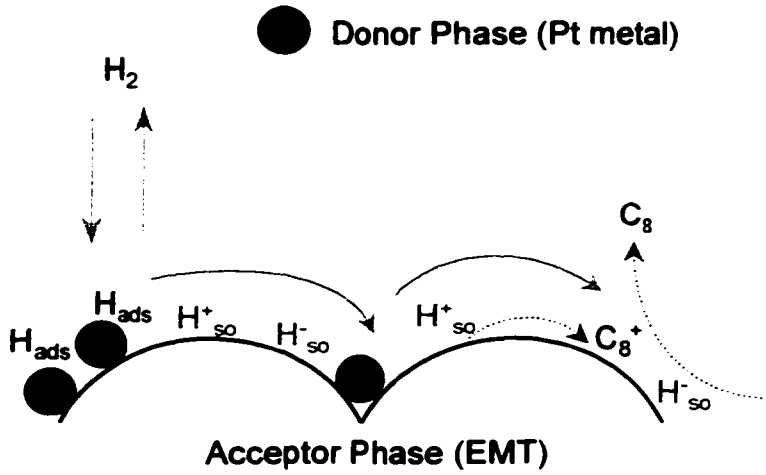



**Figure 2.4:** Proposed Mechanism for Hydrogen Spillover Participation in Butene/Isobutane Alkylation

It is proposed that an adsorbed octyl carbenium ion could accept a spillover hydride ion ($H^-_{so}$) and desorb as an octane product. The spillover hydrogen proton ($H^+_{so}$) could regenerate the acid site on the catalyst surface, thus completing the cycle

according to Equation 2-6 (see Figure 2.4).

$$i\text{-}C_8^{+}{}_{(surf)} + H^{+}{}_{so} + H^{-}{}_{so} \longrightarrow i\text{-}C_8 + H^{+}{}_{(surf)} \qquad (2\text{-}6)$$

This mode of hydride transfer could supplement that provided by the isobutane.

Spillover could provide additional benefits towards alkylation. During oxidative regeneration, the noble metal could facilitate oxygen spillover, such that lower temperatures could be employed to achieve the efficient removal of retained hydrocarbons. Incorporation of a metal into the catalyst design thus serves a multi-purpose.

### 2.4.2 Mode of Incorporation of Spillover Activator into Catalyst Design

There is considerable evidence that the rate-determining step of spillover is the diffusion of the spillover species from the donor phase to the acceptor (Conner & Falconer, 1995). For example, isomerization of *n*-$C_5$ demands intimate contact of the noble metal with the acidic support (Fujimoto, 1993; Aimoto et al, 1993). However, other reactions appear to be less sensitive to the span of separation (Conner & Falconer, 1995).

The noble metal, Pt, will be impregnated directly onto EMT and Y zeolites, to provide the minimum possible separation distance for spillover movement. The performance of the Pt impregnated materials will be compared to the parent materials, where no noble metal is present. Although hydrogen spillover can not be conclusively proven using this approach, it is expected that Pt will increase the amount of reactive hydrogen in the vicinity of the acid sites. Therefore, the benefit of Pt incorporation into the catalyst design with respect to reactive hydrogen concentration, can be assessed.

# Chapter 3

# Catalyst Preparation

Pure cubic polymorph of faujasite (FAU) can be synthesized from aluminosilicate hydrogels containing high concentrations of sodium ($Na_2O$/ $Al_2O_3$ = 3.1). The framework Si/Al ratio of the faujasite product ranges from 1.5 to 3 (Delprato et al, 1990), but impurity phases such as gismondine or gmelinite-type zeolites are often present in the crystalline product at the upper Si/Al limit.

The amount of aluminum incorporation into the matrix can be suppressed through the addition of an organic template to the hydrogel. Thus, the Si/Al ratio of the zeolite product can be increased without any need for post-synthesis treatment (i.e. chemical dealumination or steam dealumination). Recently, crown-ether templates have been applied successfully in this capacity, with both cubic (FAU) and hexagonal (EMT) phase polymorphs of faujasite being synthesized, with Si/Al ratio approaching 5 (Delprato et al, 1990). It is believed that the reduction of Al in the zeolite framework, is a consequence of the reaction mixture pH decreasing during aging and crystallization, in contradiction to what transpires during cubic phase synthesis from Na-rich hydrogels (Y zeolite).

FAU and EMT have similar structure types and hence, geometrical pore sizes and cages (see Figure 3.1). In FAU, the largest voids formed are called "supercages", with a diameter of 1.3 nm and a void volume of 1.15 $nm^3$ (van Santen, 1991). Accessibility to the supercage occurs through four circular 12-membered oxygen windows, each with a free dimension of 0.74 nm.

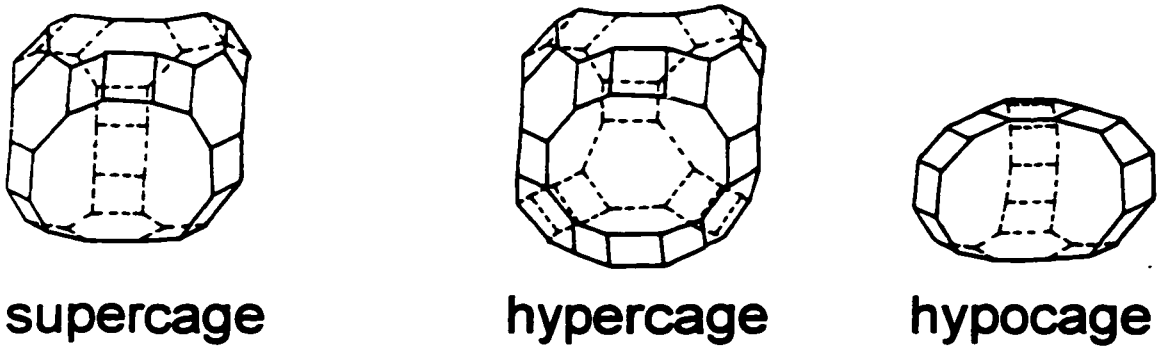



**Figure 3.1:** Polyhedral Cages occurring in cubic (Y, FAU) and hexagonal (EMT) phase Faujasites (*reprinted from Zeolites 9, Martens et al, "Investigation of the Pore Architecture of CSZ-1 Zeolites with the Decane Test Reaction", 423-427 (1989), Figure 1 only, with permission from Elsevier Science)*

EMT has an equal number of two types of large cages (Martens et al, 1989). The largest of the void spaces, called "hypercages", has a void volume of 1.24 $nm^3$, slightly greater than that of the supercages found in FAU. The "hypercages" have a free dimension of 1.3 x 1.3 x 1.4 nm and can be entered through a total of five channels: two circular channels similar to the entrances of the supercages in FAU and three elliptically shaped apertures with free diameters of 0.69 nm x 0.74 nm (Thomas et al, 1982). More importantly, the entrance to the "hypercage" is via straight channels. The smaller of the void spaces in EMT, called the "hypocages", have a void volume of 0.61 $nm^3$ which is significantly smaller than the "supercages" of FAU (van Santen, 1991). The "hypocages" have free dimensions of 0.69 x 1.3 x 1.3 nm and can be accessed through three elliptic windows (Thomas et al, 1982).

## 3.1 METHOD OF PREPARATION OF Na-EMT

The synthesis of Na-EMT appears to be more of an art than a science. Although recipes available in the literature are followed exactly, successful EMT synthesis is often elusive.

### 3.1.1 Chemical Sources and their Functions

The chemical species required for EMT synthesis and their functions, are summarized in Table 3.1 (Jansen, 1991; Feijen et al, 1994a). The choice of Al- and Si-sources does not appear to be critical for successful synthesis. Typical Si-sources include silicon alkoxides (TMAS, TEOS), water glass, colloidal silica (Ludox HS-40, Ludox AS-40) and fumed silica. Common Al-sources are gibbsite, sodium aluminate, metallic aluminum powder and pseudo-boehmite. Sodium is added in the form of sodium hydroxide with some potentially provided by the Si- and Al-sources.

Hydrated $Na^+$ cations (primary cation) direct the formation of the faujasite sheets, consisting of cubo-octahedra interconnected through hexagonal prisms. Cationic Na-18-crown-6 ether complexes act as secondary cations and facilitate the linking of the faujasite sheets into the hexagonal structure (see Figure 3.2).

**Table 3.1:** Chemical Sources and their Function in EMT Synthesis

| SOURCE | FUNCTION(S) |
|---|---|
| $SiO_2$ | • Primary building unit(s) of framework |
| $AlO_2^-$ | • Origin of framework charge |
| $OH^-$ | • Mineralizer, guest molecule |
| $Na^+$ | • charge balancing cation for framework charge<br>• primary directing cation |
| 18-crown-6 ether (see Figure 3.3) | • secondary directing cation (complexes with $Na^+$ cation) |
| Water | • solvent, guest molecule |

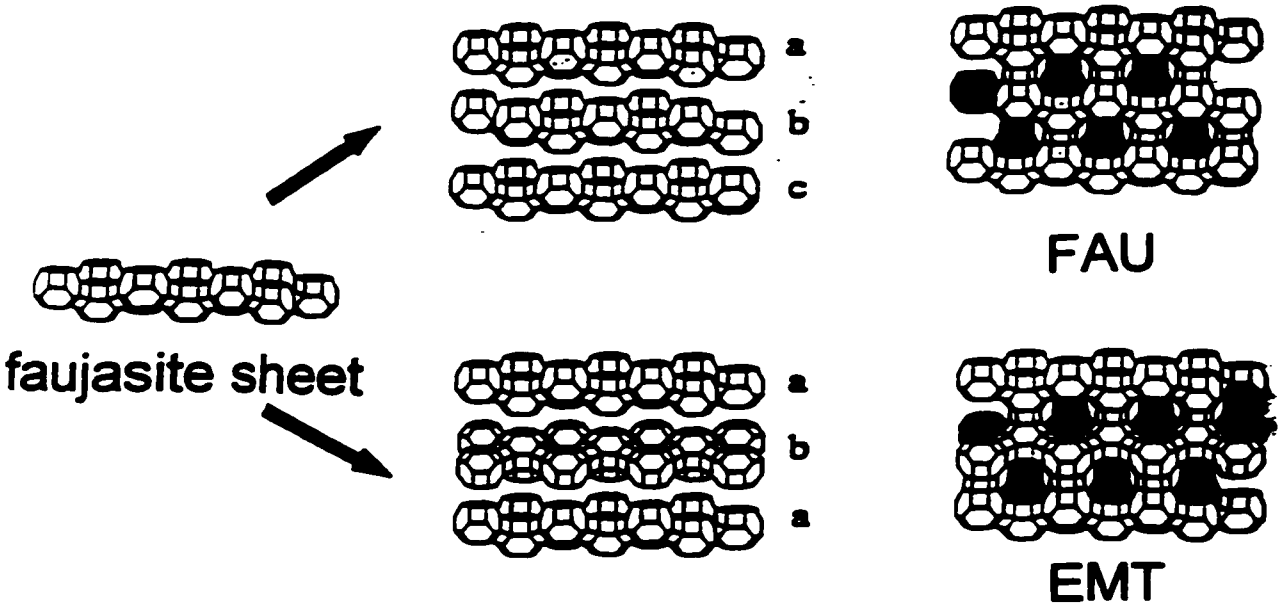



**Figure 3.2:** Assembly of Faujasite Sheets to yield FAU and EMT Phases (reprinted from J. Am. Chem. Soc. 116(7), Feijen et al, "Role of 18-Crown-6 and 15-Crown-5 Ethers in the Crystallization of Polytype Faujasite Zeolites", 2950-2957 (1994), with permission from ACS, Publications Division)

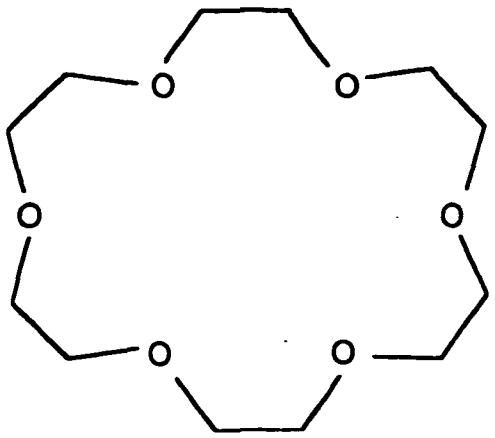


**Figure 3.3:** Structure of 18-crown-6 ether Template

Under conditions of high $Na^+$ content, the structure directing role of the crown ether is masked by the influence of the Na cation, favouring the formation of FAU (Burkett & Davis, 1993). This emphasizes the importance of the $Na_2O$/18-crown-6 ether ratio in the gel, and its crucial role in determining the outcome of the crystallization process.

The $Na_2O/Al_2O_3$ ratio is another important gel property, which is influential in determining the properties of the crystallized product. With a $Na_2O/Al_2O_3$ ratio of 2 and sufficient 18-crown-6 ether available, no crystallization occurs. At higher $Na_2O/Al_2O_3$ levels in the range of 2.4 to 3, the cubic polytype (FAU) is favoured, even in the presence of adequate 18-crown-6 ether. Pure hexagonal polytype (EMT) is produced from hydrogels containing sufficient 18-crown-6 ether and a $Na_2O/Al_2O_3$ ratio ranging from 2.0 to 2.4 (Delprato, 1990). Ideally, the $Na_2O/Al_2O_3$ level should be 2.4, to maximize the purity and crystallinity of EMT (Jansen, 1991).

### 3.1.2 List of Materials

The reagents employed in the present research are summarized in Table 3.2. Impurities such as $Fe^{3+}$ and $K^{+}$ exert minor influences compared to the effects of $Al^{3+}$ and $Na^{+}$, respectively, during the synthesis.

**Table 3.2:** List of Materials for EMT Synthesis

| Reagent | Source | Description |
|---|---|---|
| Ludox HS-40 | Aldrich | • 40 wt. % colloidal $SiO_2$ in $H_2O$<br>• Impurity: Al < 500 ppm |
| Gibbsite, $Al(OH)_3$ | Fluka | • 64-66 % $Al_2O_3$<br>• Impurity: Fe < 3 ppm |
| NaOH Pellets, Technical grade | BDH | • 97 % purity<br>• Impurities: K < 20,000 ppm, Fe < 1000 ppm, Ni < 1000 ppm |
| 18-crown-6 ether | Acros Chemicals | • 99 % purity |
| Double de-ionized water | | |

### 3.1.3 Preparation of the Hydrogel

Synthesis of EMT is difficult. Nine months worth of catalyst preparation efforts, employing six different published methods, did not produce any batches of EMT with a high degree of purity. Prof. J. A. Martens (Centre for Surface Science and Catalysis, K. U. Leuven, Belgium) is an expert in the area of catalyst synthesis, characterizaiton and catalysis. He has experience in the synthesis of EMT and has co-authored several papers on the role of the crown-ether template during the crystallization step. Prof. Martens (Gossens, 1998) provided a detailed description for EMT synthesis (modified method of Feijen et al, 1994b). Fourteen successful batches of EMT have been prepared in this laboratory, using this approach (see Appendix A1.1).

The synthesis began with the preparation of a sodium aluminate solution (Gossens, 1998; Feijen et al, 1994b). The mixture was heated, as $Al_2O_3$ is not easily dissolved. Once $Al_2O_3$ dissolution was complete, the solution was cooled to room temperature. Some of the Al may precipitate but this does not appear to affect the synthesis. Upon reaching room temperature, the amount of water that had evaporated during the heating step, was determined, and added back to the solution.

The silica sol was diluted with water and then the crown ether was added. This is necessary to ensure adequate dissolution of the crown ether in the silica sol. This mixture was added to the sodium aluminate solution and then further diluted with water. The overall composition of the hydrogel was:

$$10\ SiO_2 : 1.00\ Al_2O_3 : 2.40\ Na_2O : 0.97\ \text{18-crown-6 ether} : 140.25\ H_2O$$

### 3.1.4 The Aging Period

The resulting gel was transferred into a teflon bottle and aged at room temperature for 3 days in the absence of agitation. Maintaining the gel at a temperature below the crystallization temperature is crucial, in order to achieve the desired product within an acceptable period of time. It is possible to shorten the aging period to 1 day, as suggested by Delprato et al (1990), but a longer aging period enhances uniformity in crystal size and composition.

One important step during the aging period is the depolymerization of the silica sol, increasing the concentration of dissolved silicate species. Monomeric silicate anions condense and polymerize to produce oligomeric species in solution, which in turn react with monomeric aluminate anions to produce aluminosilicate structures. These aluminosilicate species concomitantly undergo re-dissolution and re-condensation during the aging period (Feijen et al, 1994a).

The pH of the hydrogel was found to decrease significantly during the aging period (see Figure 3.4). This behavior is not reported by Delprato et al (1990), as the

aging period of one day was used in that particular study. However, a notable drop in the pH during the crystallization period is reported by the Delprato study.

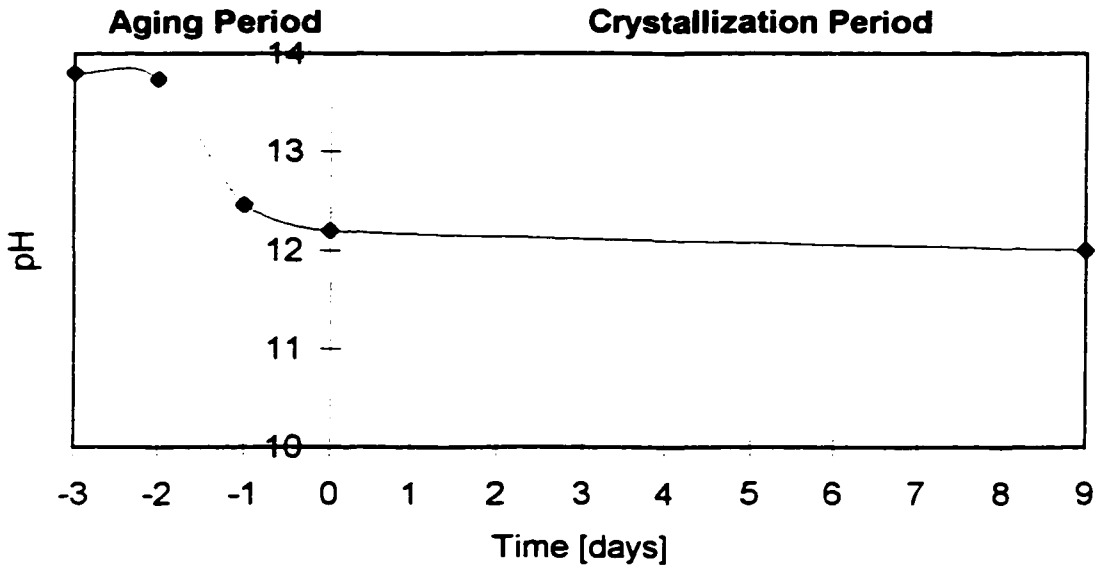



**Figure 3.4:** Evolution of pH during the Aging and Crystallization Periods

### 3.1.5 The Crystallization Step

Once the aging period had elapsed, the bottle was placed in an oven maintained at 100°C for a period of 9 days. The elevated temperature favours the formation of aluminosilicate structures, thus increasing their concentration in the solution. Eventually the solution becomes supersaturated with precursor species. Chemical aggregation of these precursors results in the formation of germ-nuclei, which can re-dissolve upon depolymerization. The germ-nuclei continue to grow over time until some nuclei achieve a critical dimension necessary to become viable and spontaneously spawn crystal growth.

Both nucleation and crystallization proceed simultaneously with both processes consuming the same precursors. Eventually, the source of precursor

species becomes depleted causing the nucleation and crystallization rates to decline.

The crystallization process follows Ostwald's rule, by which the thermodynamically least favourable phase forms first, followed by successively more stable phases. The sequence of phases which are formed during the synthesis are: amorphous $\Rightarrow$ EMT $\Rightarrow$ Na-P (Gismondine type) (Feijen et al, 1994a). Higher temperatures favour dense phase development (Na-P), as the amount of water in the liquid phase decreases.

Contrary to what takes place during Y zeolite synthesis from inorganic hydrogels, pH drops during the crystallization phase in hydrogels containing crown ethers. When a three day aging period was employed, the pH dropped slightly by 0.2 units during the crystallization phase (see Figure 3.4). With a shorter aging period, the drop in pH during the crystallization phase is more substantial. Over the course of an eight day crystallization period, the pH decreases by approximately 1.5 units (Delprato et al, 1990). This results in a Si/Al gradient in the crystals ranging from 3.5 at the center to greater than 5 at the edges. By extending the aging period to 3 days, the majority of the pH reduction occurred prior to the crystallization step, favouring a uniform Si/Al composition and size amongst the crystal population. Also, the lower pH reduces the extent of Al incorporation into the hexagonal lattice, resulting in a higher Si/Al ratio in the EMT crystals (Delprato et al, 1990; Feijen et al, 1994a).

### 3.1.6 Template Removal

After the crystallization period had elapsed, the teflon bottle was removed from the oven and cooled to room temperature. The product was recovered by filtration, washed with double de-ionized water until the pH of the filtrate was neutral, and dried overnight at 80°C.

The dried product was calcined in flowing air by increasing the temperature at a rate of 1°C/min, from room temperature to 200°C and sustained at this temperature

for 2 h. This removes the physisorbed water prior to the template combustion. The temperature was then ramped at a rate of 1°C/min to 425°C, where it was held constant for 5 h. Mass losses due to template combustion represent approximately 30 % of the calcined product mass. The average calcined product yield from a single batch is 10.50 g EMT (Na-form).

Figure 3.5 illustrates the thermogravimetric analysis/differential temperature analysis (TGA/DTA) employing 10 % $O_2$ in He gas mixture (details in Appendix A1.6). Two distinct stages of weight loss were apparent during template removal. The first mass loss is associated with an endothermic process occurring between 25 to 150°C, and represents the removal of physically adsorbed water. The second weight loss begins at approximately 325°C, and is accompanied by a steep exotherm accounting for combustion of the template. These results are similar to those reported for EMT in the literature (Feijen et al, 1994a; Annen et al, 1991).

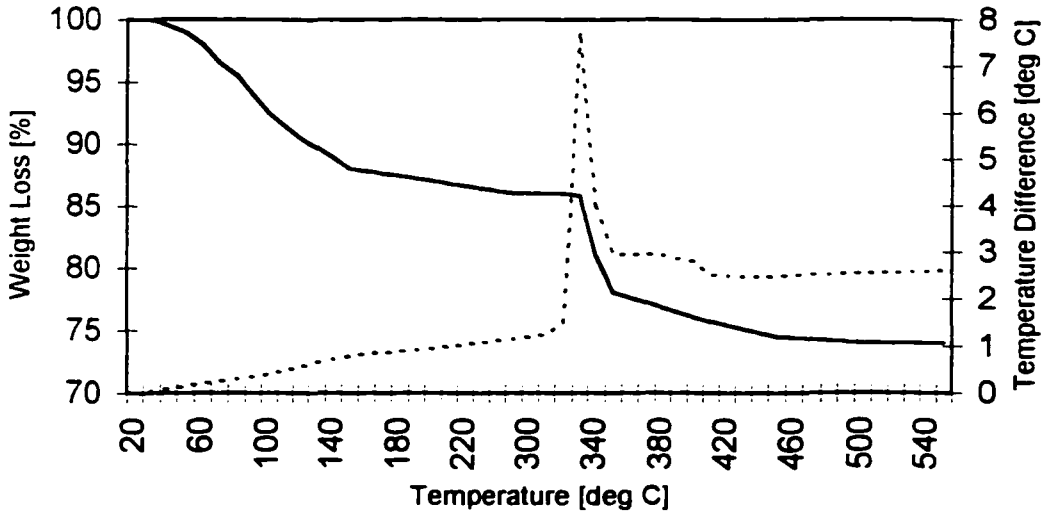



**Figure 3.5:** Thermal Decomposition Patterns for Template Removal from EMT (Batch G5019)

### 3.1.7 Phase Identification

The identification of a zeolite was made by comparing the sample powder X-ray diffraction (XRD) pattern (see Appendix A1.2 for details), with those of known standards or published patterns in the literature. The existence of EMT is validated using the diffractogram of Delprato et al (1990) as a reference. The presence of impurities or intergrowths of cubic polymorph (FAU) are indicated by the presence of major peaks of both EMT and FAU X-ray diffractograms in the sample pattern (see Figure 3.6). The XRD pattern of the final product matched that of Delprato et al (1990), confirming the identify of EMT and verifying a successful synthesis (see Figure 3.7).

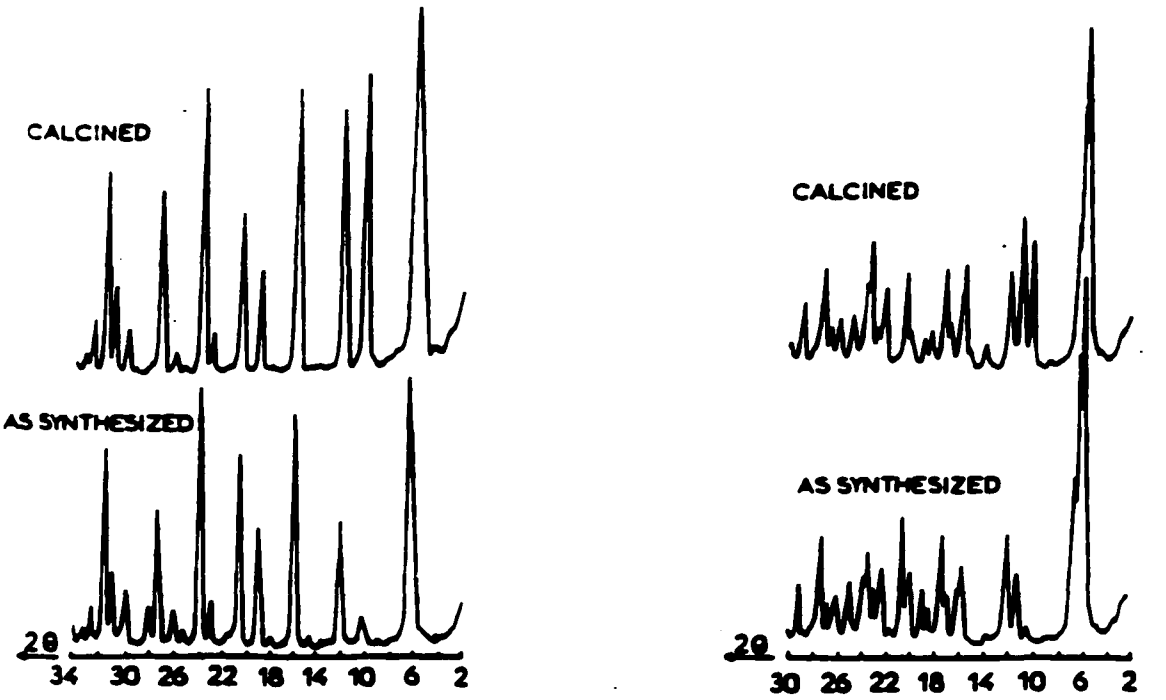



**Figure 3.6:** Published Powder X-ray Diffraction Pattern for cubic (FAU) and hexagonal (EMT) phase Faujasites (*reprinted from Zeolites 10, Delprato et al, "Synthesis of new silica-rich cubic and hexagonal faujasites using crown-ether-based supramolecules as templates", 546-552 (1990), Figures 4 & 5 only, with permission from Elsevier Science)*

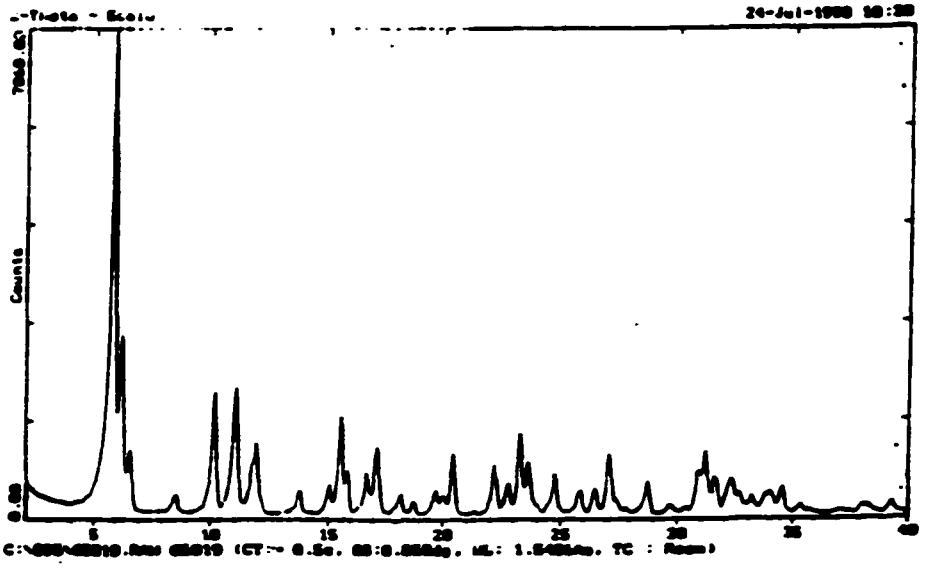


**Figure 3.7:** Powder X-ray Diffraction Pattern of Synthesized EMT (Batch G5019)

## 3.2 BATCH TO BATCH VARIATION OF EMT SYNTHESIS

The XRD patterns of all batches corresponded closely to that of Delprato et al, 1990 (Figure 3.6), confirming the existence of a hexagonal structure. No evidence of FAU impurities or intergrowths were detected in the synthesized products.

Surface area measurements confirmed the existence of a highly crystalline product (see Table 3.3). However, ANOVA analysis detected significant batch to batch variation. This conclusion was supported by a 12 % variation in XRD peak intensity for the strongest peak in the EMT diffraction pattern ($2\theta \sim 5.9°$). This emphasizes the importance of developing a strategy to minimize/eliminate the effects of batch to batch variation for the purposes of catalyst testing. This approach will be discussed in greater detail in Section 3.3.

**Table 3.3:** ANOVA Analysis on Batch Surface Area Measurements for Na-EMT

| | ANOVA Results [$m^2/g$] |
|---|---|
| Grand Average | 906 |
| *Between Batch* Standard Deviation | 25 |
| *Within Batch* Standard Deviation | 14 |
| *Equipment* Standard Deviation | 2 |

## 3.3 AMMONIUM ION EXCHANGE OF Na-EMT TO H-EMT

The H-form of EMT (H-EMT) was obtained by ion exchange of the parent material (Na-EMT) with an $NH_4NO_3$ solution, followed by calcination to drive off $NH_3$ (see Appendix A1.3 for details). In total, three exchange cycles are employed, with each exchange cycle followed by a calcination step. This is critical, as it redistributes the residual Na to new locations that are more accessible for removal during the subsequent exchange step. Literature measurements predict 71 % Na removal in the first exchange cycle, 85 % Na removal in the second exchange cycle and approximately 93 % overall Na removal is expected in the third exchange cycle (Dougnier et al, 1992).

The surface area of EMT was reduced by 17 % (from 906 $m^2/g$ for Na-EMT to 755 $m^2/g$ for H-EMT) as a result of the exchange process. The XRD measurements of H-EMT suggest that the crystallinity of the exchanged EMT improves, as indicated by an increase in the overall peak intensity on the X-ray diffractograms. This suggests that the removal of $Na^+$ does have a disruptive effect on the crystalline structure but rather causes the structure to contract with $Na^+$ removal. The material retains its structural integrity throughout the exchange process.

## 3.4 CHARACTERIZATION OF EMT AND Y

The H-EMT powder was pelletized, crushed and sieved to a particle size range of 0.25 to 0.50 mm diameter (60 US mesh and 35 US mesh respectively). Similarly, the commerical Y zeolite extrudate, was crushed and sieved to the same particle size range. A summary of the catalyst properties for both zeolites is provided in Table 3.4. Details of the analytical techniques used to characterize the catalysts, are provided in Appendix 1.

A slightly higher surface area and lower sodium content were measured for H-EMT relative to H-Y. Similar Si/Al ratios were estimated for both materials, although differences in aluminum environment were detected. A greater proportion of aluminum with one aluminum in the next-nearest neighbour position (Si(1Al)), were found to exist on H-EMT relative to H-Y. Tetrahedral and octehedral aluminum coordination were identified on both materials; however, evidence of hybrid structures were also found to exist on H-EMT.

**Table 3.4:** Summary of Catalyst Properties for EMT and Y ($T_{calc}$=425°C)

| Property | H-EMT | H-Y | Method | Appendix Reference |
|---|---|---|---|---|
| Surface Area [$m^2/g$] | 755 | 620 | 5-point BET ($N_2$ adsorption) | A1.7 |
| Na Content [ppm] | 255 | 930 | Atomic Absorption | A1.4 |
| Si/Al Ratio | 6.94 | 6.26 | $^{29}$Si MAS NMR | A1.5 |
| Si(0Al) [%] | 46.5 | 46.9 | | |
| Si(1Al) [%] | 49.7 | 42.9 | | |
| Si(2Al) [%] | 3.5 | 9.6 | | |
| Si(3Al) [%] | 0.3 | 0.6 | | |
| Si(3Al) [%] | 0.0 | 0.0 | | |
| Al Coordination | 4, 6, hybrid | 4, 6 | $^{27}$Al MAS NMR | A1.5 |

## 3.5 PREPARATION OF Pt SUPPORTED ZEOLITES

The platinum was introduced into the zeolite by contact of the support, with an aqueous solution containing hexachloroplatinate (Aldrich). The method employed for impregnation was the incipient wetness technique, whereby, just enough solution is provided to completely fill the pores of the freshly calcined solid.

### 3.5.1 Method of Preparation

The zeolite was freshly calcined, weighed and stored in a dessicator. The amount of $H_2PtCl_6 \cdot xH_2O$ (38.7 wt. % Pt) (Aldrich) needed to achieve the desired Pt loading was calculated. Similarly, the amount of water which was required to exactly fill the pores of the zeolite, was determined, using pore volume measurements from nitrogen adsorption studies (see Appendix A1.9 for details).

The water was added to $H_2PtCl_6 \cdot xH_2O$ solid and mixed thoroughly (see Table 3.5). Next, the zeolite was added to the solution and stirred. The wetted solids were left at room temperature for 24 h, with periodic stirring. The dried solids were placed in an oven at 80°C overnight, to remove as much water as possible prior to the calcination and reduction steps.

**Table 3.5:** Quantities used in the Preparation of Pt/EMT and Pt/Y Systems

| Catalyst System | Mass Calcined Zeolite | Mass Double De-ionized water [g] | Mass $H_2PtCl_6.xH_2O$[1] [g] |
|---|---|---|---|
| 0.1%Pt/EMT | 12.413 g EMT | 6.62 | 0.03044 |
| 0.5%Pt/EMT | 12.244 g EMT | 6.75 | 0.16293 |
| 0.5%Pt/Y | 25.000 g Y | 12.598 | 0.32301 |

1 Aldrich, 38.7 wt% Pt

### 3.5.2 Calcination and Reduction

The excess material from the impregnating solution must be removed by calcination, and the metal reduced to its active form. Conditions for these steps are crucial, in order to minimize the extent of metal agglomeration (sintering), which can lead to partial collapse of the zeolite structure (Feijen et al, 1994a)

Activation in flowing air prior to reduction is recommended, to yield a highly dispersed platinum cluster in the zeolite. A low calcination temperature is critical, with suggested temperatures ranging from 300 to 350°C. An intermediate calcination temperature in the recommended range was selected for the present research. The calcination procedure applied for catalyst activation, increased the temperature at 5°C/min to 325°C in flowing air. The temperature was maintained at this temperature for a period of 3 h.

Immediately following the calcination step, the catalyst was reduced. The recommended temperature for the reduction step ranges from 350 to 500°C (Gates, 1995). Similar to calcination conditions, an intermediate temperature in the recommended range was chosen. The temperature was increased from 325°C to 425°C at a rate of 5°C/min in a flowing 10.1 % $H_2$/Ar gas mixture, and maintained at 425°C for 3 h. Both the calcination and reduction steps were performed externally prior to catalyst use in the reactor. When the catalyst was to be used for an experiment, the calcination and reduction were repeated *in situ*.

## 3.6 CHARACTERIZATION OF Pt/EMT AND Pt/Y

Hydrogen chemisorption measurements were performed on all Pt loaded catalysts, repeating the calcination and reduction cycles *in situ*, prior to chemisorption measurements. This data was used to determine the fraction of active Pt atoms exposed on the surface (see Appendix AI.8). This property is important as atoms

located within the metal particles are not active for surface reactions, and are inert with respect to catalytic processes.

The metal dispersion is defined as the percentage of metal atoms exposed on the surface of active metal particles, relative to all the metal atoms present in the sample (denoted by Pt loading). Calculated values for Pt dispersion ranged from 74 to 91 %. Note that the Pt loading is estimated from amount of Pt provided in the impregnating solution per gram of calcined solid.

Incorporation of Pt into the pore network reduces the available surface area for reaction. The loss incurred by Pt presence is more noticeable on EMT relative to Y zeolite, at the same Pt loading. This may be a result of the improved Pt dispersion achieved on Y zeolite. A summary of the relevant properties measured for Pt impregnated catalysts is provided in Table 3.6.

**Table 3.6:** Summary of Catalyst Properties for Pt/EMT and Pt/Y Systems ($T_{calc}$=325°C; $T_{red}$=425°C)

| Property | EMT | 0.1%Pt/ EMT | 0.5%Pt/ EMT | Y | 0.5%Pt/ Y | Appendix Reference |
|---|---|---|---|---|---|---|
| Pt Loading [%] | n.a. | 0.1 | 0.5 | n.a. | 0.5 | |
| Surface Area [$m^2/g$] | 755 | 616 | 589 | 620 | 581 | A1.7 |
| Pt Dispersion [%] | n.a. | 74 | 76 | n.a. | 91 | A1.8 |

# Chapter 4

# Set-up of Microflow Reactor

The BTRS-Jr/PC reactor system is a new product line offered by Autoclave Engineers (AE), a Division of Snap-Tite. A basic form of the software control package, had been successfully demonstrated on other AE reactor systems, and was modified to meet the unique demands of our catalysis research. A complex sampling system was designed collaboratively with AE, permitting 15 samples to be collected with a minimum sampling frequency of 1 minute. This allows detailed evaluation of catalyst activity for the purpose of kinetic studies as well as monitoring the course of events leading to deactivation processes.

This chapter will provide a brief description of the capabilities of the equipment and the hardware and software challenges encountered during the design, installation and operational phases. The strategy for interfacing the reactor with the on-line GC will also be outlined, as well as the design of a split injector. A chronological log documenting the milestones and set-backs encountered from the design phase through the installation stage and concluding with the last experiment, is provided in Appendix 2.

## 4.1 AE BTRS-Jr/PC MICROFLOW REACTOR DESCRIPTION

### 4.1.1 Overview of System

The BTRS-Jr/PC reactor system is a bench-top reactor constructed entirely of 316 stainless steel (SS). It employs two mass flow controllers (MFC) and two high pressure liquid (HPL) pumps, for independent regulation of two gas and two liquid streams respectively (see Figure 4.1). The separate streams are pre-heated in the oven cabinet prior to mixing. The Reactor Status Valve, a 2-position 8-port valve located in the oven cabinet, facilitates the option of either diverting the pre-mixed feed stream off-line for feed analysis, or directing it to the reactor system for reaction.

The 0.413 in I.D. tubular style reactor is 12 in. in length, and is situated in the oven cabinet. A single thermowell runs down the center of the reactor with three separate thermocouples inserted at varying depths to measure the upper, middle and lower sections of the reactor bed. The total volume of void space in the reactor (excluding space occupied by thermowell) is 23 $cm^3$.

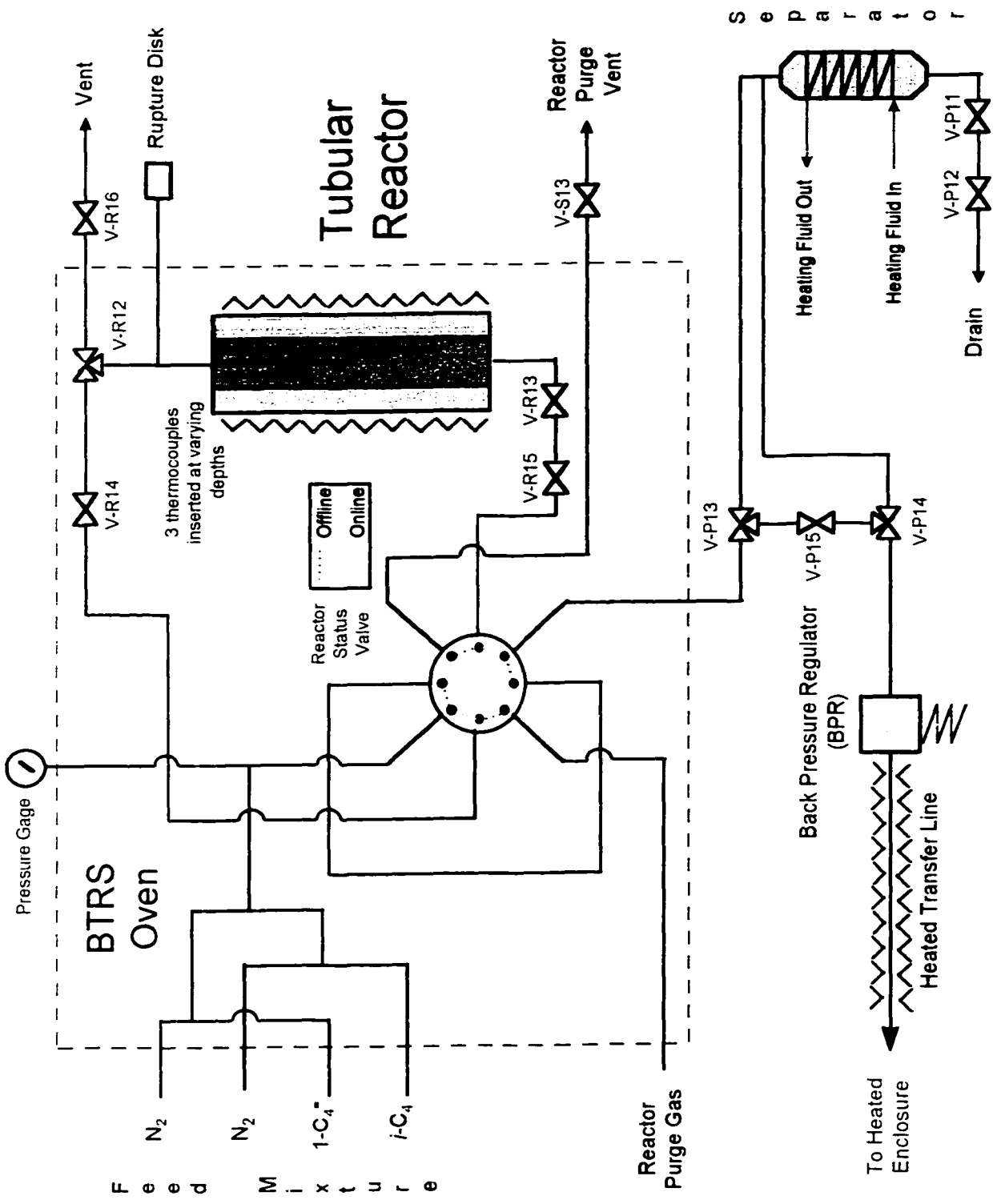



**Figure 4.1:** Flow Schematic of BTRS Reactor System

A single-zone clam-style furnace ($T_{max}$ = 650°C) jackets the reactor, permitting high temperature operation. Reactor pressure is regulated through a manually controlled back pressure regulator (BPR), mounted on the inside of the reactor oven. The system is rated for a maximum operating pressure of 2500 psig at 650°C.

Effluent from the reactor passes through the BPR and out the oven cabinet (see Figure 4.1). The de-pressurized gas travels through a heated transfer line (HTL) into a Heated Sample Enclosure (see Figure 4.2), which contains a Sample Valve (2-position, 6-port valve) and a Multiposition Trapping Valve (16-loops, each of 0.25 mL volume).

If the Sample Valve is in the *Collect* position, the sample gases flush through the loop of the Multiposition Trapping Valve, and exit through the Vent line. Simultaneously, helium flows through a HTL connected to the on-line GC, providing carrier gas flow for the installed capillary column. Alternatively, when the Sample Valve is in the *Transfer* position, helium flow flushes out the loop of the Multiposition Trapping valve and transports the sample to the on-line GC for analysis. Concurrently, sample gases from the reactor system are directly vented from the system.

Efforts were made to collect a bulk liquid sample from the reaction, to provide an estimate of catalyst yield. The Vent line from the Sample valve was coiled and immersed in an acetone/ice water bath, with the end of the tubing placed in a partially submerged Erlenmeyer flask. The liquid product condensed and collected in the flask over the duration of the reaction period. At the conclusion of the experiment, the flask was removed from the acetone/ice water bath and weighed. Some samples were analyzed using PE Trio-1 GC-MS system equipped with VG Lab-Base software, for the purpose of component identification (see Section 4.2.4).

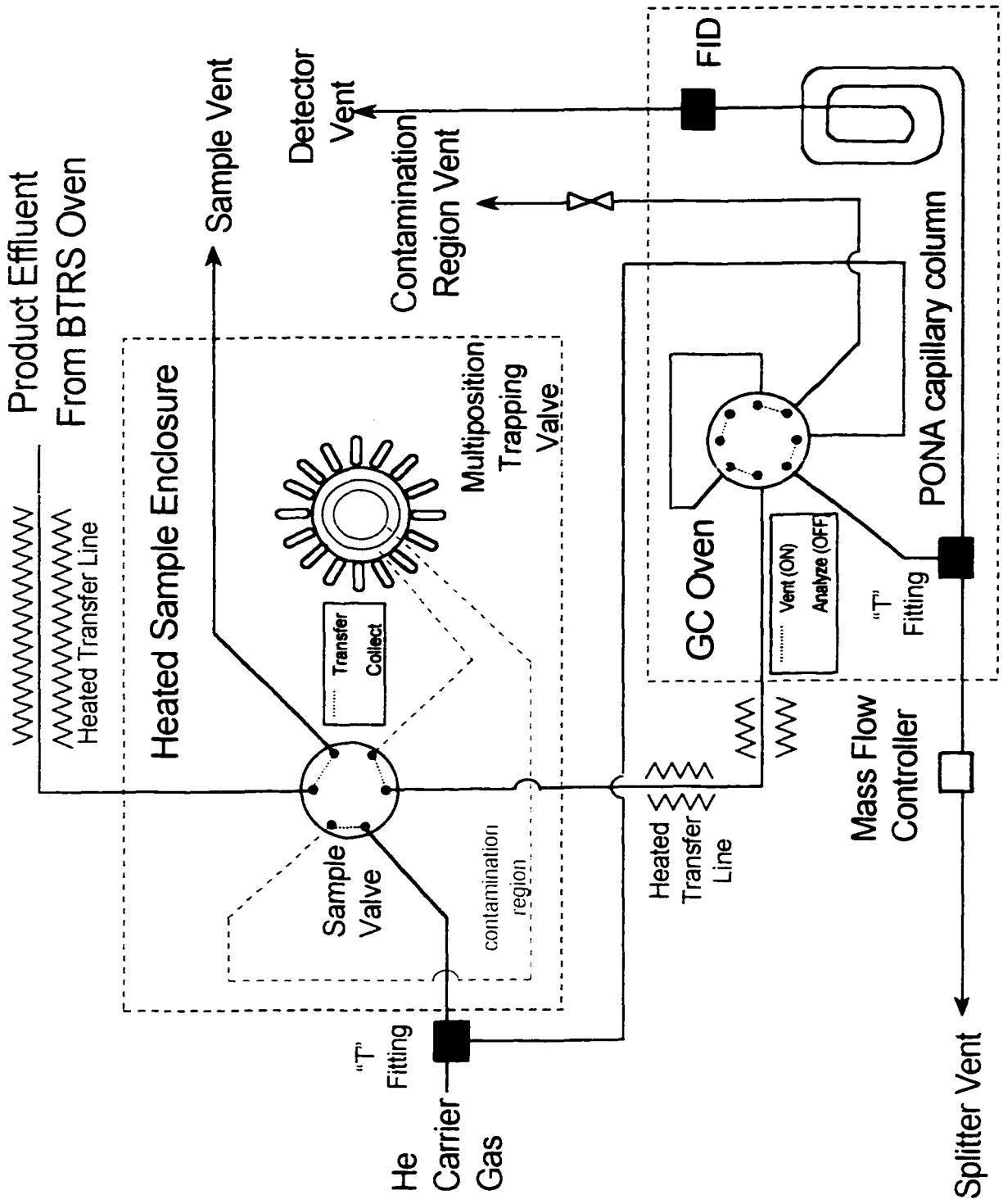



**Figure 4.2:** Flow Schematic of BTRS Sampling System

### 4.1.2 Software Capabilities

The reactor and sampling systems, with the exception of system pressure and GC programming, are computer controlled using a dual computing architecture strategy (see Figure 4.3). The Programmable Logic Controller (PLC) is dedicated to controlling the process, including implementing set point changes, switching valve positions, activating alarms and shutting down the equipment in the event of a dangerous operating condition. The (PC) workstation (using Wonderware software) acts as an interface between the operator and the equipment, facilitating manual entry of set point changes as well as activating programmed recipes for unattended operation. Details of the software capabilities are outlined in Appendix A3.1.1.

## 4.2 INTERFACING THE BTRS REACTOR SYSTEM WITH THE ON-LINE GC

The reactants and products from the BTRS system were analyzed on-line, using a Perkin Elmer (PE) Autosystem GC equipped with a PE NELSON 1020 GC Integrator. However, interfacing the GC with the reactor system was not included in the AE BTRS equipment purchase. The BTRS software could receive a READY (5 V) signal from the GC and send a START (24 V) signal to the GC, provided a GC READY signal was detected. These signals were to be received/sent from a module in the PLC. The procedure for wiring the connections to the GC were not provided in the purchasing contract with AE, and were part of the current research.

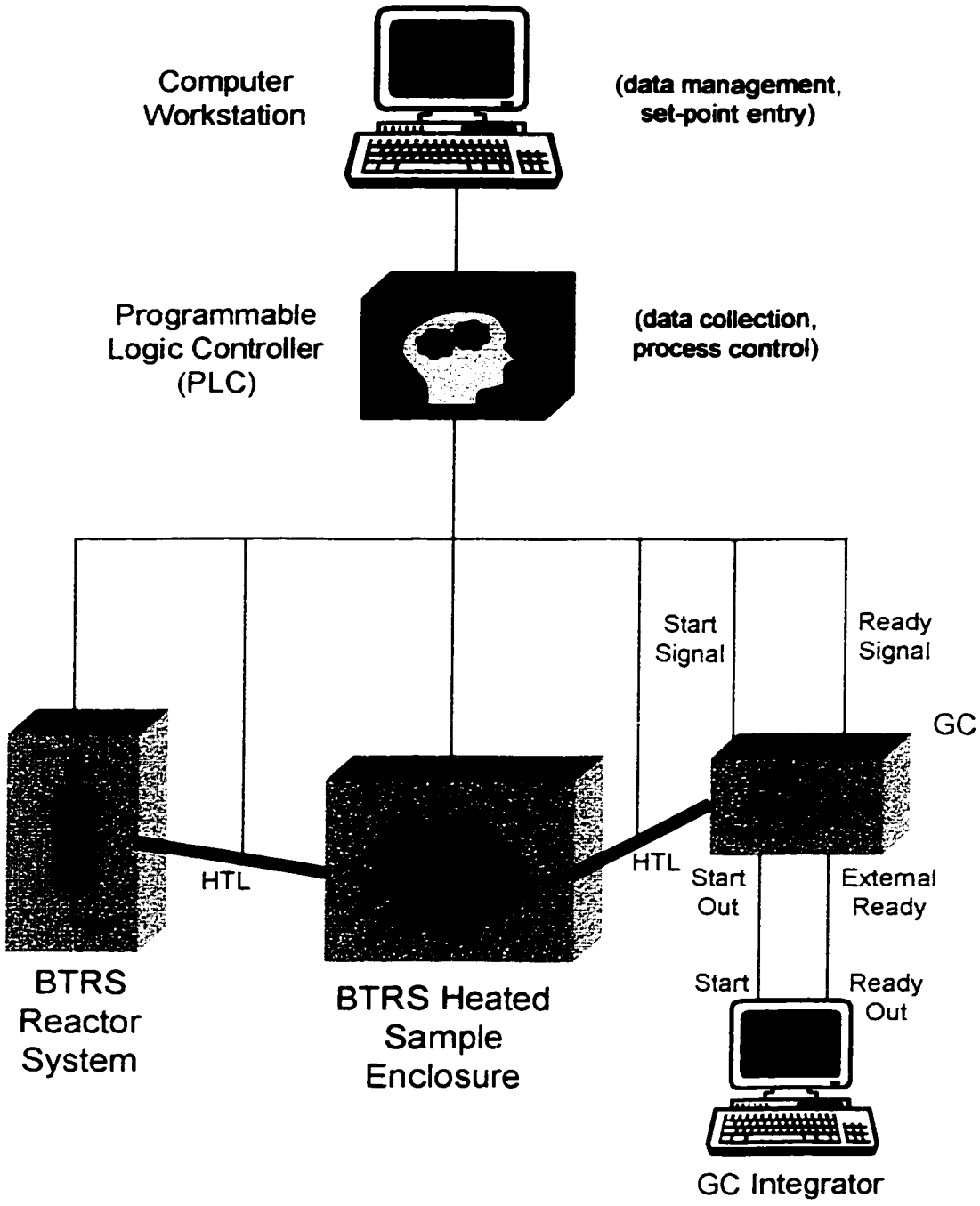



**Figure 4.3:** Information Flow and Control Strategy of BTRS

### 4.2.1 Electronic Communication between PLC, GC and Integrator

The Integrator and the GC have terminal strips with the following contact functions:

| | |
|---|---|
| READY OUT | signals an external device that the instrument is READY |
| START OUT | used to start an external device |
| EXT. READY | prevents the instrument from becoming READY until the external device is READY |
| EXT. START | provides a means to start the instrument from an external device (equivalent to pressing the RUN key) |

The terminal strips for the BTRS, GC and Integrator use the "NO" policy for contact closure, which means that the contact is normally open, but closed when READY.

Consultation with PE, resulted in a strategy to interface the Integrator to the GC and the GC to the PLC (see Figure 4.4). In this arrangement, the PLC displays the READY/NOT READY status of the GC. The GC does not achieve READY status until the integrator is READY. Therefore, a READY status at the PLC is only displayed when both the GC and Integrator are ready.

The PLC issues a START signal through the ENABLE command for GC Status. Note that a START signal for GC analysis cannot be sent unless a READY signal is detected by the PLC. If a READY signal is detected, the START signal from the PLC will initiate the active program loaded on the GC. Similarly, activation of the START signal at the GC automatically relays a START signal to the Integrator. This activates data collection and processing of peaks, according to the active program loaded on the Integrator.

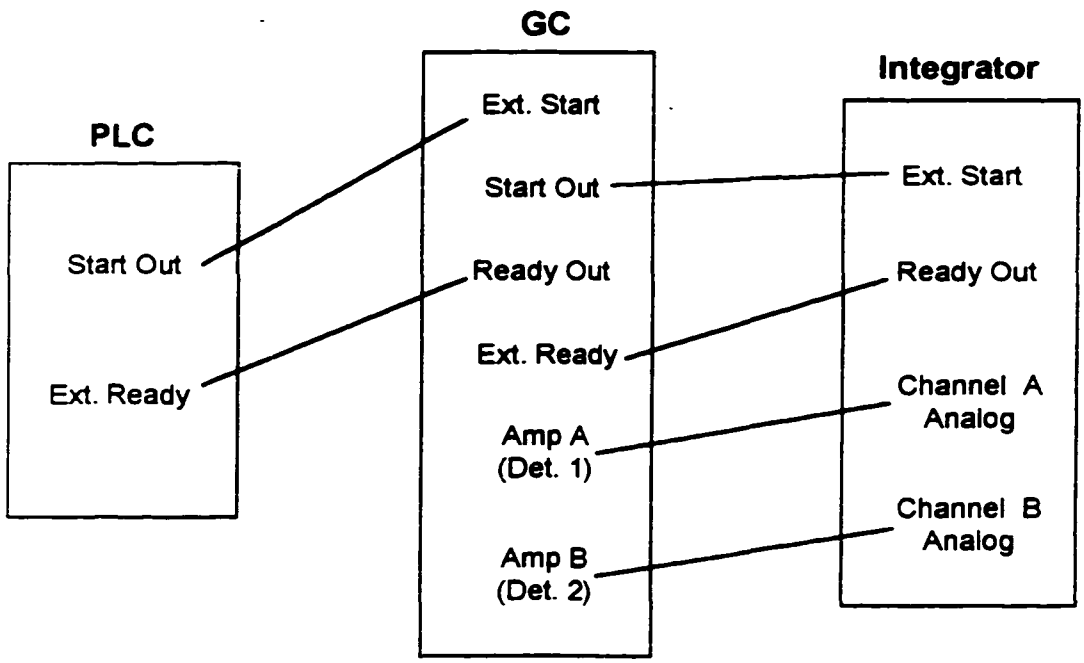



**Figure 4.4:** Interface between PLC, GC and Integrator

### 4.2.2 Flow Connection between Heated Enclosure and GC

The Autosorb GC system, equipped with one splitless injector, was installed adjacent to the BTRS equipment. A flow path between the Heated Enclosure and the GC was established, using a HTL provided by AE for this purpose. A hole (diameter slightly larger than the HTL) was drilled through the cap, covering the vacant injector port of the GC, to provide access for the HTL to the GC injector (see Section 4.2.3).

One end of the HTL was connected to the Sample Valve in the Heated Enclosure. The other free end was passed through the hole drilled in the GC injector

cap, and connected to an 8-port, 2 position valve (GC Valve) located in the GC oven (see Figure 4.2). Actuation of this valve is facilitated through a touch pad, located on the top panel of the GC instrument.

When the GC Valve is in the OFF position, flow follows the solid line path. Alternatively, the ON position chooses the dotted flow path. This valve serves an important role to flush the "contamination region" (dashed line flow path in Figure 4.2), between the Sample Valve and the Multiposition Valve, prior to sample injection. Before this function can be considered, provisions for carrier flow for both valve positions must be designed.

The carrier flow line was split using a "Tee" fitting after the MFC in the GC, to ensure uniform head pressure (see Figure 4.2). One branch from the "Tee" directed carrier flow to the Sample Valve in the Heated Enclosure. The second carrier branch was connected to the GC Valve in the GC oven. If the GC Valve was in the OFF position, carrier flow to the column was provided by the helium flow passing through the HTL to the GC. Simultaneously, the second carrier branch connected directly to the GC was directed to vent.

A needle valve with fine flow control was essential to create resistance to flow on the Vent line. Otherwise, the carrier flow would choose the path of least resistance and flow solely through the second branch (Vent). This would result in no flow passing through the column.

If the GC Valve is in the ON position, carrier gas from the Heated Enclosure is directed to Vent, and the second carrier branch supplies flow to the column. To collect a sample, the GC Valve is kept in the OFF position and the Sample Valve assumes the COLLECT position. Flow from the BTRS reactor flushes through a loop (for example, loop 1) in the Multiposition Trapping Valve, and exits to vent. After a minimum of one minute, the Multiposition Trapping Valve is actuated to a new loop position (for example, loop 2), trapping the sample in the previous active loop (loop 1). The GC Valve is then switched to the ON position sending the carrier flow from the Heated Enclosure to vent. The Sample Valve is switched to the INJECT position which flushes the contamination region and loop 2 contents out to vent, via the GC

valve. Once this task has been accomplished, the GC Valve is switched back to the OFF position. The "contamination" region is now filled with carrier gas and is sample free. The Sample Valve is switched to the INJECT position and simultaneously the Multiposition Valve is actuated back to loop 1. The sample is flushed out of loop 1 and sent via the HTL to the GC for sample analysis.

Adjustment of the needle valve position, used to create back pressure on the Vent line from the GC Valve, was a delicate process. Sufficient resistance must be created such that optimal carrier flow for sample analysis is established through the column, when the GC Valve is in the OFF position. However, this resistance must not be so great that it restricts flushing of the "contamination" region. Achieving a balance between these opposing needs, involved a tedious trial-and-error process. The final needle valve position achieved a carrier flow of 1 to 2 mL/min through the column, when the GC valve was in the OFF position. When the GC valve was in the ON position, the same needle valve position successfully flushed the entire "contamination" region to Vent, in a period of 5 minutes.

### 4.2.3 Design of the Split Injector

The GC did not possess a split injector, which is a requirement for capillary column applications to avoid sample overloading. Three different splitter designs were developed and tested for the current research.

The first two strategies located the splitter in the Heated Enclosure, between the Sample Valve and the HTL carrying flow to the GC. A "Tee" fitting served as the splitter, with the GC column attached to one branch and the Splitter Vent attached to the other. The difference between the two strategies was the method of imposing a resistance on the Splitter Vent line, to ensure adequate flow to the capillary column.

The first design utilized a fine-control needle valve to regulate Splitter Vent flow. The resulting split ratio was too small, resulting in sample overloading on the column. The second design used a capillary column, whose length was adjusted to

achieve the desired split ratio. It was found that Splitter Vent flow control was sporadic and reproducible GC results for standard injections were impossible. A large part of the failure of both of these designs, was the misleading temperature measurement in the Heated Enclosure (see Section 4.3.6).

The final design accommodated the splitter in the GC oven, between the GC Valve and the capillary column. Control of the Splitter Vent flow was achieved using a MFC, which was provided as a component of the Heated Enclosure. A split ratio of 100:1 was established and reliably sustained using this design.

### 4.2.4 Development of GC Temperature Program

A flame ionization detector (FID) was used for product analysis. Pre-purified helium, supplied by Praxair, was used as the carrier gas. Praxair zero hydrogen and compressed bench air (University of Waterloo) were used as combustion gases for the FID. A J & W Scientific PONA column (100 m x 0.25 mm ID x 0.5 μm film thickness) performed the sample separation. This column elutes compounds in the order of paraffins, olefins, naphthalenes and aromatics, with a minor degree of overlap. This is helpful in the present reaction, as several $C_8$ products are formed. The elution order assists in the separation and identification of olefins from paraffins. Component identification was accomplished through retention time matching of pure components (2-methylhexane, 2,2,4-TMP, 2,5-DMH, 2,3,4-TMP – all supplied from Aldrich) and GC-MS of bulk liquid samples. A sample chromatogram is illustrated in Figure 4.5.

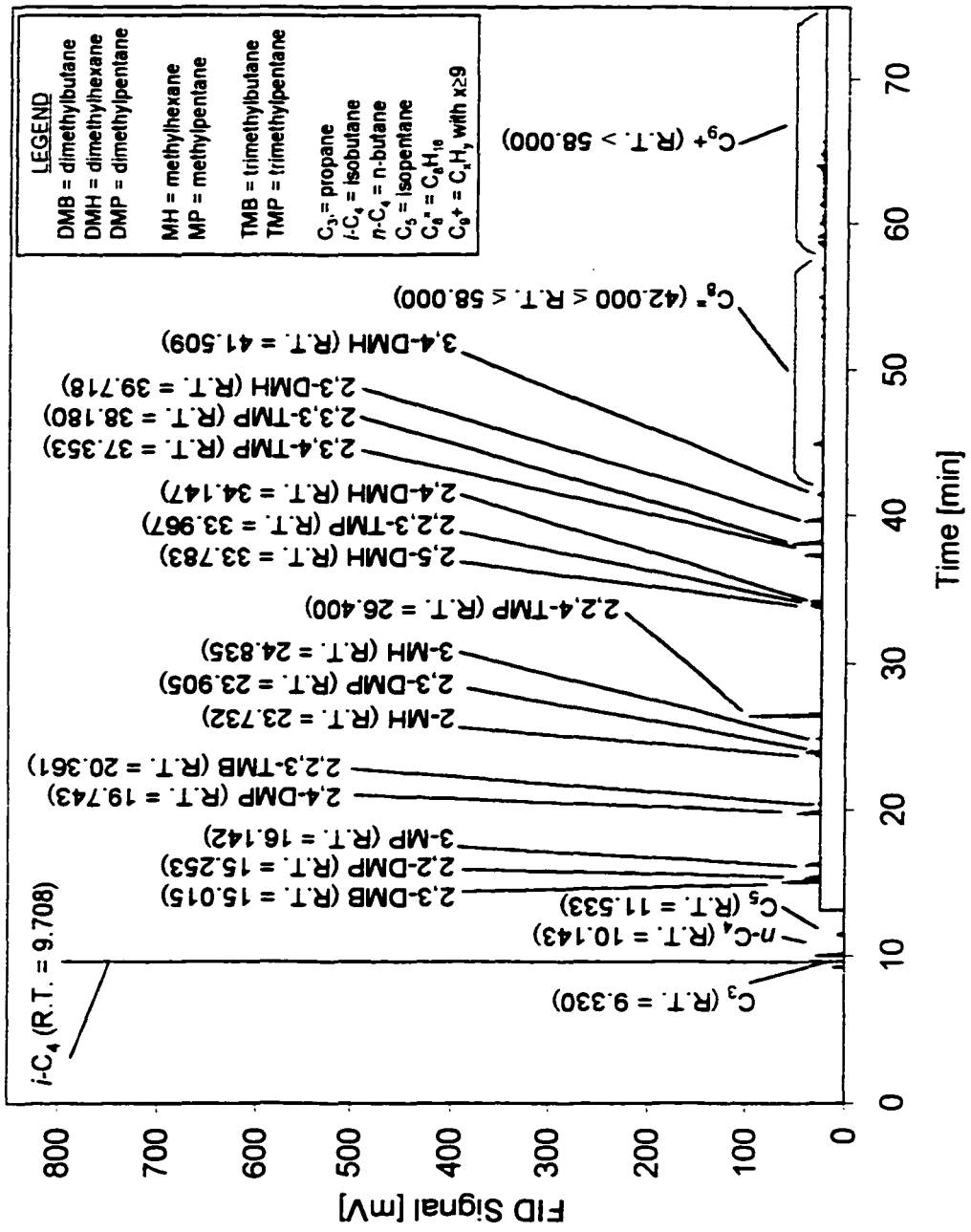



**Figure 4.5:** Sample Chromatogram of Alkylate Product (F31EMT; $T_{rxn}$=77°C; $T_{calc}$=425°C; P=382psig; I/O=11; t=1h; $C_4^=$ WHSV=2.7$h^{-1}$; $m_{cat}$=2.78g)

The procedure used for separation of the alkylate is a multi-staged temperature program. It was derived from the ASTM D-2699 standard method for alkylate analysis. The program maintains an initial temperature of 35°C for 10 min. and then ramps the temperature at a rate of 1°C/min to 45°C. This temperature is maintained for 15 min. The oven is ramped a second time at 1°C/min to 60°C, where it is maintained isothermally for 2 min. The oven temperature is increased at a rate of 15°C/min to 250°C where it is held constant for 5 min.

The entire program requires 75 min. This excludes the cool down time, of approximately 20 minutes, which is necessary to bring the oven temperature back to 35°C. The operating conditions of the GC and Integrator are summarized in Table 4.1.

**Table 4.1:** Operating Conditions of GC and Integrator for Alkylate Analysis

| | Setting |
|---|---|
| Inlet Pressure of Carrier Gas [psi] | 30 |
| Injector Temperature [°C] | 280 |
| Detector Temperature [°C] | 280 |
| Attenuation | 4 |
| FID Range<br>Initial<br>13.0 min. | <br>20 (low)<br>1 (high) |
| Peak Width | Automatic |
| Area Sensitivity | 50 |
| Base Sensitivity | 8 |

The detector is operated at low sensitivity for the initial 10 minutes of the program to allow the large excess of isobutane and unreacted butene to elute. After this time, the detector sensitivity is switched to high, in order to increase sensitivity to the smaller product peaks. Total peak areas for the sample are calculated by multiplying the peak areas at low sensitivity by 20, and adding them to the peak areas at high sensitivity.

## 4.3 MAJOR HARDWARE CHALLENGES

Numerous hardware challenges were faced during the installation and operation phases of the equipment. A chronological history of events is provided in Appendix 2.

### 4.3.1 Inlet Check Valves for HPL Pumps

Isobutane ($T_{nb}$ = -11.85°C) and 1-butene ($T_{nb}$ = -6.25°C) are gaseous at atmospheric conditions, but the liquid state can be maintained under a nitrogen blanket. The pumping of these pressurized liquids is made possible using feed tanks, equipped with dip tubes. The inlet check valve of the HPL pump presents a unique design challenge, as it must withstand pressure on the upstream side of the inlet check valve. The standard valve provided with the BTRS unit, is designed for atmospheric pressure operation on the upstream side. This valve was not suitable for the present application. A prototype, designed by Scientific Systems, Inc. (SSI), retrofitted the conventional inlet valve, with a metal ferrule, for a gas tight connection. SSI hypothesized that pump operation would not be jeopardized using an inlet pressure up to 125 psig, although no data were available to support this pressure limitation.

Preliminary testing on-site found that a 125 psig inlet pressure gave unreliable pump operation. Firstly, opening the prime/purge valve effectively caused a stream of gas to spew uncontrollably out the luer port in the stem assembly. In order to prime the pump, this flow must be regulated through the collection of the effluent in a liquid syringe, and manually controlling plunger withdrawal until the syringe is full. This proved to be quite a challenging task when working against a pressure of 125 psig! Secondly, employment of 125 psig inlet pressure, resulted in excessive pressure on the pump piston. This often forced the pump out of control and frequently resulted in motor stalling (i.e. pump losing prime). For this reason, the inlet

pressure (feed tank pressure) was reduced to 75 psig and more reliable operation achieved. Motor stalling continued to be problematic, but at a reduced incidence rate. A more important concern was unpredictable stroke or flow rate. Pump flow rate is based on the volume of a pressurized liquid passing through the pump. However, after the BPR, the feed is de-pressurized to atmospheric conditions, making verification of flow measurement next to impossible.

### 4.3.2 Seat Material for AE Brand Manual Operated Valves

After three months of operation, pressure tests failed, due to severe leakage from the manual operating valves (AE) isolating the reactor (V-R12, V-R13, V-R14, V-R15) and those closing the Reactor Line Vent (V-R16) and the Reactor Purge Vent (V-S13). The manufacturer expected that the thermal mass of the tubing and valve bodies would sufficiently cool the gases to warrant the use of a lower temperature seat design. This hypothesis proved incorrect and severe leakage occurred. The valves were replaced with high temperature valves with teflon packing producing satisfactory results.

### 4.3.3 Seat Materials for Multiposition Valves: Valcon T vs. Valcon E

The reactor system was originally delivered with Valcon T (polyimide / PTFE / carbon composite) seats installed in all Valco multiposition valves:

- Reactor Status Valve (BTRS Oven)
- Sample Valve (Heated Enclosure)
- Multiposition Trapping Valve (Heated Enclosure)

Valcon T permitted a maximum operating temperature of 280°C at 2500 psig. During preliminary testing, it was found that the Reactor Status Valve leaked at temperatures less than ~150°C with reliable sealing only evident at higher temperatures. After approximately one month of operation, complete seat failure

resulted with no sealing provided at any temperature. Consultation with Valco, the valve manufacturer, indicated that Valcon T is best suited for temperatures above 200°C. A plastic transition temperature occurs at ~150°C, above which the material softens and swells. Below this temperature, the material is brittle and tends to stick to the valve body making it difficult to turn. Although Valcon T is functional at lower temperatures, seat lifetime is severely reduced.

Valcon E (polyaryletherketone/PTFE composite) is a similar material to Valcon T providing reliable sealing from room temperature to 220°C at 2500 psig. Although the upper temperature limit is lower than that of Valcon T, reliable operation is provided throughout the temperature range. A new Valcon T seat had been installed in the Reactor Status Valve and operated reliably for 14 months. After this time period, leakage from the Reactor Status Valve was detected again. The Valcon T seat was removed from the Reactor Status Valve, and replaced with a Valcon E seat. The BTRS oven high temperature and alarm limits were adjusted to reflect the tolerance of the new seat material. After alignment, the valve has provided reliable sealing and actuation.

As mentioned previously, Valcon T was also installed in the Multiposition Trapping Valve. After a few months of operation, actuation of this valve became difficult due to sticking of the seat. This problem arised as a result of actuating the valves at temperatures below 150°C (see faulty Heated Enclosure Design in section 4.3.5). Valco recommended re-conditioning the valve at a high temperature, causing some of the Teflon to extrude to the surface and re-lubricate the valve. A modification to the Wonderware software was supplied by AE, to permit operation of the equipment at the elevated temperatures demanded by the re-conditioning step. The re-conditioning procedure was successful on two separate occasions, but a third sticking incidence ultimately caused the Valcon T seat to seize completely. The Multiposition valve was removed from the Heated Enclosure and sent to Valco for servicing. The Valcon T seat was replaced with a Valcon E type, thus compromising the upper temperature limit slightly. However, the new seat material is designed to provide reliable operation from 25 to 200°C. The Heated Enclosure high temperature

and alarm limits of the software were modified, to reflect the reduced temperature ceiling of the new seat material.

### 4.3.4 Manual Control of Liquid Feed Flow

Manual control of the liquid feed flow is regulated by a metering valve (V-F31 for Feed 3 and V-F41 for Feed 4), a 3-way ball (V-F32 for Feed 3 and V-F42 for Feed 4) and a check valve (CV-F31 for Feed 3 and CV-F41 for Feed 4). These valves are labelled on the AE BTRS Reactor Flow blueprint. The 3-way ball valves are an important component in the liquid feed system, as they are essential for isolation of the liquid pumps during priming. In addition, they provide a quick means for venting liquid feed in an emergency situation. The metering valve serves to manually regulate the fluid flow. The check valves are also an essential element as they ensure safe and accurate delivery of the liquid feed. They are also vital to prevent back flow of fluid, guaranteeing reliable fluid flow and preventing contamination in the feed cylinders.

Severe leakage resulted from the stems of both needle valves during the priming of one of the liquid pumps (note that all valves were supposedly in the closed position). This not only revealed leaking in the 3-way valves and catastrophic failure of the needle valves, but also exposed malfunctioning of the check-valves.

The 3-way valves in the original design employed a TFE packing, which offered an operational temperature range of 10 to 65°C. It is believed that the vapourization of the pressurized liquid feed may have lowered the temperature below the lower limit. This would induce the development of burrs on the Teflon seat, if the valve was switched under these conditions. Continual erosion of the seat would cause an overall deterioration in the quality of the sealing surface and eventually result in valve failure.

The reason for check valve failure is not completely clear. The failed "O" ring appeared slightly brittle and revealed definite evidence of wear. The original check

valves employed a Kalrez "O" ring, which easily accommodates the expected operating conditions of the liquid feed system. Review of the chemical incompatibilities for Kalrez, suggest that chemical attack is also unlikely. The most probable explanation for check valve failure is that incorrect "O" rings were assembled in the check valve by the equipment manufacturer, as the colour of the failed "O" rings differed from that of a fresh Kalrez "O" ring.

The failure of all valves prompted the re-design of the liquid delivery system. It was concluded that manual regulation of liquid flow rate was redundant, as operation of the equipment (i.e. mass flow controllers, liquid pumps, multiposition valve actuation, temperature controllers, etc.) is only possible using the computer software. For this reason, the failed needle valves regulating liquid flow rate, were not replaced.

The original 3-way ball valves were substituted with a spring-loaded version (Whitey), which minimizes the contacting area of the system fluid with the valve sealing materials. It utilizes a PFA packing, extending the lower temperature limit to -54°C, without compromising the upper temperature ceiling. The "O" ring of the check valves was replaced with a Teflon TFE type ,which is more chemically inert than the Viton "O" ring employed in the original design. A slightly higher cracking pressure is required to activate fluid flow through the valve, but this did not appear to affect operation. Reliable functioning of the liquid delivery system was confirmed and no subsequent leakage problems have been encountered.

### 4.3.5 Heated Enclosure Design

The Heated enclosure is an insulated box in which the Sample Valve and the Multiposition Trapping Valve are mounted. This unit is designed for sample collection, storage and injection at elevated temperatures. The orignial design is a standard Valco product, which utilizes a heater block equipped with a heater cartridge for thermal output. A hole is drilled in the side of the block and a thermocouple installed. Temperature measurements serve to regulate heater output and

maintaining temperature control. The Heated Enclosure was rated for 125 W/350°C service.

Persistent difficulties in sample injection quality to the on-line GC, prompted investigation into the reliability of the sample collection system. It was identified that a maximum temperature of 210°C could be reached at the maximum heater output, which was well below the upper temperature limit of 280°C specified by the AE BTRS blueprint. A higher wattage cartridge was supplied by AE and installed into the heater block. Sample injection problems persisted. The heater block temperature signal was verified using independent thermocouple measurements, to eliminate faulty heater operation as a possible explanation. A review of the Heated Enclosure blueprint revealed a definite weakness in the design. No mechanism for heat circulation (i.e. fan) is provided, implying that energy transfer from the heater block must be facilitated by conduction only. Independent temperature measurements revealed a significant temperature gradient from the heater block to the surrounding air space in the box. At a heater block temperature of 250°C, independent thermocouple measurements sense a temperature of less than 150°C in the surrounding air space. This would explain the sample injection problems.

The Heated Enclosure was returned to AE, as the unit failed to meet the maximum temperature specifications. A new unit was provided utilizing the same motor and blower assembly as well as insulation (1 inch thick), as the design of the BTRS oven. The temperature of the newly designed Heated Enclosure was confirmed with independent thermocouple measurements.

## 4.4 SOFTWARE ISSUES

### 4.4.1 Software "Bugs"

The addition of software control to a highly complex system greatly increases the level of difficulty in troubleshooting problems. Several bugs in the software were identified during the installation phase (see Appendix 2). Program seizures, at certain steps in the recipes of both the Automatic Control and Sample Control windows, were encountered. In addition, it was found that some set points were not adjustable under automatic control. "Ghost" commands were being issued by the software, without any prompt from the operator. A dangerous response in furnace output was diagnosed as a result of skin temperature thermocouple failure. All of these problems were isolated and demanded rectification before proper use of the equipment could be achieved.

Corrections to Wonderware software require the use of a proprietary design key, which is accessible to AE personnel only. When a software bug was identified, AE personnel were contacted and the corrections were coded at their facility. The revised software was sent and installed onto the PC. Testing of the re-coded software was required to confirm safe and proper operation of the equipment.

### 4.4.2 Faulty PLC Module

The thermocouple, which detects Reactor Skin Temperature, periodically failed with no signal being sent to the PLC. It is expected that this condition would DISABLE the system. However, the opposite action occurred. A failed furnace thermocouple was registered by the PLC, as a temperature below the set point temperature, triggering 100 % output from the furnace. Once the reactor temperature exceeded the High Limit of the equipment, the system was DISABLED.

Simultaneous to the skin temperature problem, the MFCs experienced similar behaviour. One MFC would suddenly shut off for no explainable reason. Complicating the issue further, were a malfunctioning BPR, sticking Multiposition valve and chronic pump problems. Several problems were happening simultaneously, making the diagnostic process highly complicated.

The skin temperature problem was attacked first. A new reactor skin thermocouple was installed to see if this corrected the problem. Thermocouple failure recurred, suggesting the source of the problem was either a software bug or a failed module in the PLC. The final diagnosis was a faulty PLC module. A replacement part was sent by AE and installed in the PLC and no subsequent problems were encountered with either the skin temperature or MFC operation. The problems with the pumps, BPR and Multiposition valves were unrelated software issues and were resolved sequentially as discussed in the Section 4.3.

# Chapter 5

# Preliminary Batch Reactor Studies using Y Zeolite

## 5.1. CATALYST PRE-TREATMENT AND STORAGE

The catalyst Y Zeolite (Si/Al ratio of 6.26; S.A. = 620 $m^2/g$) was generously donated by UOP (Y-84, Lot 966094061003~S). This material has been extruded into 1/8" pellets and was ion-exchanged by the manufacturer. Atomic absorption measurements estimate Na levels to be 930 ppm (see Appendix A1.4). The catalyst was crushed and sieved to a particle diameter range of 250 to 500 μm, and calcined in flowing air at 500°C for 5 h prior to use. Upon completion of the calcination program, the catalyst was cooled in flowing ultra-high purity (UHP) $N_2$ and

immediately transferred into a glove bag. Samples were measured into 3 g allotments and stored in sample vials.

## 5.2 BATCH REACTOR DESCRIPTION AND EXPERIMENTAL PROCEDURE

The batch alkylation experiments were performed in a 316 SS 300 mL Parr reactor equipped with a magnetic stirrer, internal water cooling coil and a dual action temperature controller. The reactor was loosely sealed and purged several times with UHP $N_2$ to remove air from the reactor. If heptane was used for catalyst storage (see Section 5.4), the excess heptane was decanted into a beaker. The reactor sealing clamps were loosened, the reactor top lifted slightly and the catalyst was quickly added to the reactor. The reactor top was replaced immediately, tightened and then the reactor was purged several times with nitrogen to remove residual air.

The reactants, *i*-$C_4$ (CP grade, Linde) and 1-$C_4^=$ (CP grade, Linde), were pre-weighed into separate sample bombs and pressurized to 800 psig with UHP $N_2$ at room temperature. The *i*-$C_4$ sample cylinder was connected to the reactor system, and the contents introduced into the reactor. Next, 1-$C_4^=$ was added in the same manner. The system was heated from ambient conditions to the reaction temperature, increasing the temperature at a rate of 5°C/min.

No duplicates were performed on batch experiments. The data presented depicts the results from a single run.

## 5.3 PRODUCT COLLECTION AND ANALYSIS

Reaction time zero was defined as the time at which the reaction temperature reached the set-point value. At the conclusion of the reaction, the furnace was lowered and the reactor submerged in an acetone-ice water bath. Cooling water flow was activated through the internal cooling coil to accelerate the cooling process.

Once the internal reactor temperature reached approximately 6°C, the pressure was slowly vented to ambient conditions. The autoclave was quickly opened and the product collected and weighed. Mass balance was poor, averaging at approximately 68 %. This is primarily a consequence of the excess isobutane employed in the feed, which vapourized when the reactor was opened at the conclusion of the experiment, incurring alkylate product losses.

The liquid product was separated from the spent catalyst and stored in a sample bottle, immersed in an acetone/ice water bath. The cap was loosely attached to the bottle, allowing excess isobutane to slowly evaporate over a period of 4 h. This step is necessary to successfully inject samples into the GC. Excessive amounts of isobutane in the product, result in complete evaporation of the sample from the syringe prior to injection. However, product analysis is sensitive to the duration of the evaporation step, with longer times favouring higher $C_9^+$ levels. This emphasizes the importance of employing consistent evaporation periods to permit comparison between experiments.

Once the evaporation time had expired, a 1.0 μL sample of residual liquid was aspirated using a chilled syringe. The sample was injected into a Perkin Elmer (PE) Autosystem GC equipped with a PE Nelson 1020 GC Plus Integrator. Pre-purified helium (Praxair) was used as the carrier gas in the separation, and Zero grade hydrogen (Praxair) and compressed bench air (University of Waterloo) were employed for the combustion gases of the FID detector. Separation was achieved using a DB-1 (J&W Scientific) capillary column (60 m x 0.325 mm OD x 1.0 μM film), using the temperature program described in Section 4.2.4.

## 5.4 EFFECT OF STORING CATALYST IN HEPTANE

Zeolites are known to be very hygroscopic, and hence, negligible conversion of butene was obtained when the catalyst was exposed to ambient air prior to reaction. For this reason, two methods of catalyst storage were explored. The first method employed a glove box for catalyst addition and reactor sealing, in order to avoid exposure to moisture in ambient air. The desired mass of catalyst was measured, added to the reactor and the autoclave sealed.

The second approach, stored the catalyst in pre-treated heptane (stored in a bottle containing freshly calcined 3A zeolite to remove any dissolved moisture). A mass of 3 g of catalyst was measured into a vial, and heptane added to completely submerge the catalyst. These steps were performed in a glove bag. The vial was capped, the stopper secured with electrical tape and the sample stored no longer than 48 hours prior to use.

The influence of storage methods on catalyst performance is summarized in Table 5.1. Pre-filling the catalyst pores with heptane, favoured the formation of $C_8$ products at the expense of $C_9^+$ products. The TMP/DMH ratio improved slightly in the presence of heptane, indicating that hydride transfer was enhanced under these conditions. It is possible that heptane is acting as a source of hydride transfer, thus suppressing deactivation processes. Alternatively, heptane may serve to dilute the concentration of the olefin in the pores. This reduces the probability of oligomers forming, thereby enhancing the opportunity for isobutane participation.

A higher surface area of the spent catalyst would be expected if polymerization reactions are reduced through enhanced hydride transfer. The experimental data support this hypothesis in that the catalyst surface area was better preserved employing heptane for storage, relative to the catalyst stored under a nitrogen blanket. No discernible change in yield was observed using either catalyst storage method. All subsequent batch experiment employed heptane for catalyst storage.

**Table 5.1:** Effect of Catalyst Storage Method on Batch Reactor Alkylate Composition (Y zeolite; $T_{rxn}$=80°C; P=450psig; I/O=10; t=30 min; $m_{cat}$=3.00 g)

| Catalyst Storage Method | $N_2$ blanket | Heptane |
|---|---|---|
| Yield [g $C_5^+$/g $C_4^=$ fed] | 0.254 | 0.267 |
| *$C_5^+$ Liquid [mass%]* | | |
| $C_5$ - $C_7$ | 5 | 9 |
| $C_8$ | 42 | 47 |
| $C_9^+$ | 53 | 44 |
| *$C_8$ Fraction [mass%]* | | |
| TMP | 26 | 38 |
| DMH | 16 | 17 |
| Other $C_8$ Saturates | 4 | 2 |
| $C_8^=$ | 54 | 43 |
| *TMP Fraction [%]* | | |
| 2,2,4-TMP | 29 | 34 |
| 2,2,3-TMP | 9 | 9 |
| 2,3,4-TMP | 32 | 28 |
| 2,3,3-TMP | 30 | 29 |
| *Indicator [mass fraction]* TMP / DMH | 1.6 | 2.2 |
| S.A. Spent Catalyst[1] [$m^2$/g] | 304 | 359 |

1 SA fresh = 620 $m^2$/g

## 5.5 EFFECT OF PRE-SOAKING CATALYST WITH ISOBUTANE

The olefin preferentially adsorbs onto solid acids, favouring oligomerization and polymerization reactions rather than alkylation with the paraffin. For this reason, two different approaches were evaluated for 1-$C_4^=$ addition. The first method added 1-$C_4^=$ immediately after *i*-$C_4$ addition, at ambient temperature (see Figure 5.1). In the second technique, 1-$C_4^=$ addition was delayed until the reaction temperature was reached. In this manner, the catalyst was pre-soaked with *i*-$C_4$ (in the absence of 1-$C_4^=$) thus allowing it to adsorb alone onto the catalyst surface.

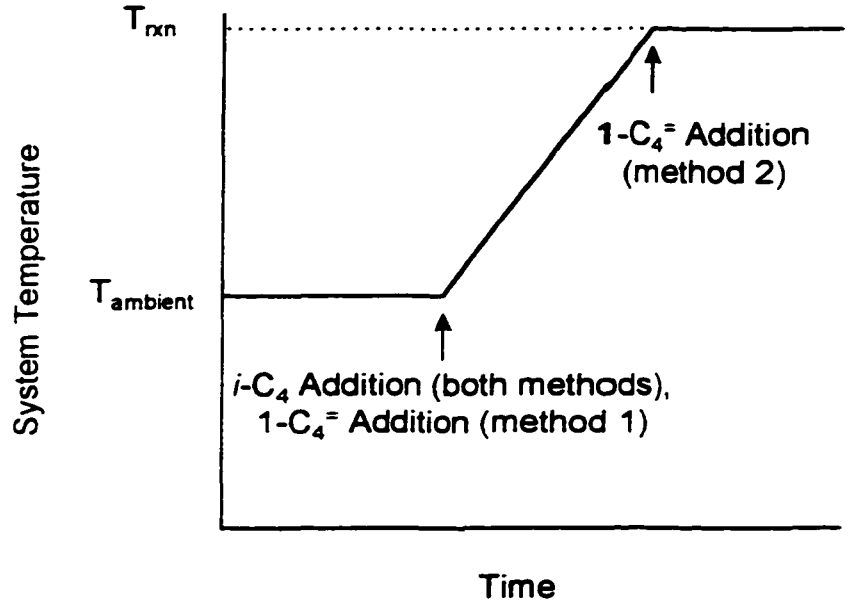



**Figure 5.1:** Timing of 1-$C_4^=$ Addition for Batch Reaction

Delaying the addition of 1-$C_4^=$ protected the strong acid sites responsible for cracking and alkylation reactions, and enhanced the selectivity to 2,2,4-TMP (see Table 5.2). Pre-soaking the catalyst in *i*-$C_4$, favours a high I/O ratio in the vicinity of the acid sites. This promoted the alkylation of 1-$C_4^=$ with *i*-$C_4$ rather than oligomerization of the olefin, during the initial stages of the reaction. This environment would also favour self-alkylation of isobutane. This offers a possible explanation for the elevated levels of 2,2,4-TMP, as this TMP isomer is the primary product of self-alkylation of *i*-$C_4$.

The content of $C_8^=$ and $C_9^+$ levels, suggest that oligomerization and polymerization reactions were favoured with earlier butene addition. This is not surprising in view of the adsorption preference of olefins over paraffins on solid acid sites. This observation is supported by the larger surface area measurement, when 1-$C_4^=$ addition was delayed (see Table 5.2). Reduced polymerization activity would suggest a slower rate of catalyst deactivation and higher product yield, which is supported by the data.

**Table 5.2:** Effect of Pre-soaking Catalyst (stored in heptane) with Isobutane on Batch Reactor Alkylate Composition
(Y zeolite; P=450psig; I/O=10; t=30 min; $m_{cat}$=3.00 g)

| Timing of 1-$C_4^=$ Addition | immediately after *i*-$C_4$ | once $T_{rxn}$ reached |
|---|---|---|
| Yield [g $C_5^+$/g $C_4^=$ fed] | 0.239 | 0.267 |
| *$C_5^+$ Liquid [mass%]* | | |
| $C_5$ - $C_7$ | 2 | 9 |
| $C_8$ | 43 | 47 |
| $C_9^+$ | 55 | 44 |
| *$C_8$ Fraction [mass%]* | | |
| TMP | 19 | 38 |
| DMH | 15 | 17 |
| Other $C_8$ Saturates | 3 | 2 |
| $C_8^=$ | 63 | 43 |
| *TMP Fraction [%]* | | |
| 2,2,4-TMP | 13 | 34 |
| 2,2,3-TMP | 7 | 9 |
| 2,3,4-TMP | 40 | 28 |
| 2,3,3-TMP | 40 | 29 |
| *Indicator [mass fraction]* TMP / DMH | 1.3 | 2.2 |
| S.A. Spent Catalyst[1] [$m^2$/g] | 111 | 359 |

1 SA fresh = 620 $m^2$/g

## 5.6 EFFECT OF REACTION TEMPERATURE

The effect of temperature was evaluated at 80 and 100°C, maintaining the I/O ratio constant at 10 for both experiments (see Table 5.3). Reaction temperatures in excess of 100°C, encourage excessive gas production and were therefore, not explored. Catalysts were stored in heptane for all experiments. In addition, butene addition was delayed until the reaction temperature was reached.

**Table 5.3:** Effect of Reaction Temperature on Batch Reactor Alkylate Composition (Y zeolite; $T_{rxn}$=80°C; P=450psig; I/O=10; t=30min; $m_{cat}$=3.00g, catalyst stored in heptane, catalyst pre-soaked with isobutane)

| Temperature [°C] | 80 | 100 |
|---|---|---|
| Yield [g $C_5^+$/g $C_4^=$ fed] | 0.267 | 0.276 |
| *$C_5^+$ Liquid [mass%]* | | |
| $C_5$ - $C_7$ | 9 | 12 |
| $C_8$ | 47 | 47 |
| $C_9^+$ | 44 | 41 |
| *$C_8$ Fraction [mass%]* | | |
| TMP | 38 | 35 |
| DMH | 17 | 19 |
| Other $C_8$ Saturates | 2 | 1 |
| $C_8^=$ | 43 | 44 |
| *TMP Fraction [%]* | | |
| 2,2,4-TMP | 34 | 34 |
| 2,2,3-TMP | 9 | 13 |
| 2,3,4-TMP | 28 | 27 |
| 2,3,3-TMP | 29 | 26 |
| *Indicator [mass fraction]* TMP / DMH | 2.2 | 1.9 |
| SA Spent Catalyst[1] [$m^2$/g] | 359 | 265 |

1 SA fresh = 620 $m^2$/g

A higher reaction temperature produced an increase in $C_5$-$C_7$ levels and a decrease in $C_9^+$ levels, suggesting that heavier products were cracked to form smaller fragments. Deterioration in alkylate quality (TMP/DMH ratio) was also observed at the higher reaction temperature. It appears that the stability of alkylate precursors was jeopardized under these conditions. Surface area loss of the spent catalyst was more pronounced at the elevated reaction temperature. However, no significant effect on product yield was detected.

## 5.7 EFFECT OF REACTION DURATION

The commercial success of solid acids for alkylation of butene with isobutane is elusive, due to rapid catalyst deactivation. It was of interest to explore the effect of reaction duration on the product distribution and selectivity of the reaction. Two separate experiments were performed at 80°C and I/O of 10, varying the duration of the experiment from 15 to 30 minutes (see Table 5.4). Heptane was employed for catalyst storage in both experiments. Similarly, the catalysts were pre-soaked in isobutane for both runs.

**Table 5.4:** Effect of Reaction Duration on Batch Reactor Alkylate Composition (Y zeolite; $T_{rxn}$=80°C; P=450psig; I/O=10; t=30min; $m_{cat}$=3.00g, catalyst stored in heptane, catalyst pre-soaked in isobutane)

| Run Number | B6 | B4 |
|---|---|---|
| Duration [min.] | 15 | 30 |
| Yield [g $C_5^+$/g $C_4^=$ fed] | 0.214 | 0.267 |
| *$C_5^+$ Liquid [mass%]* | | |
| $C_5$ - $C_7$ | 10 | 9 |
| $C_8$ | 47 | 47 |
| $C_9^+$ | 43 | 44 |
| *$C_8$ Fraction [mass%]* | | |
| TMP | 42 | 38 |
| DMH | 17 | 17 |
| Other $C_8$ Saturates | 1 | 2 |
| $C_8^=$ | 39 | 43 |
| *TMP Fraction [%]* | | |
| 2,2,4-TMP | 33 | 34 |
| 2,2,3-TMP | 9 | 9 |
| 2,3,4-TMP | 28 | 28 |
| 2,3,3-TMP | 29 | 29 |
| *Indicator [mass fraction]* TMP / DMH | 2.4 | 2.2 |
| SA Spent Catalyst[1] [$m^2$/g] | 344 | 359 |

1 SA fresh = 620 $m^2$/g

A 44 % loss in catalyst surface area occurred during the first 15 minutes of the reaction period. Extending the reaction duration to longer times does not reduce the surface area further. A slight increase in product yield was observed with longer reaction times, but the latter 15 minutes of the reaction favoured oligomerization activity rather than TMP production. This suggests that the ability to facilitate hydride transfer to the octyl carbenium ion was hindered as the reaction progressed. Instead of promoting hydride transfer from isobutane for desorption of a saturated $C_8$ product, a proton was returned to the surface, with an olefin desorbing as the final product.

# Chapter 6

# Effect of Process Parameters on Alkylation Yield and Selectivity for EMT and Y Zeolites in a Flow Reactor

This chapter investigates the effect of calcination temperature, reaction temperature, olefin WHSV, cyclical feed addition and catalyst type (EMT or Y) in a flow reactor. The influence of these operating conditions on the Useful Catalyst Lifetime period and alkylate quality will be investigated. The preferred operating conditions (of the levels tested), will be identified for EMT and Y zeolites.

## 6.1 EXPERIMENTAL PROCEDURE

The micro-reactor employed for the flow reaction studies is described in Chapter 4. A detailed description of the experimental procedure for its use is reviewed in Appendix 3.1. Sample calculations are outlined in Appendix A3.2. Raw data for all flow experiments are presented in Appendix 4.

The catalyst was pelletized, crushed and sieved to a particle diameter range of 0.25 (60 US mesh) to 0.50 (35 US mesh) mm. Due to the exothermicity of the reaction, 2.78 g of zeolite were diluted with inert 1 mm borosilicate glass beads (50/50 by weight). The pre-heat and cool down zones of the reactor bed were also filled with glass beads.

The reactor was re-attached to the BTRS system and the catalyst was calcined *in situ*. The reactor was heated to the calcination temperature and maintained isothermally for 5 h in a 50 sccm stream of nitrogen. After the calcination step, the catalyst bed was switched to the off-line position, and cooled under a nitrogen blanket to the reaction temperature level.

Prior to initiating the reaction, the feed mixture was sent off-line for analysis. Once constant feed composition was achieved, the mixture was directed on-line to the reactor to initiate the experiment. All runs employed a nitrogen flow rate of 35 sccm and a reaction pressure of 382 psig. The flow through the Vent line from the Sample Valve was measured using a bubble flow meter, after the Reactor Valve was switched to the on-line position. A dramatic increase in flow rate occurred once the liquid front reached the Heated Enclosure, indicating the break-through of the reaction front. This point defined the start of the reaction, or 0 min time-on-stream (0 min TOS). At this time, the sample program was activated and collection of the first sample was initiated.

## 6.2 STAGES OF CATALYST ACTIVITY AND SELECTIVITY ON EMT AND Y ZEOLITES

The reaction of isobutane with 1-butene in a flow reactor exhibits four distinct stages of catalyst activity and selectivity (Taylor & Sherwood, 1997). These four stages were distinguishable in the catalytic profiles of EMT and Y zeolites. The $C_5$+ product distributions are illustrated in Figures 6.1 and 6.3 for EMT and Y zeolites respectively. Selectivities within the $C_8$ fraction are shown in Figure 6.2 for EMT zeolite and Figure 6.4 for Y zeolite.

The first stage, termed "Initial Activity", is very short and is characterized by the highest catalyst activity. This stage is often not observed due to the brevity of the phase, as well as, restrictions on sample collection frequency of the reactor system (Taylor & Sherwood, 1997). This activity period was assumed to occur between 0 and 1 min TOS for the present study.

The second stage of catalyst activity represents the "Useful Catalyst Lifetime", and features butene conversion greater than 80 % (Taylor & Sherwood, 1997). Figures 6.1 and 6.3 demonstrate that the $C_5$+ liquid produced from EMT and Y zeolites, consisted of predominantly $C_8$ compounds, which in turn, are composed of primarily TMPs (see Figures 6.2 and 6.4). Typically, the alkylate ($C_5$+ liquid) consisted of 40 to 60 % $C_8$ compounds, with 60 to 80 % of the $C_8$ fraction being TMPs. Actual product levels depend upon the operating conditions (i.e. reaction temperature, olefin WHSV, etc.) employed. The $C_5$-$C_7$ fraction was also significant in this phase, suggesting that cracking of alkylation, oligomerization and polymerization products to smaller components, was occurring extensively. Levels of $C_5$-$C_7$ fraction, ranged between 20 to 50 % of the $C_5$+ liquid, with higher amounts observed at operating temperatures approaching 100°C. The TMP fraction was composed of primarily 2,2,4-TMP, with typical levels ranging from 40 to 60 %. The primary product of 1-butene/isobutane alkylation is 2,2,3-TMP. However, this product represented approximately 10 % of the TMP fraction and was consistently the least preferred of all

TMP isomers, for all operating conditions tested. Under similar operating conditions, EMT zeolite typically produced lower $C_5$-$C_7$ levels and higher $C_8$ and $C_9$+ amounts in the alkylate, relative to Y zeolite. Comparable $C_8$ and TMP selectivities were observed on both catalyst systems.

As the catalyst deactivated with longer TOS, butene conversion decreased and selectivity towards $C_8$ products in the $C_5$+ product declined. This was accompanied by a corresponding increase in $C_5$-$C_7$ levels as well as amounts of $C_9$+ products. Saturated $C_8$ compounds still remained the dominant fraction during this period; however, the selectivity within the $C_8$ fraction was increasingly favoured towards DMHs.

During the third stage of catalyst activity, termed "Rapid Deactivation", butene conversion dropped rapidly as the catalyst lost activity, but was sustained above 40 % (Taylor & Sherwood, 1997). Production of saturated $C_8$ products (TMP and DMH) declined sharply, due to a rapid decrease in TMP levels. This was particularly true on Y zeolite (see Figure 6.4), where the deactivation process appeared to proceed a faster rate relative to EMT (see Figure 6.2). The content of DMH in the $C_8$ fraction remained relatively unchanged from the levels observed during the Useful Catalyst Lifetime period. Levels of $C_9$+ products in the alkylate were high during this period, representing between 50 to 60 % of the alkylate composition. A dramatic increase in $C_8$ olefin production occurred during this phase, with levels reaching 60 to 70 % of the $C_8$ fraction. Cracking activity was lost completely during this phase. This suggests that deactivation occurred on the strongest acid sites first, resulting in a loss in cracking and alkylation activities. The rate of this process appeared to be suppressed on EMT relative to Y, resulting in a longer deactivation period observed on EMT.

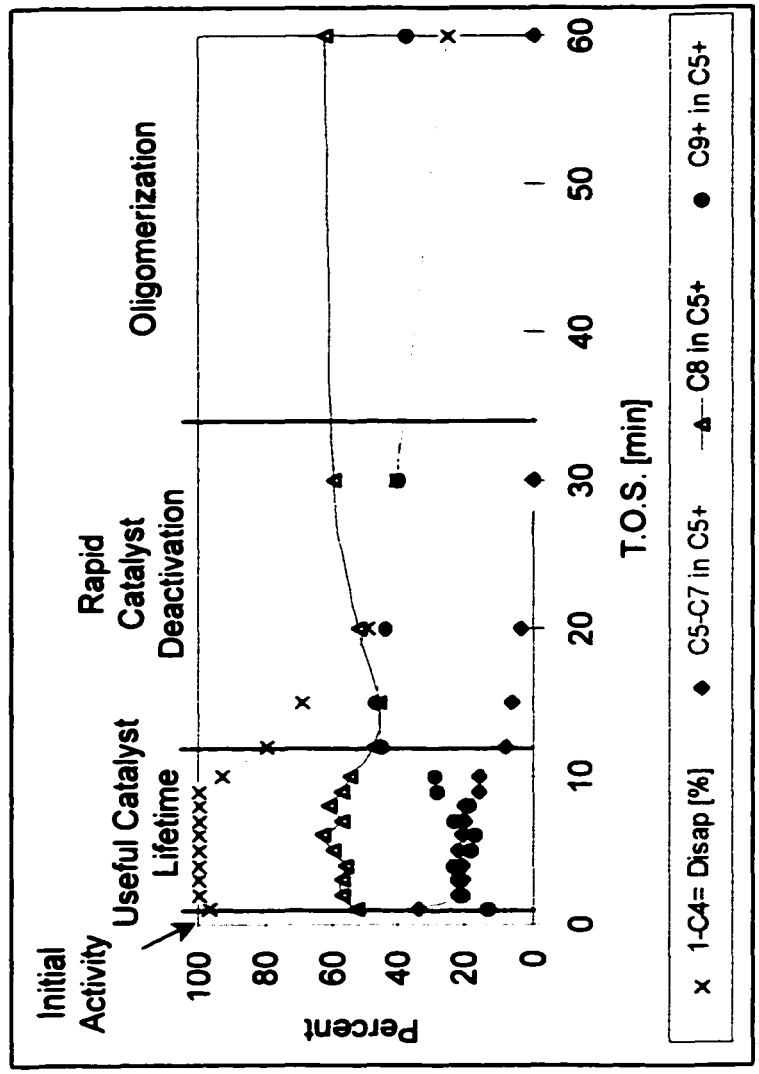



**Figure 6.1:** Stages of Catalyst Activity on EMT Zeolite with respect to $C_5$+ Product Distribution (F66EMT; $T_{rxn}$=50°C; $T_{calc}$=425°C; P=382psig; I/O=15; t=1h; $C_4^=$ WHSV=2.0$h^{-1}$; $m_{cat}$=2.78g)

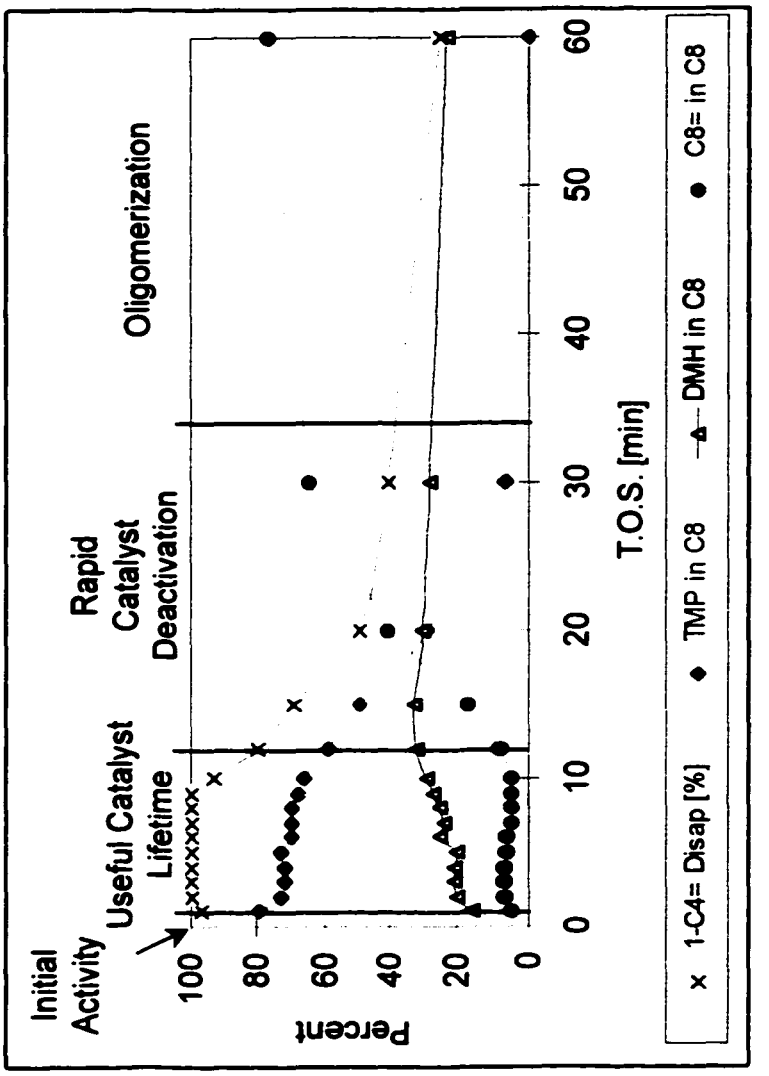



**Figure 6.2:** Stages of Catalyst Activity on EMT Zeolite with respect to $C_8$ Fraction Distribution (F66EMT; $T_{rxn}$=50°C; $T_{calc}$=425°C; P=382psig; I/O=15; t=1h; $C_4^=$ WHSV=2.0$h^{-1}$; $m_{cat}$=2.78g)

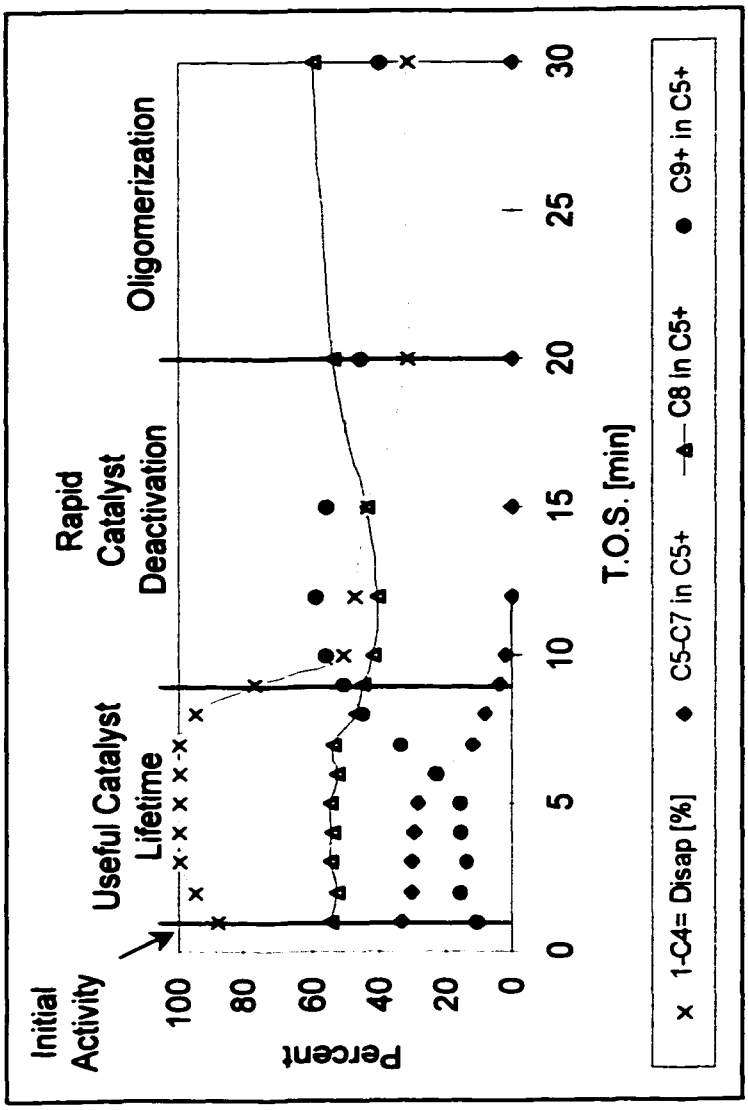



**Figure 6.3:** Stages of Catalyst Activity on Y Zeolite with respect to $C_5$+ Product Distribution (F54Y; $T_{rxn}$=50°C; $T_{calc}$=425°C; P=382psig; I/O=15; t=1h; $C_4^=$ WHSV=2.0$h^{-1}$; $m_{cat}$=2.78g)

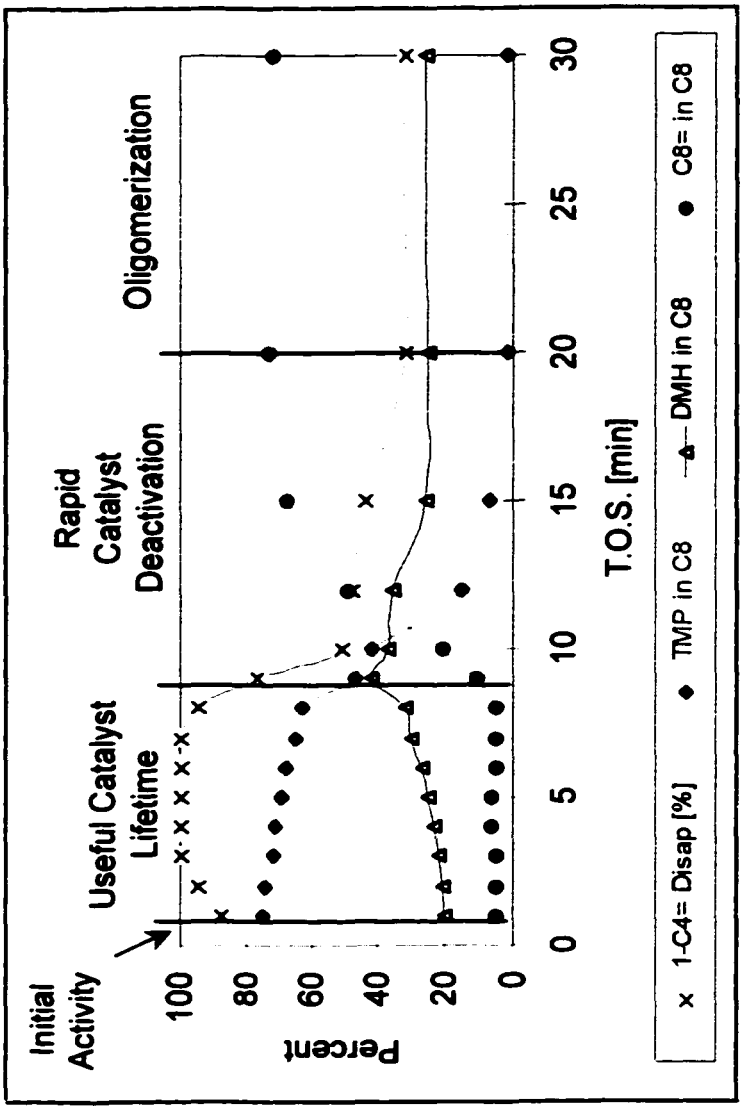



**Figure 6.4:** Stages of Catalyst Activity on Y Zeolite with respect to $C_8$ Fraction Distribution (F54Y; $T_{rxn}$=50°C; $T_{calc}$=425°C; P=382psig; I/O=15; t=1h; $C_4^=$ WHSV=2.0$h^{-1}$; $m_{cat}$=2.78g)

The fourth and final stage of catalyst activity is termed the "Oligomerization" phase. This period was characterized by a low but measurable amount of butene conversion (Taylor & Sherwood, 1997). The $C_5$+ liquid consisted of mainly $C_8$ olefins with some $C_9$+ products observed. Saturated $C_8$ production was low, and restricted to DMHs only. A typical alkylate composition from this phase was composed of 60 % $C_8$ products, of which 80 % were $C_8$ olefins. Similar behaviour was shown by EMT and Y zeolites during this final phase of catalyst activity.

## 6.3 SENSITIVITY ANALYSIS FOR EMT AND Y ZEOLITES

Sensitivity analysis is based on 3 sets of duplicated experiments and 1 set of triplicated results (see Appendix A4.3). These replicates involved catalyst systems of EMT, fresh 0.5%Pt/Y, regenerated 0.1%Pt/EMT and regenerated 0.5%Pt/EMT. Standard deviations were calculated during the initial 7 min of the Useful Catalyst Lifetime period. An overall average of the standard deviations was determined for all measures of catalyst performance (see Table 6.1). These values were used to assess the significance of experimental differences.

**Table 6.1:** Sensitivity Analysis for Measures of Catalyst Performance of Flow Runs using EMT and Y Zeolites

| Measure of Catalyst Performance | Standard Deviation |
|---|---|
| Useful Catalyst Lifetime [min] | ± 0.7 |
| Yield [g $C_5$+/gcat/min] | ± 0.016 |
| *$C_5$+ Product Distribution [mass %]* | |
| $C_5$ - $C_7$ | ± 2.3 |
| $C_8$ | ± 2.5 |
| $C_9^+$ | ± 3.7 |
| *$C_8$ Fraction Distribution [mass %]* | |
| TMP | ± 3.3 |
| DMH | ± 2.7 |
| $C_8^=$ | ± 0.8 |
| *TMP Isomer Distribution [mass %]* | |
| 2,2,4-TMP | ± 2.5 |
| 2,2,3-TMP | ± 2.1 |
| 2,3,3-TMP | ± 2.4 |
| 2,3,4-TMP | ± 2.1 |
| *Indicators [mass fraction]* | |
| $\frac{\text{TMP}}{\text{DMH}}$ | ± 0.57 |
| $\frac{\text{TMP + DMH}}{C_8^= + C_9^+}$ | ± 0.63 |
| $\frac{\text{2,2,3-TMP + 2,2,4-TMP}}{\text{2,3,3-TMP + 2,3,4-TMP}}$ | ± 0.20 |
| S.A. Spent Catalyst [$m^2$/g] | ± 28.3 |

## 6.4 EFFECT OF CALCINATION TEMPERATURE ON EMT AND Y ZEOLITES

The calcination temperature has an effect on the relative amounts of Bronsted and Lewis acid sites in zeolites, as described in Section 2.1.1.1. Maximum Bronsted acidity is achieved at a calcination temperature of approximately 425°C for Y zeolite (Ward, 1967). Above this temperature, Bronsted acidity declines and Lewis acid sites increase in concentration. Once a calcination temperature of approximately

725°C is reached, Lewis and Bronsted acidity are approximately equal. As the calcination temperature is increased above 725°C, partial collapse of the zeolite structure occurs and the total number of acid sites decreases with only Lewis acid sites prevailing. No published information on the influence of EMT calcination temperature, with respect to Lewis and Bronsted acidity, is available. However, analogous behavior is expected, as both EMT and Y belong to the same faujasite family (see Chapter 3).

Calcination conditions for EMT and Y zeolites were tested at two levels: 425 and 540°C. The effect of calcination temperature was examined within the reaction temperature range of 55 to 100°C, at a reaction pressure of 382 psig and employing an I/O ratio of 11. Raw data for all experiments are found in Appendix 4.

### 6.4.1 Effect of Calcination Temperature on Butene Disappearance

The Useful Catalyst Lifetime of EMT was reduced by 40 % when the calcination temperature was increased from 425 to 540°C at a reaction temperature of 55°C (see Table 6.2). Calcination temperature effects were significantly diminished at higher reaction temperatures, on both EMT and Y zeolites. The Useful Catalyst Lifetime appeared to be compromised at higher temperatures; however, additional data are required to substantiate this claim.

These observations suggest that a calcination temperature of 540°C, which favours a higher concentration of Lewis acid sites and lower Bronsted acidity, expedited the onset of catalyst deactivation. This validates the approach to catalyst design, in which a primary screening criteria for potential candidates is maximizing Bronsted acidity and minimizing Lewis acidity. The data suggest that catalyst lifetime would be enhanced by employing a calcination temperature of 425°C, particularly when a low reaction temperature of 55°C is employed in the experiment.

**Table 6.2:** Effect of Calcination Temperature on Useful Catalyst Lifetime period of EMT and Y Zeolites (P=382psig, I/O=11; $C_4^=$ WHSV=2.6$h^{-1}$; $m_{cat}$=2.78g)

| Catalyst | $T_{rxn}$ [°C] | Useful Catalyst Lifetime period [min] | |
|---|---|---|---|
| | | $T_{calc}$=425°C | $T_{calc}$=540°C |
| EMT | 55 | 10.6 | 6.5 |
| | 77 | 7.6 | n.a. |
| | 88 | n.a. | 6.9 |
| | 100 | 6.8 | n.a. |
| Y | 70 | 8.4 | n.a. |
| | 86 | n.a. | 4.5 |
| | 100 | 4.5 | n.a. |

It is interesting that the effect of calcination temperature was more apparent at a lower reaction temperature, and became less significant as the temperature was elevated. It is possible that the hydrophilicity of the catalyst surface was influenced by calcination temperature (Kaliguine, 2000), with lower calcination temperatures favouring reduced desorption rates of *i*-$C_4$. As reaction temperature was increased, the desorption rate of *i*-$C_4$ increased, making the effect of calcination temperature less distinguishable. The reaction became less selective towards alkylation and therefore, the effect of acid site type was less significant.

Alternatively, pore volume may also be modified by calcination temperature affecting the concentration of reactants in the catalyst pores or rate of adsorption of *i*-$C_4$. These modifications to the local environment, may be more significant at lower reaction temperatures. These aspects were not considered in the present work and could be explored in future investigations.

### 6.4.2 Effect of Calcination Temperature on $C_5$+ Product Distribution

Calcination temperature demonstrated a measurable effect on alkylate composition during the Useful Catalyst Lifetime period. The fraction of $C_5$-$C_7$ components in the alkylate was reduced and polymerization levels were elevated, for the catalyst calcined at 540°C. This behaviour was found to be more significant on EMT at a reaction temperature of 55°C (see Figure 6.5) and Y zeolite between 70 and 100°C (see Figure 6.7). The effects were less notable on EMT between 77 to 100°C (see Figure 6.6).

The content of $C_8$ compounds in the alkylate, was not significantly altered by the calcination temperature. EMT achieved comparable $C_8$ levels at 55°C for both calcination temperatures (see Figure 6.5). However, these levels were sustained for a longer duration under the milder calcination conditions (i.e. $T_{calc}$=425°C). The content of $C_8$ compounds in the alkylate was reduced slightly at higher reaction temperatures on both EMT (see Figure 6.6) and Y (see Figure 6.7) zeolites, when the severity of the calcination step was increased to 540°C.

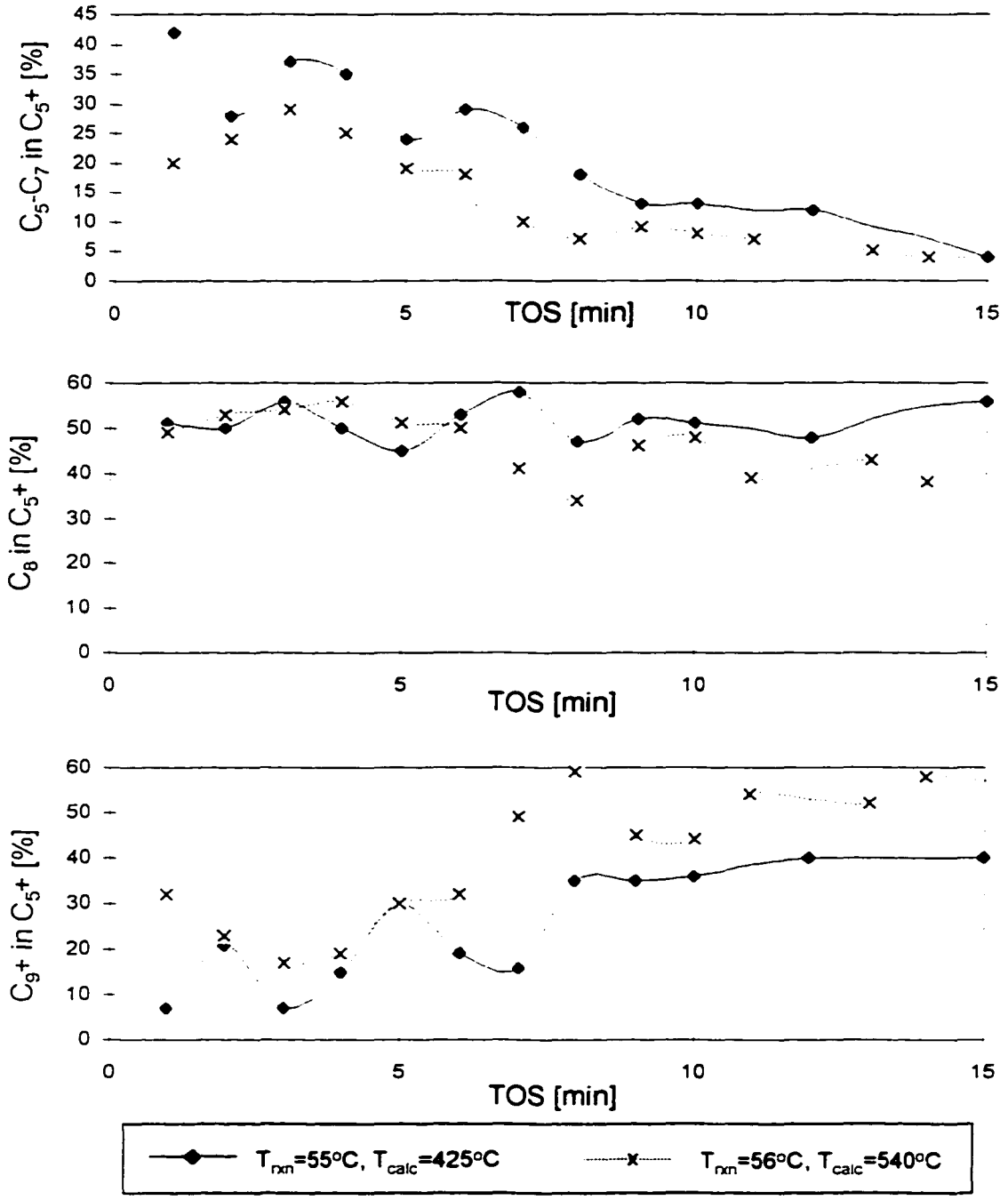



**Figure 6.5:** Effect of EMT Calcination Temperature on $C_5$+ Product Distribution at a Reaction Temperature of 55°C (P=382psig; I/O=11; $C_4^=$WHSV=2.60$h^{-1}$; $m_{cat}$=2.78g)

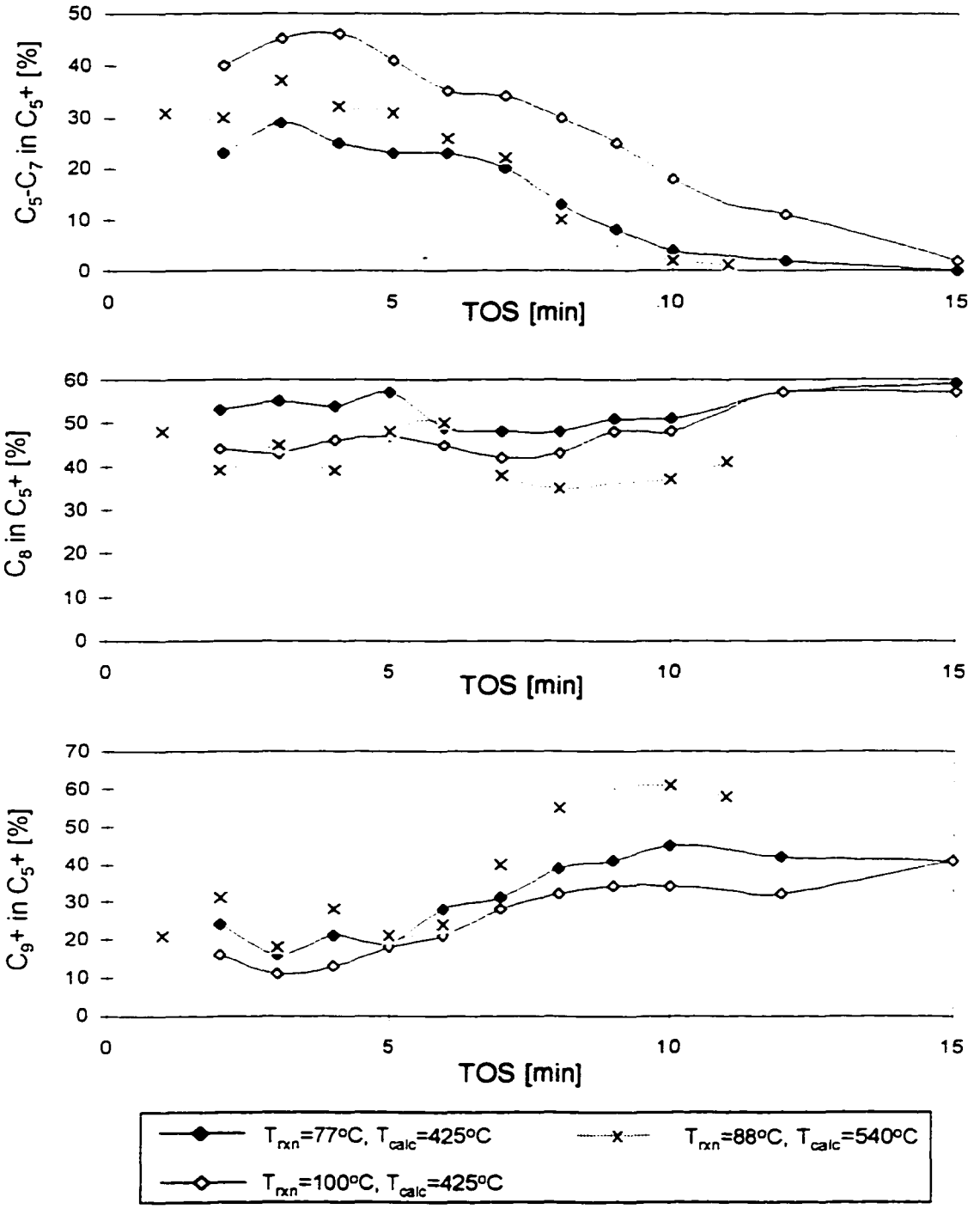



**Figure 6.6:** Effect of EMT Calcination Temperature on $C_5$+ Product Distribution for Reaction Temperatures between 77 and 100°C

(P=382psig; I/O=11; $C_4^=$WHSV=2.60$h^{-1}$; $m_{cat}$=2.78g)

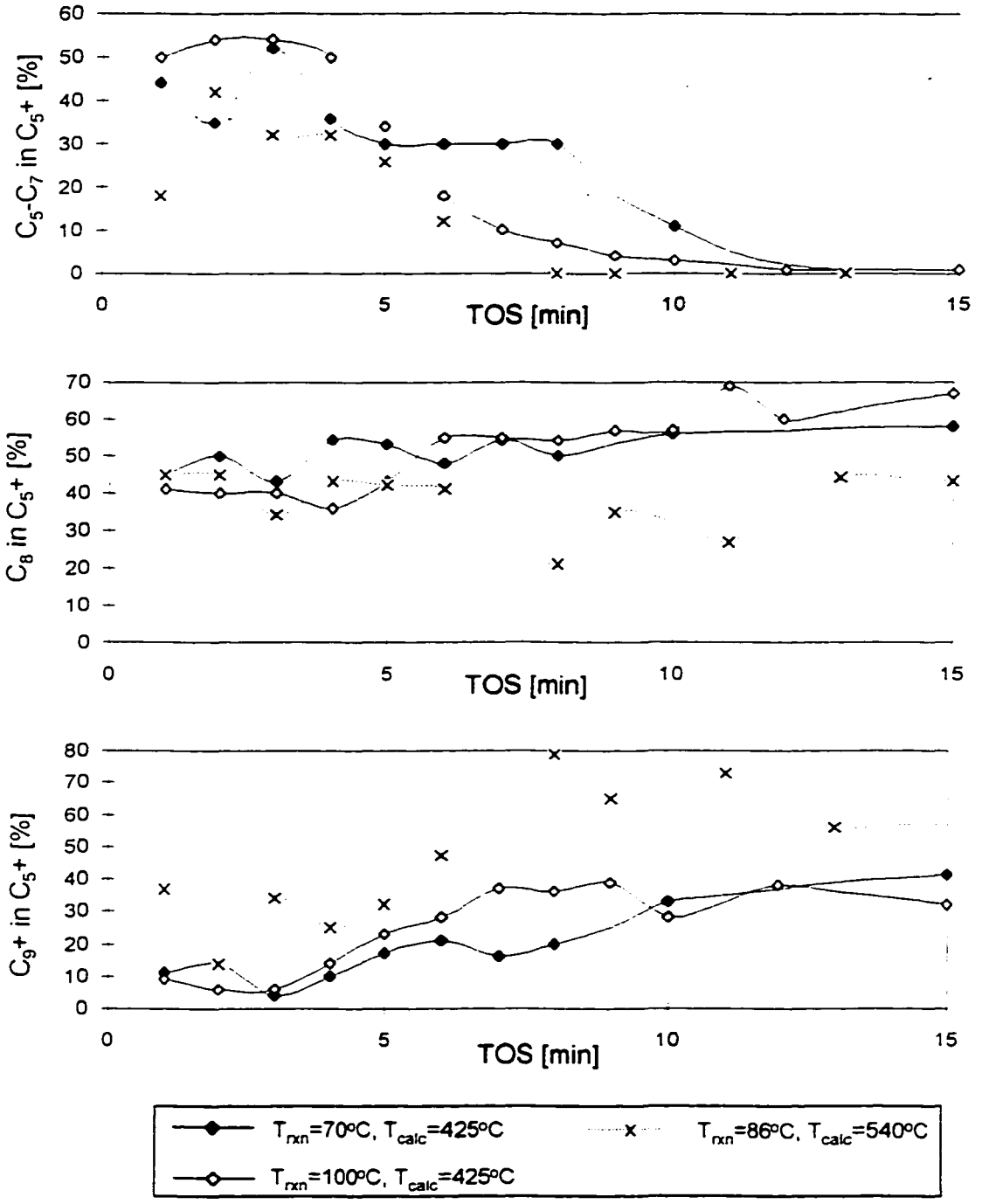



**Figure 6.7:** Effect of Y Calcination Temperature on $C_5$+ Product Distribution for Reaction Temperatures between 70 and 100°C (P=382psig; I/O=11; $C_4^=$WHSV=2.60$h^{-1}$; $m_{cat}$=2.78g)

### 6.4.3 Effect of Calcination Temperature on $C_8$ Selectivity

No significant change in TMP levels was noted during the Useful Catalyst Lifetime period on EMT, when the calcination temperature was increased from 425 to 540°C. However, TMP levels were sustained for a longer duration at 55°C, when the milder calcination temperature was employed (see Figure 6.8). The lower calcination temperature favoured increased DMH production, as compensated by suppressed oligomerization formation. Overall, more saturated $C_8$ products (TMPs and DMHs) were detected from EMT with higher Bronsted acidity, at a reaction temperature of 55°C. An increase in calcination temperature enhances Lewis acidity on EMT, which favoured oligomerization products over DMHs. Elevated levels of olefins are expected to enhance polymerization activity, which was observed for EMT calcined at 540°C.

The effects of calcination temperature were greatly diminished at elevated reaction temperatures on EMT (see Figure 6.9). A calcination temperature of 425°C produced slightly lower amounts of TMPs with increased levels of DMHs, for reaction temperatures of 77 and 100°C. This differs slightly from the behaviour at 55°C, where TMP levels were independent of calcination conditions.

Y zeolite behaved in a manner similar to EMT at higher reaction temperatures (see Figure 6.10). The catalyst calcined at 425°C produced less TMPs and more DMHs during the Useful Catalyst Lifetime period. Although the TMP content was improved by calcining at 540°C, the total amount of saturated $C_8$ products (TMPs and DMHs) was greatly reduced.

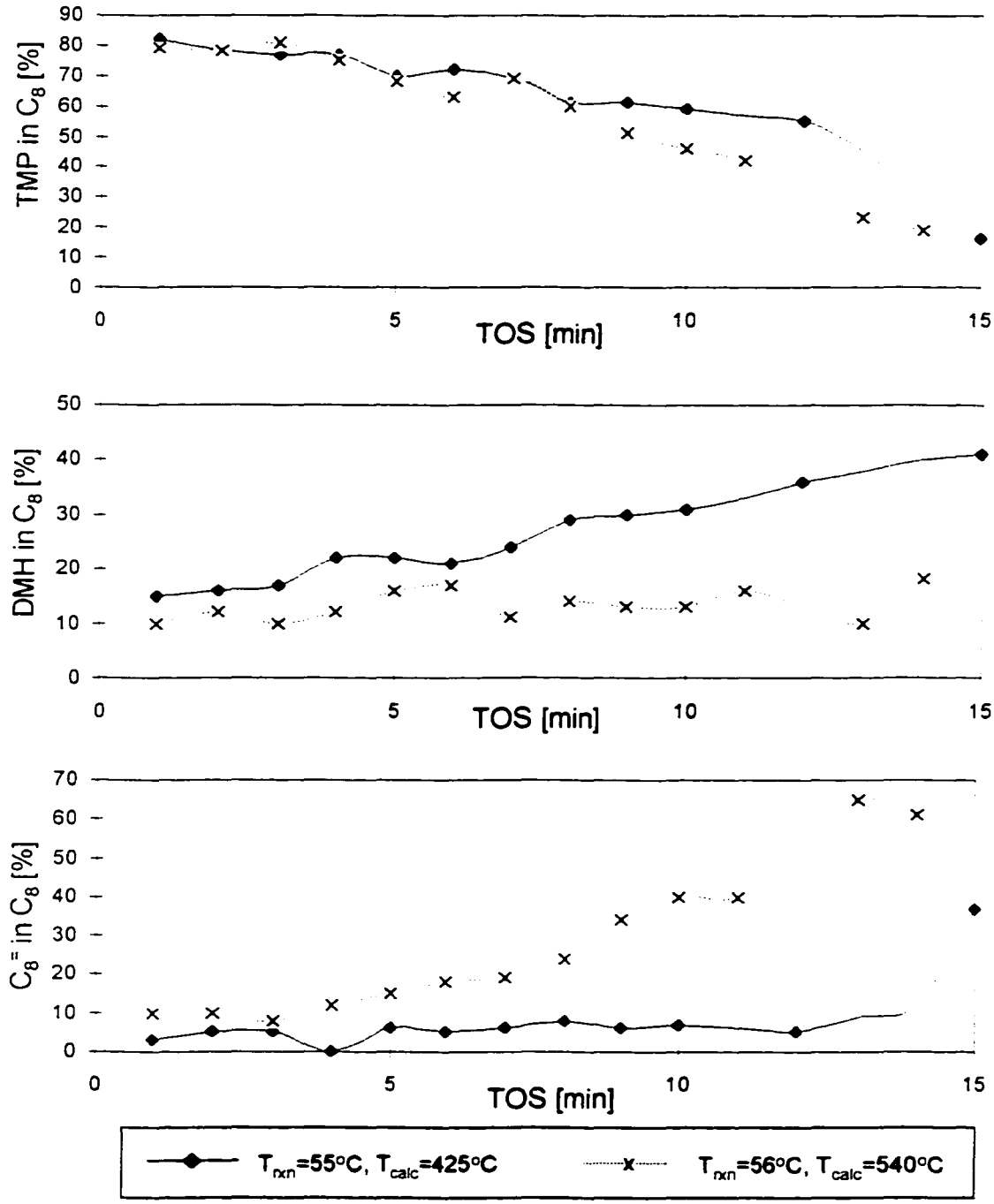



**Figure 6.8:** Effect of EMT Calcination Temperature on $C_8$ Selectivity at a Reaction Temperature of 55°C
(P=382psig; I/O=11; $C_4^=$WHSV=2.60$h^{-1}$; $m_{cat}$=2.78g)

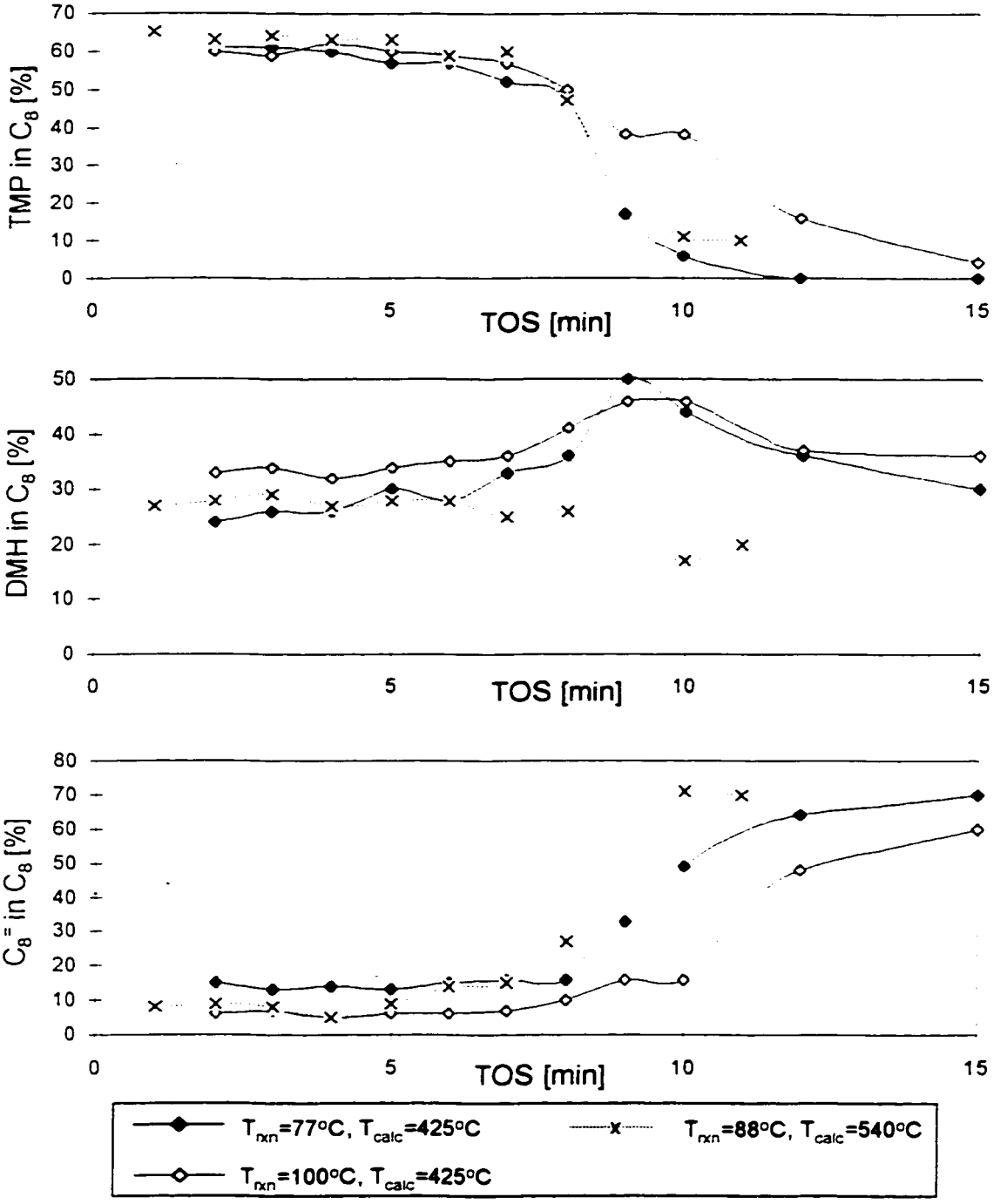



**Figure 6.9:** Effect of EMT Calcination Temperature on $C_8$ Selectivity For Reaction Temperatures between 77 and 100°C (P=382psig; I/O=11; $C_4^=$WHSV=2.60$h^{-1}$; $m_{cat}$=2.78g)

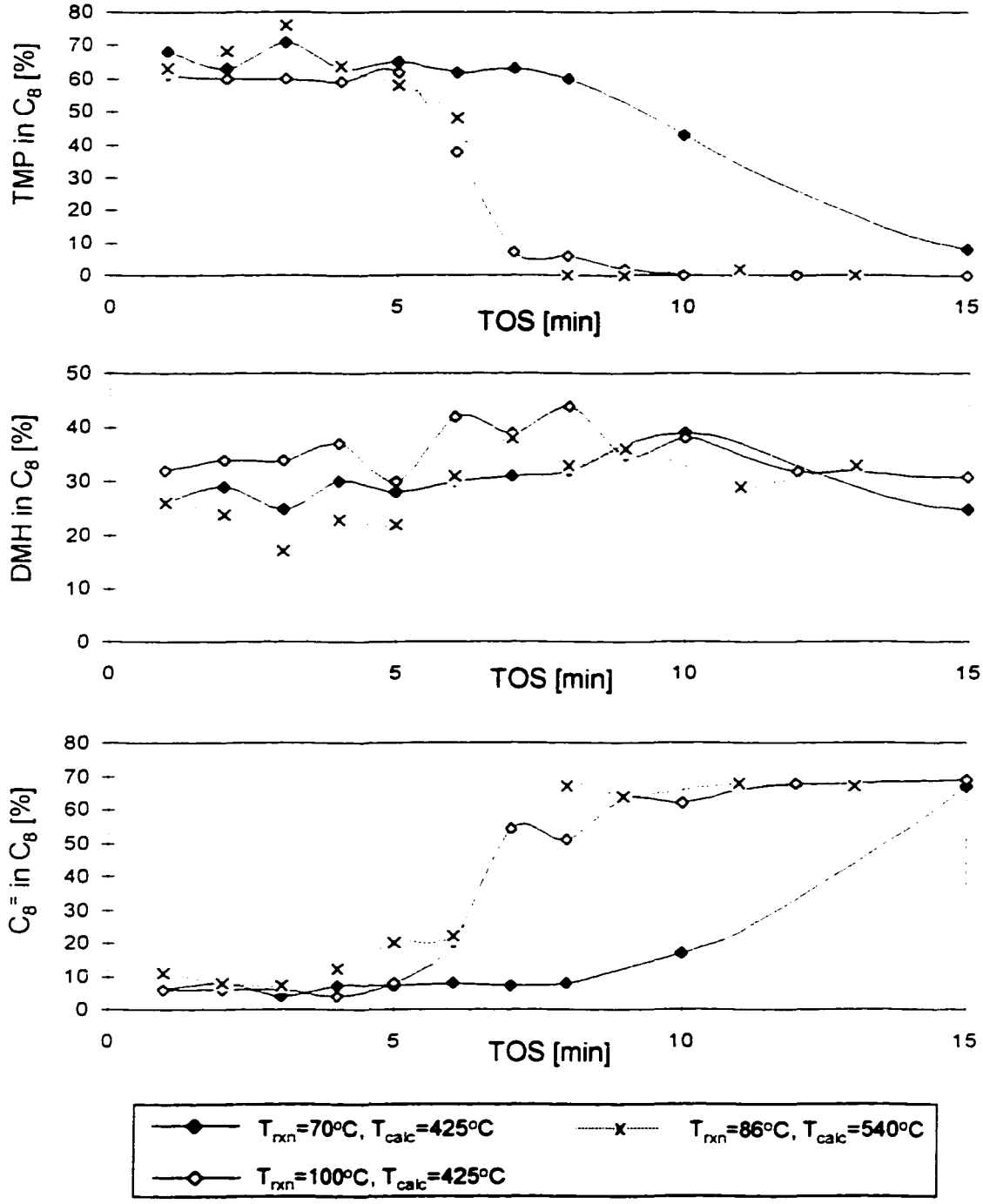



**Figure 6.10:** Effect of Y Calcination Temperature on $C_8$ Selectivity for Reaction Temperatures between 70 and 100°C (P=382psig; I/O=11; $C_4^=$WHSV=2.60h$^{-1}$; $m_{cat}$=2.78g)

Comparable behaviour between EMT and Y zeolites was observed during the other phases of catalyst activity (see Figures 6.8 to 6.10). The production of TMP was sustained more effectively during the Deactivation period on the catalysts calcined at 425°C. Elevated levels of DMH formation were noted during the Useful Catalyst Lifetime, for catalysts subjected to milder calcination treatment. This behaviour continued during the Deactivation phase, except on Y zeolite at reaction temperatures above 70°C. This catalyst favoured TMPs during the Deactivation phase when calcined at 425°C. The levels of $C_8^=$ were comparable during the Useful Catalyst Lifetime period, for all calcination conditions. However, content of $C_8^=$ was notably less during the Deactivation Period, for catalysts calcined at 425°C.

These results support the notion that the nature of the acid sites resulting from a calcination temperature of 425°C were better equipped to maintain a strong hydride transfer function, particularly at a reaction temperature of 55°C. Predominantly saturated products were detected in the $C_8$ fraction, which were less reactive towards undesirable side reactions. This delayed the onset of catalyst deactivation, allowing alkylation activity to be sustained for longer duration and favouring an extended Useful Catalyst Lifetime.

### 6.4.4 Effect of Calcination Temperature on 2,2,4-TMP Level in the TMP Fraction

The most valuable octane product, 2,2,4-TMP, can result from self-alkylation of *i*-$C_4$, isomerization of $TMP^+$ isomers formed or cracking of $C_{12}^+$ products. If cracking of $C_{12}^+$ components is the primary route of 2,2,4-TMP formation, it is expected that higher levels of 2,2,4-TMP would result at a higher reaction temperature and lower calcination temperature, as these conditions favour high cracking activity. This is contrary to what was observed experimentally (see Figure 6.11). This suggests that other routes of 2,2,4-TMP formation, such as self-alkylation of *i*-$C_4$, were being promoted on EMT.

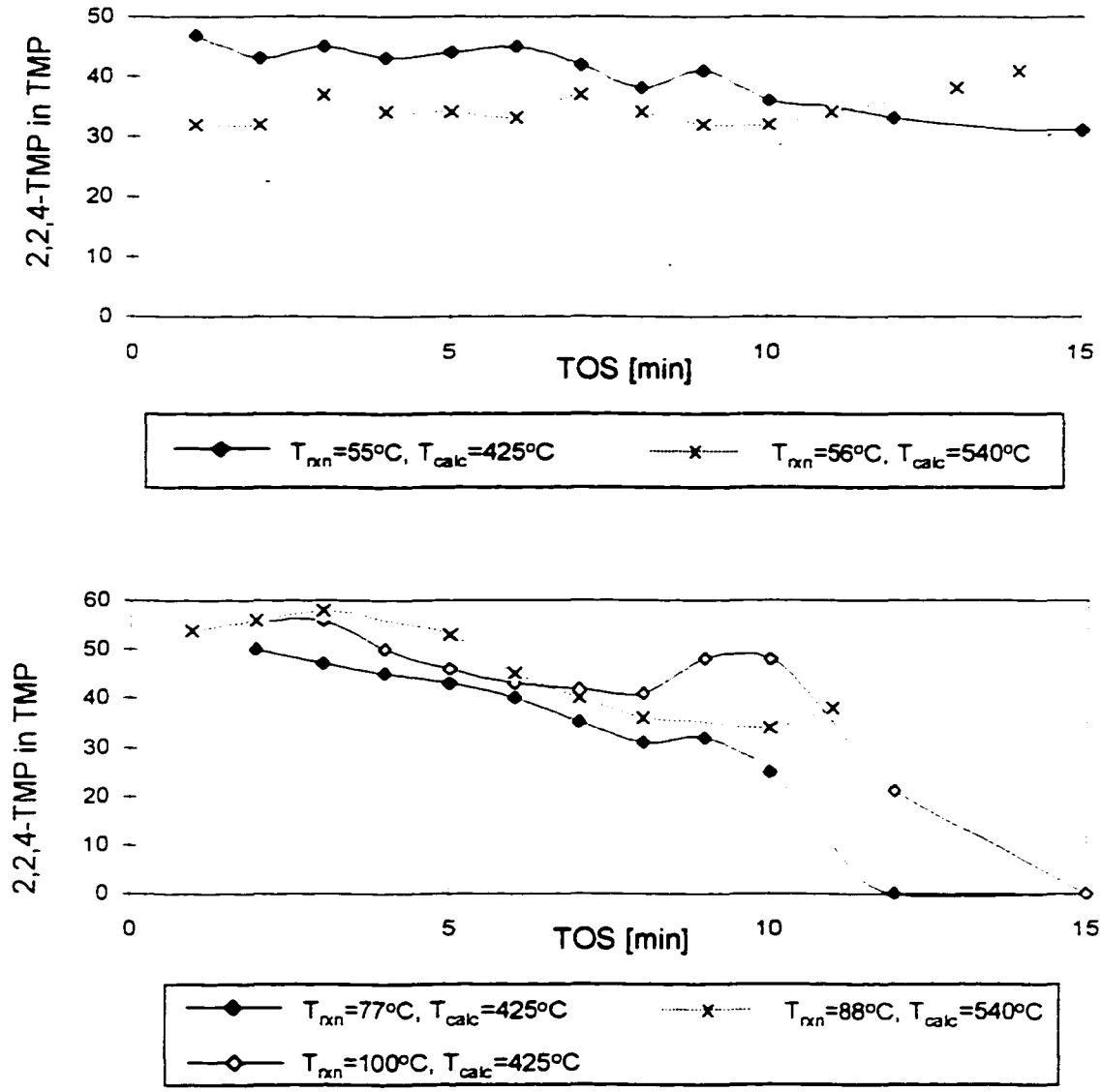



**Figure 6.11:** Effect of EMT Calcination Temperature on 2,2,4-TMP Content in TMP Fraction for Reaction Temperatures between 55 and 100°C (P=382psig; I/O=11; $C_4^=$WHSV=2.60$h^{-1}$; $m_{cat}$=2.78g)

Results on Y zeolite contrasted with those obtained on EMT, at higher reaction temperatures. A lower calcination temperature of 425°C favoured higher levels of 2.2.4-TMP in the TMP fraction, relative to those obtained on Y zeolite calcined at 540°C (see Figure 6.12). It may be that the primary route of 2,2,4-TMP formation on Y zeolite occurred through cracking of $C_{12}^+$ compounds. Since the lower calcination temperature enhanced cracking activity, it is expected that 2,2,4-TMP levels would be greatest under these conditions. It is also possible that acid sites which could potentially facilitate other routes of 2,2,4-TMP production (i.e. self alkylation of isobutane), were converted to Lewis acid sites during the more severe calcination treatment at 540°C. These possibilities were not pursued in the present work, and could be considered in subsequent investigations.

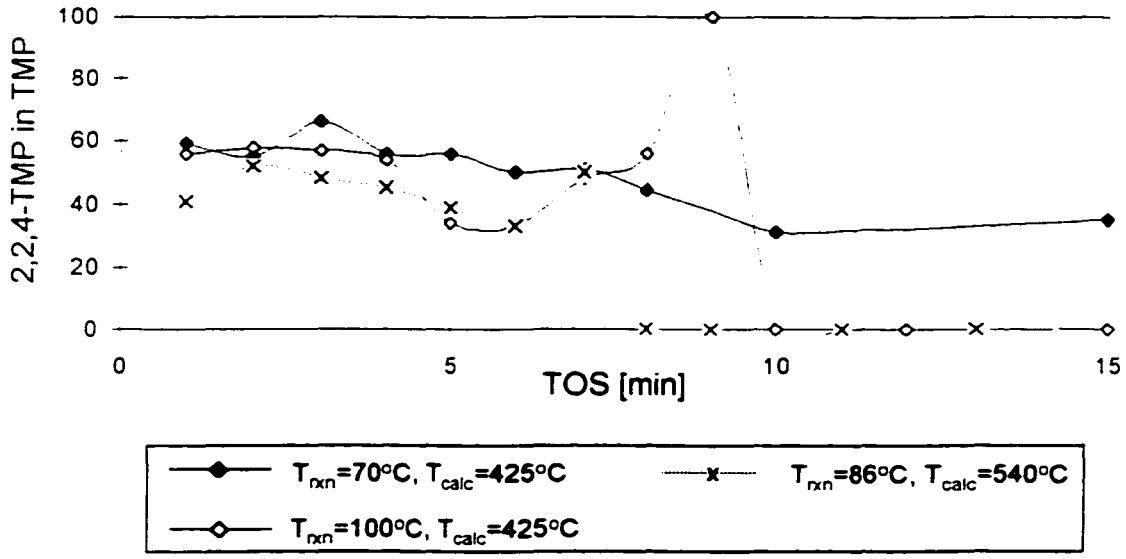



**Figure 6.12:** Effect of Y Calcination Temperature on 2,2,4-TMP Content in TMP Fraction for Reaction Temperatures between 70 and 100°C (P=382psig; I/O=11; $C_4^=$WHSV=2.60$h^{-1}$; $m_{cat}$=2.78g)

### 6.4.5 Synopsis of Effect of Calcination Temperature

The effect of calcination temperature is consistent with the hypothesis that the alkylation mechanism is facilitated by a Bronsted acid site. A calcination temperature of 425°C, which favours the maximum density of Bronsted acid sites, sustained catalyst activity for a longer duration on EMT and Y zeolites. This result is supported by other work in the literature. Simpson et al (1996) observed a striking correspondence between the relative number of Bronsted acid sites on Y zeolite and time-zero butene conversion, providing corroborating evidence of the nature of the acid site activating this reaction using solid acids.

Catalyst performance varied with changes in calcination temperature on both EMT and Y zeolites. Table 6.3 summarizes average alkylate quality during the first 5 min of the Useful Catalyst Lifetime period. A lower calcination temperature of 425°C promoted cracking activity whereas, a catalyst calcined at 540°C favoured polymerization reactions on both EMT and Y zeolites.

Although the TMP/DMH ratio was augmented by a calcination temperature of 540°C on EMT at a reaction temperature 55°C, the selectivity to saturated $C_8$ products was very poor ((TMP + DMH)/($C_8^=$ + $C_9$+)) (see Table 6.3). Similar behavior appeared to be demonstrated by Y zeolite at higher operating temperatures, between 70 and 100°C. However, this behaviour was not conclusively observed on EMT between 77 and 100°C. Additional experiments are required to definitively assess the influence of calcination treatment on catalyst performance at higher reaction temperatures.

All of the effects discussed above were more significant at a reaction temperature of 55°C when employing EMT. As the reaction temperature was increased, the effects of calcination temperature were found to be less important, with respect to maximizing saturated $C_8$ production levels and suppressing oligomerization activity. However, the lower calcination temperature still demonstrated superior catalyst performance in terms of maximizing the Useful Catalyst Lifetime period.

**Table 6.3:** Effect of Calcination Temperature on Catalyst Performance and Average Alkyate Quality (first 5 min of Useful Catalyst Lifetime period) using EMT and Y Zeolites (P=382psig, I/O=11; $C_4^=$ WHSV=2.6$h^{-1}$; $m_{cat}$=2.78g)

| Catalyst | EMT | | | | | | Y | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| $T_{calc}$ [°C] | 425 | | | 540 | | | 425 | | | 540 |
| Run | F28EMT | F31EMT | F34EMT | F23EMT | F22EMT | | F29Y | F33Y | | F21Y |
| $T_{rxn}$ [°C] | 55 | 77 | 100 | 56 | 88 | | 70 | 100 | | 86 |
| Useful Catalyst Lifetime [min] | 10.6 | 7.6 | 6.8 | 6.5 | 6.9 | | 8.1 | 4.5 | | 4.5 |
| *$C_5$+ Liquid [mass %]* | | | | | | | | | | |
| $C_5$ - $C_7$ | 33 | 25 | 41 | 23 | 32 | | 39 | 49 | | 30 |
| $C_8$ | 51 | 55 | 45 | 53 | 45 | | 49 | 40 | | 42 |
| $C_9$+ | 16 | 20 | 14 | 24 | 23 | | 12 | 11 | | 28 |
| *$C_8$ Fraction [mass %]* | | | | | | | | | | |
| TMP | 77 | 60 | 61 | 76 | 64 | | 66 | 61 | | 66 |
| DMH | 19 | 26 | 33 | 13 | 28 | | 27 | 33 | | 22 |
| $C_8^=$ | 4 | 14 | 6 | 11 | 8 | | 7 | 6 | | 12 |
| *TMP Distribution [%]* | | | | | | | | | | |
| 2,2,4-TMP | 44 | 46 | 52 | 34 | 55 | | 58 | 53 | | 45 |
| 2,2,3-TMP | 15 | 10 | 12 | 11 | 13 | | 9 | 10 | | 5 |
| 2,3,4-TMP | 15 | 17 | 14 | 23 | 11 | | 12 | 15 | | 22 |
| 2,3,3-TMP | 26 | 27 | 22 | 32 | 21 | | 21 | 22 | | 28 |
| *Indicators [mass %]* | | | | | | | | | | |
| TMP / DMH | 4.13 | 2.29 | 1.81 | 6.10 | 2.29 | | 2.42 | 1.82 | | 3.03 |
| TMP+DMH / $C_8^=$ + $C_9$+ | 3.57 | 1.74 | 2.49 | 1.65 | 1.61 | | 3.63 | 3.20 | | 1.26 |
| 2,2,4-TMP+2,2,3-TMP / 2,3,3-TMP+2,3,4-TMP | 1.49 | 1.30 | 1.82 | 0.81 | 2.15 | | 2.05 | 1.68 | | 1.01 |

These results support the notion that the nature of the acid sites resulting from a calcination temperature of 425°C were better equipped to maintain a strong hydride transfer function. Predominantly saturated products were detected in the $C_8$ fraction which were less reactive towards undesirable side reactions. This delayed the onset of catalyst deactivation allowing alkylation activity to be sustained for a longer duration thus extending the Useful Catalyst Lifetime period.

The severity of the calcination treatment influenced the distribution of TMP isomers. More severe calcination temperatures favoured the least sterically hindered isomers, 2,3,3-TMP and 2,3,4-TMP, at 55°C on EMT and on Y between 70 and 100°C (see Table 6.3). No significant effect of calcination temperature on TMP distribution was noted on EMT at reaction temperatures above 77°C. The most valuable octane isomer, 2,2,4-TMP, predominated on both catalysts under all conditions tested, reaching levels between 34 and 58 % of the TMP fraction. Cracking of $C_{12}$+ compounds was identified as the most probable route for 2,2,4-TMP formation, with self-alkylation of *i*-$C_4$ being suggested as a possible alternative on EMT.

Note that the product distribution observed is a qualitative assessment, on the basis of instantaneous product effluent analysis. This approach does not consider catalyst yield (i.e. g $C_5$+ produced/g $C_4^=$ fed/h) with TOS, which provides a measure of the quantity of alkylate collected. Since liquid product was not collected for these experiments, the most reliable indication of yield is the duration of the Useful Catalyst Lifetime. That is, a catalyst facilitating effective hydride transfer will desorb products efficiently, operate for a longer TOS and favour alkylation products. In contrast, catalysts which are deficient in this ability, will retain products on the catalyst surface and deactivate in a shorter period of time. On this basis, a catalyst calcined at 425°C is expected to achieve a higher yield and EMT is expected to behave in a superior manner relative to Y zeolite.

The explanations provided to rationalize the experimental data are further validated by surface area (SA) measurements of the spent catalyst (see Table 6.4). Those calcined at 425°C were less susceptible to SA loss despite the fact that catalyst exposure to the feed was four times longer. It appears that calcination

conditions promoting Bronsted acidity, yielded a catalyst which demonstrated superior resistance to catalyst deactivation. In contrast, a calcination temperature of 540°C, favouring increased Lewis acidity, promoted olefin adsorption. This favoured oligomerization and polymerization activities, promoting rapid surface area loss upon exposure to the feed.

**Table 6.4:** Effect of Calcination Temperature on Surface Area of Spent Catalyst (P=382 psig; I/O=11, $C_4^=$ WHSV=2.6$h^{-1}$; $m_{cat}$=2.78g)

| Catalyst | Calcination Temperature [°C] | Reaction Temperature [°C] | Experiment Duration [min.] | Surface Area of Spent Catalyst [$m^2/g$] |
|---|---|---|---|---|
| EMT | 425 | 55 | 60 | 377 |
| | | 77 | 60 | 348 |
| | | 100 | 60 | 309 |
| EMT | 540 | 56 | 15 | 148 |
| | | 88 | 15 | 121 |
| Y | 425 | 70 | 60 | 374 |
| | | 100 | 60 | 329 |
| Y | 540 | 80 | 15 | 205 |

S.A. fresh EMT = 755 $m^2/g$; S.A. fresh Y = 620 $m^2/g$

TGA/DTA of the spent catalyst provided further evidence of increased susceptibility to deactivation on EMT, when pre-treatment promoted increased Lewis acidity (see Table 6.5). The loss in active surface area was more significant for EMT calcined at 540°C, despite the brief exposure to the butene feed mixture. It is possible that adsorbed species on this catalyst are active in facilitating hydride transfer during the reaction, leading to polyaromatic deposits plugging the catalyst pores. In contrast, EMT calcined at 425°C, favouring increased Bronsted acidity, was better equipped to facilitate hydride transfer. Consequently, adsorbed species were less reactive towards polymerization reactions. The content of adsorbed species was suppressed and active surface area was preserved in a superior manner.

**Table 6.5:** TGA/DTA Analysis of Spent EMT as a Function of Calcination Temperature ($T_{rxn}$=55°C; P=382psig; I/O=11; $C_4^=$ WHSV=2.6$h^{-1}$; $m_{cat}$=2.78g)

| Run | $T_{calc}$ [°C] | Duration [min] | TGA [mass %] Desorption Temperature [°C] $T_d \leq 200$ | $200 < T_d < 300$ | $T_d \geq 300$ | Total | SA Spent Catalyst [$m^2/g$] |
|---|---|---|---|---|---|---|---|
| F28EMT | 425 | 60 | 3.8 | 2.5 | 3.0 | 9.3 | 377 |
| F23EMT | 540 | 15 | 2.8 | 2.7 | 3.0 | 8.5 | 148 |

S.A. fresh EMT = 755 $m^2/g$

Overall, a calcination temperature of 425°C promoted hydride transfer for a longer period of time and deferred the onset of catalyst deactivation. This resulted in high butene conversion being maintained for a longer TOS. Additional experiments, with the objective to optimize the calcination temperature for EMT and Y zeolite, were not attempted. All subsequent experiments utilized a calcination temperature of 425°C, unless otherwise specified.

## 6.5 EFFECT OF REACTION TEMPERATURE ON EMT AND Y ZEOLITES

Reaction temperature was not found to exercise a significant effect on the product distribution between 80 and 100°C in batch experiments. It is of interest to determine whether similar behavior is observed in a continuous flow environment. Flow experiments were performed in the temperature range of 29 to 100°C at 382 psig, using EMT and Y zeolites calcined at 425°C, and employing an I/O ratio of 11 ($C_4^=$ WHSV = 2.6 $h^{-1}$).

### 6.5.1 Effect of Reaction Temperature on Butene Disappearance

Of the reaction temperatures considered, a preferred level of 55°C was identified for EMT, whereas 70°C was concluded best on Y zeolite (see Figures 6.13). The result on Y zeolite closely matches that found by other authors utilizing a continuous stirred reactor (Taylor & Sherwood, 1997). Butene conversion was sustained for a longer duration under these preferred conditions, maximizing the length of the Useful Catalyst Lifetime period. Clearly, the optimum reaction temperature is specific to the nature of the catalyst (i.e. catalyst type, $T_{calc}$) and operating conditions (i.e. I/O, olefin WHSV, reactor geometry) employed for the experiment. This suggestion has been emphasized by other authors (Corma & Martinez,1993).

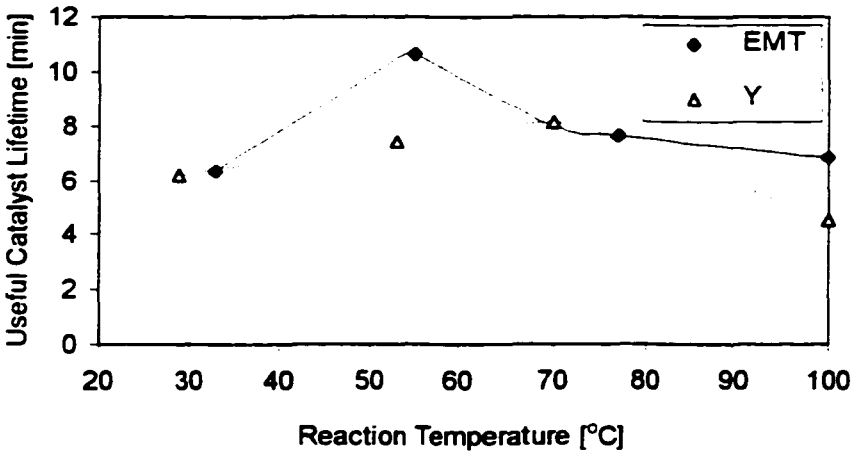



**Figure 6.13:** Effect of Reaction Temperature on Useful Catalyst Lifetime for EMT and Y Zeolites ($T_{calc}$=425°C; P=382psig; I/O=11; $C_4^=$WHSV=2.6$h^{-1}$; $m_{cat}$=2.78g)

EMT demonstrated superior ability over Y, and extended the Useful Catalyst Lifetime for a longer duration at their respective preferred temperature conditions. The Useful Catalyst Lifetime for EMT was more adversely affected at reaction temperatures below 55°C, relative to those above this preferred level. This trend was reversed when employing Y zeolite. The Useful Catalyst Lifetime was significantly reduced at temperatures above 70°C, and less sensitive to operating conditions below this preferred reaction temperature.

### 6.5.2 Effect of Reaction Temperature on $C_5$+ Product Distribution

At the preferred reaction temperature, cracking activity and alkylation activities were maximized and polymerization activity was suppressed for EMT and Y zeolites (see Figures 6.14 to 6.15). Since alkylation and cracking reactions demands similar acid site strength (Corma et al, 1994b; Corma & Wojciechowski, 1982; Corma et al, 1994a; O'Young et al, 1994; Corma et al, 1996a), it is difficult to promote one type of reaction without encouraging the other. Therefore, the optimum reaction temperature represents a compromise between two opposing forces. The reaction temperature must be sufficiently high to facilitate high olefin conversion for a long duration and crack bulky polymerization products. However, it cannot be excessively high, such that the stability of alkylate precursors is compromised. This complicated kinetic balance is a function of the process parameters employed, including catalyst type, calcination temperature and I/O ratio to name a few. Therefore, the preferred reaction temperature which has been identified, is specific to the process parameters which have been fixed in the experimental procedure.

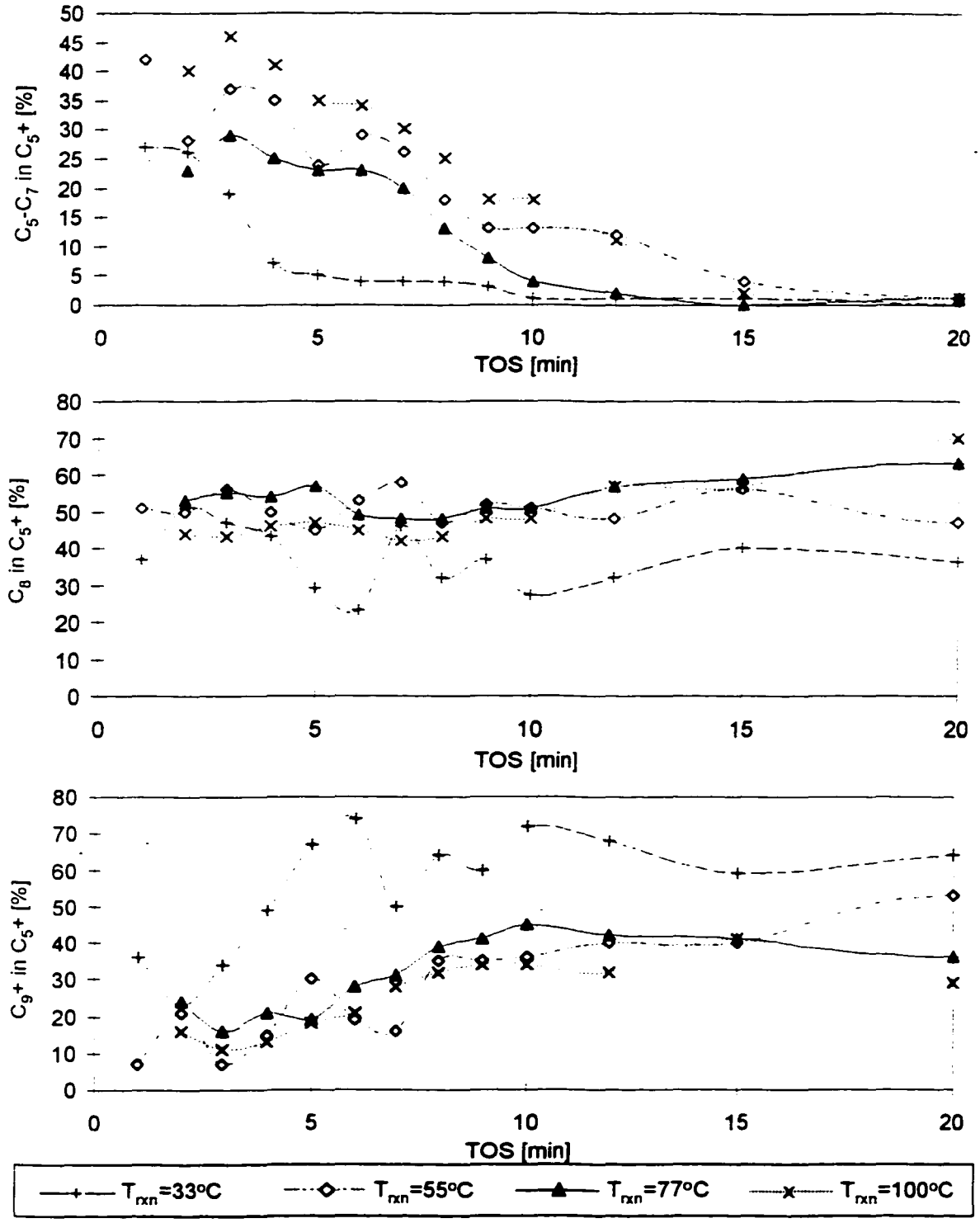



**Figure 6.14:** Effect of Reaction Temperature on $C_5$+ Product Distribution on EMT Zeolite ($T_{calc}$=425°C; P=382psig; I/O=11; $C_4^=$WHSV=2.6$h^{-1}$; $m_{cat}$=2.78g)

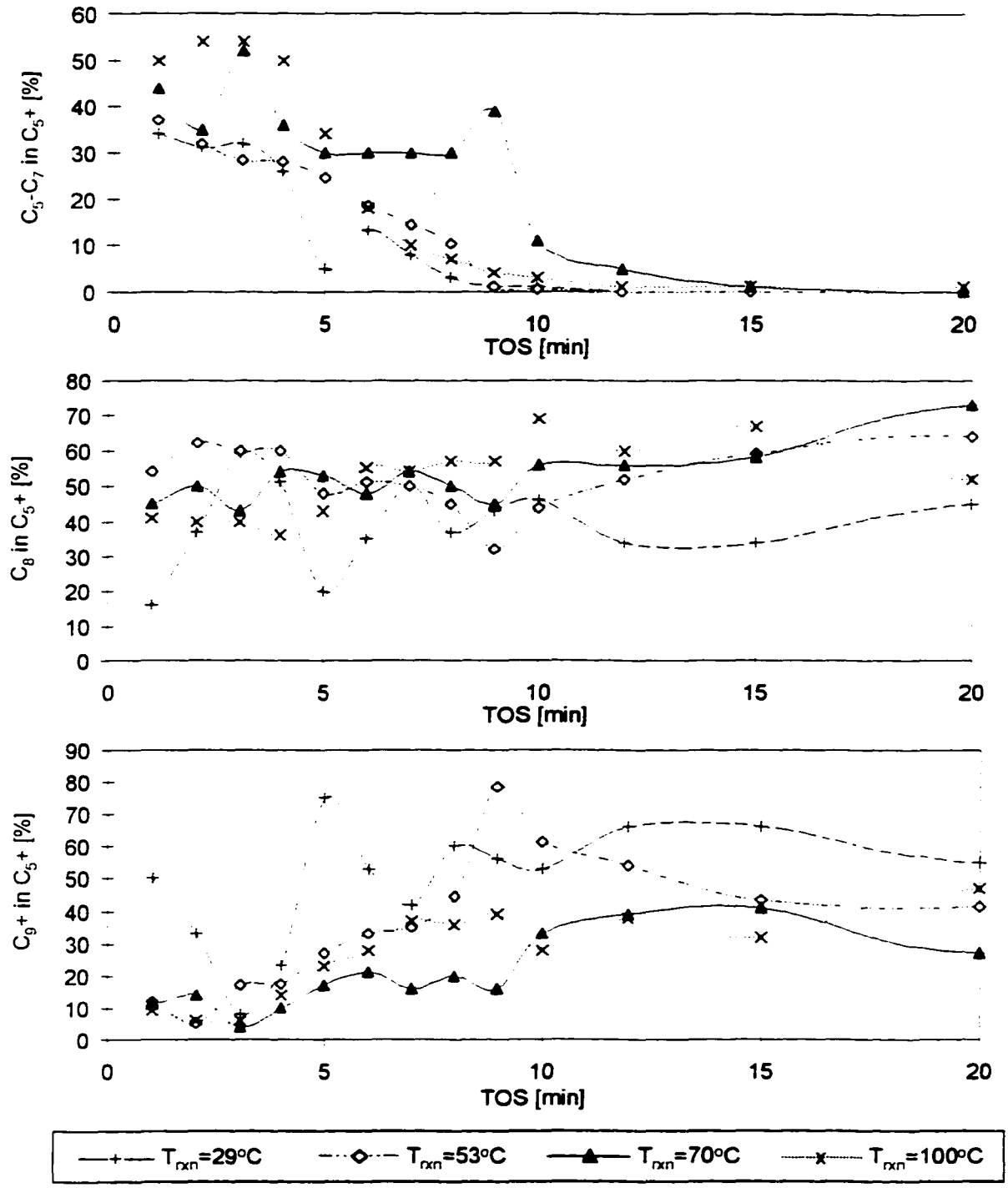



**Figure 6.15:** Effect of Reaction Temperature on $C_5$+ Product Distribution on Y Zeolite ($T_{calc}$=425°C; P=382psig; I/O=11; $C_4^=$WHSV=2.6$h^{-1}$; $m_{cat}$=2.78g)

Although the preferred reaction temperature was specific to the catalyst type, catalytic behavior was similar for EMT and Y zeolites as the reaction temperature was varied away from preferred levels. At temperatures lower than the preferred condition, cracking activity was diminished. Therefore, accumulation of polymerization was observed, agreeing with the results obtained by other authors (Taylor & Sherwood, 1997). It appears that the proportion of acid sites with sufficient strength for facilitating cracking reactions, is reduced at lower temperatures, resulting in more sites being active for less demanding activities such as polymerization reactions.

At reaction temperatures greater than the preferred level, cracking activity increased notably, on both EMT and Y zeolites. Polymerization activity was relatively unchanged from the levels obtained at the preferred reaction temperature, with the exception of experiments at approximately 30°C, where polymerization product levels were notably higher. Catalyst performance was unstable on both zeolites at approximately 30°C, as evidenced by irregular $C_5$+ liquid composition profiles. This is most likely a consequence of enhanced deactivation rates, favoured by elevated concentrations of polymerization products in the catalyst pores.

Batch reaction results were modestly affected by a change in reaction temperature from 80 to 100°C. Results from the flow reactor studies display similar behavior. Cracking activity was slightly elevated at the higher temperature in the flow experiments, agreeing with preliminary batch reactor data. A decrease in the polymerization activity was observed in the flow reactor results rather than the $C_8$ production levels, as was observed in batch experiments. This difference reflects the changes in residence time of the product on the catalyst surface, in a flow versus batch reactor geometry.

### 6.5.3 Effect of Reaction Temperature on $C_8$ Selectivity

The production of TMP was maximized at approximately 78 % of the saturated $C_8$ fraction (DMHs plus TMPs), using EMT at 55°C (see Figure 6.16). In contrast, only 69 % of the saturated $C_8$ fraction was TMP on Y zeolite at 29°C (see Figure 6.17). Both of these results differ considerably from the thermodynamic prediction of 10 to 12 % of $C_8$ paraffins in the $C_8$ fraction (Corma & Martinez, 1993). It is unknown what factors are controlling the reaction mechanism, preventing equilibrium from being attained. Important considerations include the strong adsorption capacity of zeolites, even at low temperatures, which equates to a high solubility of the reactants in a liquid acid. This factor, in conjunction with the concentration effect inherent in zeolite pores, as well as the preferential adsorption of olefins over paraffins, results in a product distribution significantly different from thermodynamic predictions.

Low reaction temperatures favoured elevated TMP levels, during the Useful Catalyst Lifetime on EMT (see Figure 6.16) and Y (see Figure 6.17) zeolites, agreeing with the results of other authors (Taylor & Sherwood, 1997). It was found that butene isomerization occurred rapidly on fresh and aged Y zeolite (Chu & Chester, 1986). Measured levels of butene isomers, found that 1-butene formation was suppressed at lower reaction temperatures on Y zeolite (Simpson et al, 1996). Reaction of 1-butene with *tert*-butyl carbenium ion leads to $DMH^+$ isomers, whereas combination of 2-butene with *tert*-butyl cation produces $TMP^+$ species. Therefore, increased isomerization of 1-butene to 2-butene is expected to enhance TMP formation at lower reaction temperatures. Alternatively, the improved stability of the *tert*-butyl cation relative to the *sec*-butyl cation, may exercise greater importance at low reaction temperatures, accounting for higher TMP levels.

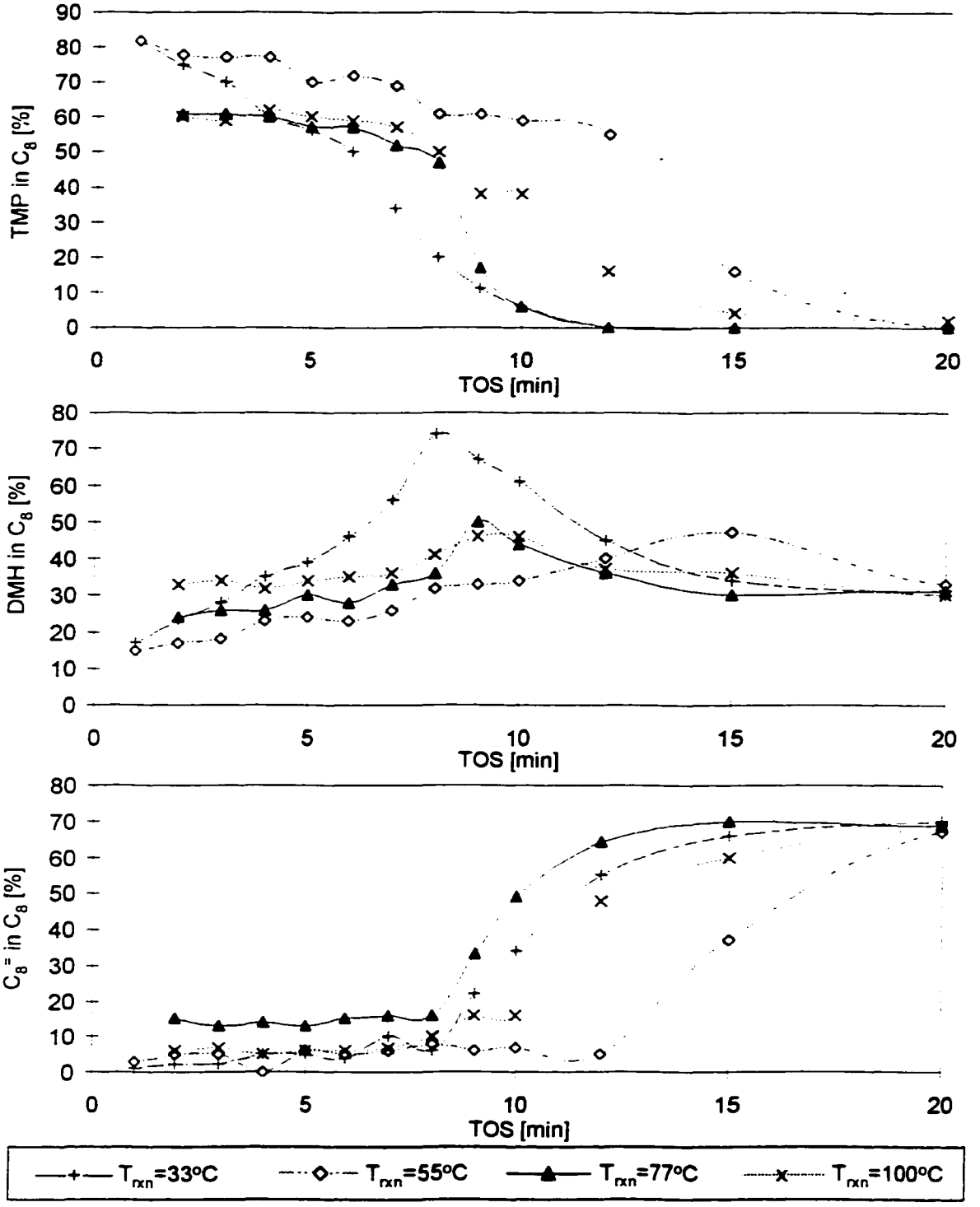



**Figure 6.16:** Effect of Reaction Temperature on $C_8$ Selectivity on EMT Zeolite ($T_{calc}$=425°C; P=382psig; I/O=11; $C_4^=$WHSV=2.6$h^{-1}$; $m_{cat}$=2.78g)

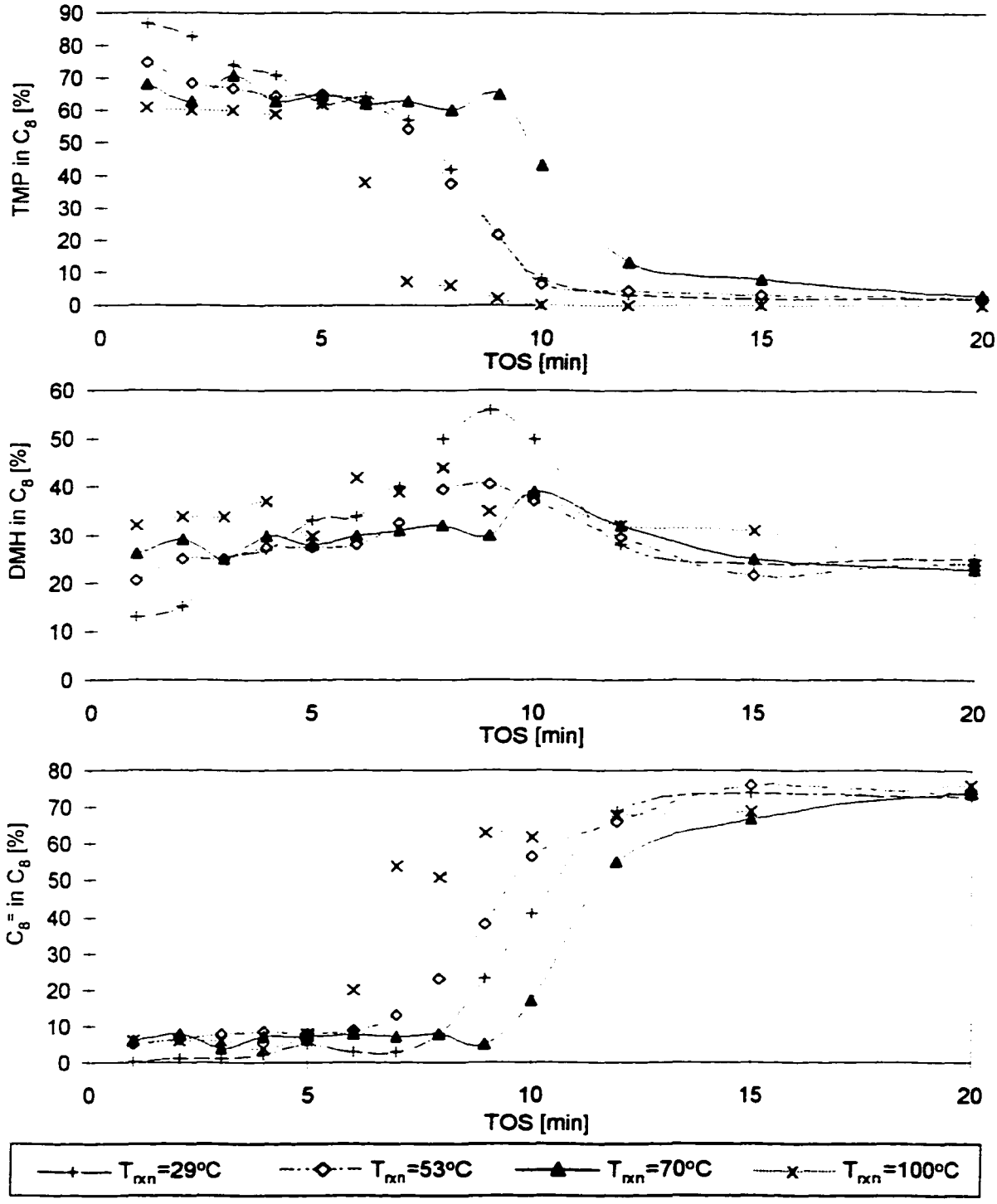



**Figure 6.17:** Effect of Reaction Temperature on $C_8$ Selectivity on Y Zeolite ($T_{calc}$=425°C; P=382psig; I/O=11; $C_4^=$WHSV=2.6$h^{-1}$; $m_{cat}$=2.78g)

Increasing the operating temperatures above 30°C, promoted cracking activity during the Useful Catalyst Lifetime period, jeopardizing the stability of $TMP^+$ species on both zeolites. Isomerization of *trans*-2-butene to 1-butene was found to be more favourable at higher reaction temperatures (Simpson et al, 1995), promoting the formation of $DMH^+$ isomers. In addition, polymerization of alkylate precursors ($TMP^+$ cations) at elevated temperatures, compromises catalyst selectivity to alkyate. Both of these factors likely contribute to lower TMP levels and higher DMH content, at higher reaction temperatures.

The production of TMP was sustained for the longest duration at the preferred reaction temperature of 55°C on EMT (see Figure 6.16). Similar behaviour was demonstrated by Y zeolite at 70°C (see Figure 6.17). As the reaction temperature deviated from the preferred level, DMH production increased at the expense of reduced TMP production, with little variation in oligomerization activity on both EMT (see Figure 6.16) and Y (see Figure 6.17).

Batch reactor results indicate a slight decrease in TMP levels as compensated by modest increase in DMH and $C_8^=$ levels when the reaction temperature is increased from 80 to 100°C. This agrees with results from the flow reactor in that TMP production is adversely affected by reaction temperatures in the vicinity of 100°C.

### 6.5.4 Effect of Reaction Temperature on TMP Selectivity

The content of 2,2,4-TMP in the TMP fraction increased as reaction temperature was elevated, following cracking activity trends (see Table 6.6). This behaviour supports literature claims that, 2,2,4-TMP is the predominant $C_8$ isomer produced from cracking of $C_{12}$+ species (Corma & Martinez, 1993). Levels of 2,3,3-TMP and 2,3,4-TMP decreased with increasing operating temperature, on both EMT and Y zeolites (see Table 6.6).

**Table 6.6: Effect of Reaction Temperature on Average Alkylate Quality**
(first 5 min of Useful Catalyst Lifetime period) using EMT and Y Zeolites
($T_{calc}$=425°C; P=382psig; I/O=11; $C_4^=$WHSV=2.6$h^{-1}$; $m_{cat}$=2.78g)

| Catalyst | EMT | | | | Y | | | |
|---|---|---|---|---|---|---|---|---|
| Run | F25EMT | F28EMT | F31EMT | F34EMT | F27Y | F24Y F36Y | F29Y | F33Y |
| $T_{rxn}$ [°C] | 33 | 55 | 77 | 100 | 29 | 53 | 70 | 100 |
| Useful Catalyst Lifetime [min] | 6.3 | 10.6 | 7.6 | 6.8 | 6.2 | 7.4 | 8.1 | 4.5 |
| *$C_5$+ Liquid [mass %]* | | | | | | | | |
| $C_5$ - $C_7$ | 17 | 33 | 25 | 41 | 26 | 28 | 39 | 49 |
| $C_8$ | 41 | 51 | 55 | 45 | 37 | 51 | 49 | 40 |
| $C_9$+ | 42 | 16 | 20 | 14 | 37 | 21 | 12 | 11 |
| *$C_8$ Fraction [mass %]* | | | | | | | | |
| TMP | 69 | 77 | 60 | 61 | 75 | 68 | 66 | 61 |
| DMH | 28 | 19 | 26 | 33 | 23 | 25 | 27 | 33 |
| $C_8^=$ | 3 | 4 | 14 | 6 | 2 | 7 | 7 | 6 |
| *TMP Distribution [%]* | | | | | | | | |
| 2,2,4-TMP | 29 | 44 | 46 | 52 | 22 | 37 | 58 | 52 |
| 2,2,3-TMP | 5 | 15 | 10 | 12 | 5 | 5 | 9 | 10 |
| 2,3,4-TMP | 30 | 15 | 17 | 14 | 33 | 25 | 12 | 16 |
| 2,3,3-TMP | 36 | 26 | 27 | 22 | 40 | 33 | 21 | 22 |
| *Indicators [mass %]* | | | | | | | | |
| $\frac{TMP}{DMH}$ | 2.77 | 4.13 | 2.29 | 1.81 | 3.91 | 2.76 | 2.42 | 1.82 |
| $\frac{TMP+DMH}{C_8^= + C_9+}$ | 1.11 | 3.57 | 1.74 | 2.49 | 2.07 | 2.99 | 3.63 | 3.20 |
| $\frac{2,2,4\text{-}TMP+2,2,3\text{-}TMP}{2,3,3\text{-}TMP+2,3,4\text{-}TMP}$ | 0.53 | 1.49 | 1.30 | 1.82 | 0.40 | 0.72 | 2.05 | 1.68 |

Temperature does not have a significant effect on thermodynamic predictions for the distribution of TMP isomers (see Figure 6.18). Thermodynamic estimates for 2.2.4-TMP levels, exceed 60 % of the TMP fraction, between 30 and 100°C. The response of the TMP distribution to reaction temperature is contrary to thermodynamic trends. Experiments employing lower temperatures favoured 2,3,3-TMP and 2,3,4-TMP, the least sterically hindered isomers (see Lennard Jones diameter calculations in Appendix A3.2.5). Higher operating conditions promoted 2,2,4-TMP production (see Table 6.6), in opposition to thermodynamic trends (see Figure 6.18).

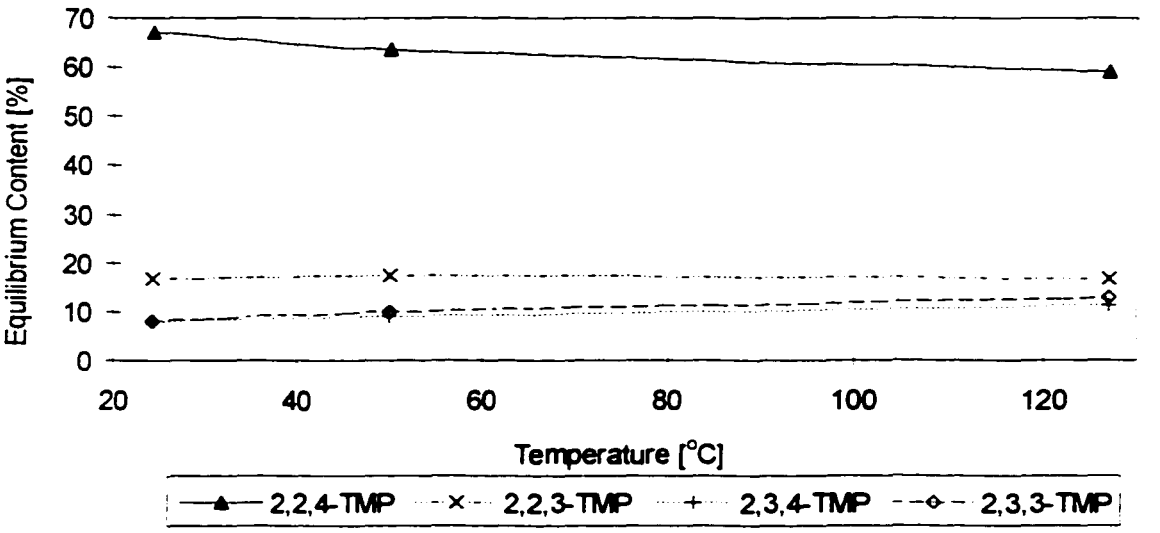



**Figure 6.18:** Effect of Temperature on Thermal Equilibrium Composition of TMPs (Cardona et al, 1995; Chu & Chester, 1986)

### 6.5.5 Synopsis of Effect of Reaction Temperature

Low reaction temperatures effected low butene conversion during the Useful Catalyst Lifetime period on EMT and Y zeolites (see Figures 6.14 and 6.15, Table 6.6). The rate of cracking reactions was reduced at lower operating temperatures, resulting in accumulation of polymerization products. This behaviour agrees with that observed by other authors (Taylor & Sherwood, 1997).

As the reaction temperature increased, olefin conversion was sustained for a longer duration. Cracking activity increased, exercising a negative effect on the stability of TMP precursors. Production of 2,2,4-TMP increased with reaction temperature, as this isomer appears to be correlated with cracking of $C_{12}$+ carbenium ions.

The preferred reaction temperature represents a balance between enhancing olefin conversion without degrading alkylate quality. The reaction temperature must be sufficiently high to suppress polymerization reactions, which are known to favour deactivation processes. However, excessive temperatures jeopardize the stability of alkylate precursors. At the preferred reaction temperature, the Useful Catalyst Lifetime period was maximized and TMP production levels were sustained for the longest duration. At an I/O ratio of 11, this temperature was concluded to be 55°C for EMT, whereas 70°C was identified for Y zeolite. These preferred temperatures are specific to the fixed operating conditions (i.e. I/O ratio of feed, $T_{calc}$, olefin WHSV, mass of catalyst, etc.) of the experiment.

The least sterically hindered TMP isomers, including 2,3,3-TMP and 2,3,4-TMP, were favoured at low reaction temperatures (see Table 6.6). These isomers offer the least resistance during formation of the activated complex, and diffuse most efficiently through the catalyst pores. At higher reaction temperatures, alternate reaction pathways become more facile. Cracking activity increased as the reaction temperature was elevated, favouring formation of 2,2,4-TMP via cracking of $C_{12}^{+}$ carbocations (Corma & Martinez, 1993).

Temperature does not appear to exert a significant effect on alkylate yield (see Table 6.7). The Useful Catalyst Lifetime period represents approximately 15 % of the total time period for liquid collection, making sensitivity to operational changes poor. Secondly, the method of liquid collection is not responsive to small changes in liquid production levels. Although a distinctive temperature effect was not evident on either catalyst, significant differences between catalysts were found. For all reaction temperatures considered, EMT achieved a notably higher yield and longer Useful Catalyst Lifetime period, relative to those observed on Y zeolite.

Analysis of the catalyst performance and properties of the spent catalyst, reveal some interesting features. As the temperature was increased, the surface area of the spent catalyst decreased, with notable losses measured at low reaction temperatures (see Figure 6.19). Temperature does not appear to have a significant effect on preserving the active surface area of the catalyst.

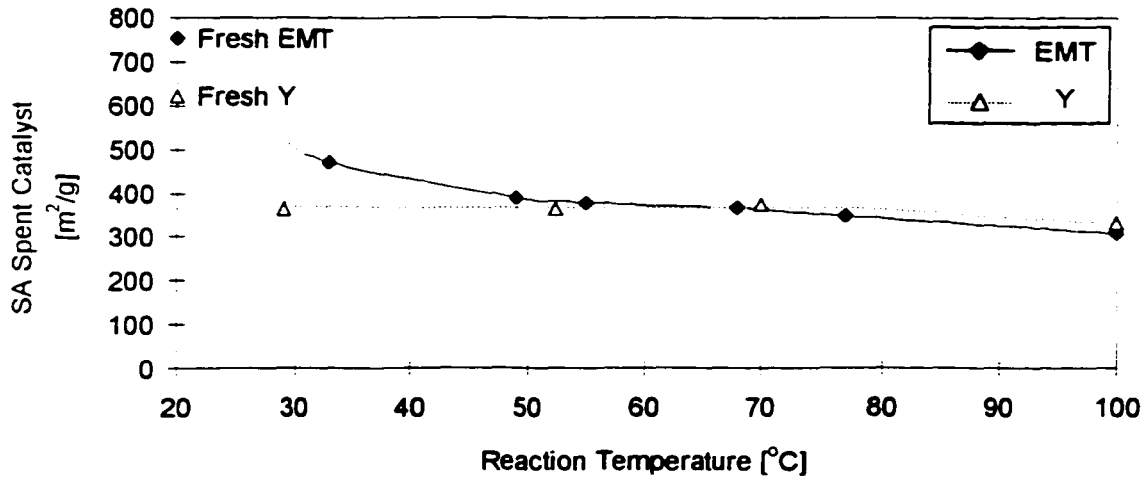



**Figure 6.19:** Effect of Reaction Temperature on Surface Area of Spent Catalyst ($T_{calc}$ = 425°C, P=382psig; I/O = 11; $C_4^=$WHSV=2.6$h^{-1}$; $m_{cat}$=2.78g)

Carbonaceous deposits on the spent catalyst, measured between 9.1 and 10.2 % on EMT, whereas a lower range of 6.8 to 7.6 % was determined for Y zeolite (see Table 6.7). Comparable levels of retained hydrocarbons on spent catalysts (40 min. TOS) were reported by Querini & Roa (1997), where carbonaceous deposits varied between 5 to 13 % on Y and La-exchanged Y zeolites.

The amount of retained hydrocarbons on the spent catalyst was minimized at the preferred reaction temperature (see Table 6.7). This occurred at 55°C for EMT and 70°C on Y. Levels of hydrocarbons retention were significant on the spent catalyst from reactions undertaken at 30°C on both EMT and Y. This suggests that the adsorption of the olefin and oligomerization of the olefin, proceed much faster than hydride transfer and desorption of the product, under these conditions.

**Table 6.7:** Effect of Reaction Temperature on Catalyst Properties
($T_{calc}$ = 425°C; I/O = 11)

| Catalyst @$T_{rxn}$[°C] | SA Spent Catalyst [$m^2$/g] | TGA of Spent Catalyst [mass %] Desorption Temperature [°C] < 200 | 200-300 | >300 | Total | Yield* [$gC_5^+$/gcat/$gC_4^=$fed] |
|---|---|---|---|---|---|---|
| EMT | | | | | | |
| 33°C | 470 | 3.9 | 3.0 | 3.3 | 10.2 | n.a. |
| 55°C | 377 | 3.8 | 2.5 | 3.0 | 9.3 | 0.094 |
| 77°C | 348 | 3.0 | 2.9 | 3.2 | 9.1 | 0.104 |
| 100°C | 309 | 3.7 | 3.2 | 3.2 | 10.1 | 0.113 |
| Y | | | | | | |
| 29°C | 364 | 2.5 | 2.3 | 2.5 | 7.3 | 0.057 |
| 56°C | 372 | 2.0 | 2.5 | 2.5 | 7.0 | 0.068 |
| 70°C | 374 | 1.2 | 2.1 | 3.6 | 6.8 | 0.084 |
| 100°C | 329 | 2.4 | 2.3 | 2.9 | 7.6 | 0.088 |

* liquid collected over a 1 hour reaction period

It is possible that high molecular weight hydrocarbons retained on the catalyst surface, act as hydride donors to other adsorbed species. The close proximity of the heavy compounds to the reactive carbocations in the zeolite cages, makes this form of hydride transfer favoured, over direct hydride transfer from isobutane (Cardona et al, 1995). Allylic carbenium ions are formed when high molecular weight hydrocarbons facilitate hydride transfer. These carbocations are more stable than the *tert*-butyl carbenium ion, which is formed upon hydride transfer from isobutane. However, the carbonaceous deposit becomes less saturated in nature and acts as a precursor to coke, favouring deactivation processes.

Weitkamp and Maixner (1987) characterized carbonaceous deposits on spent La-Y zeolite catalysts. The deposit from a catalyst operating at a reaction temperature of 80°C, appeared to be primarily paraffinic in nature, with a H/C ratio of 1.8. Higher reaction temperatures produced a carbonaceous deposit with a lower H/C ratio, indicative of an olefinic and aromatic nature. This suggests that adsorbed hydrocarbons become an important source of hydride transfer at higher reaction temperatures. The H/C ratio for the spent catalyst deposit was not analysed in the present investigation.

## 6.6 EFFECT OF 1-$C_4^=$ WHSV ON Y ZEOLITE

The preferential adsorption of olefins over paraffins in zeolites, favours oligomerization and polymerization reactions over alkylation. This phenomena, is exacerbated by the concentration effect and diffusional limitations, which are inherent in microporous solids. The I/O ratio and olefin WHSV are two process variables, which are used to circumvent these problems, and represent the most important parameters influencing alkylate quality and yield. A low concentration of the olefin (reflected by a high I/O ratio or a low 1-$C_4^=$ WHSV) increases the likelihood of alkylation reactions being facilitated. In contrast, oligomerization and polymerization

reactions are encouraged by higher concentrations of the olefin, conditions which are favoured by a low I/O ratio or a high olefin WHSV.

The importance of olefin WHSV was not studied extensively on EMT due to limited catalyst supply, but was explored on the commercially available product of Y zeolite. A calcination temperature of 540°C, a reaction temperature of 80°C and operating pressure of 382 psig, were employed for the olefin WHSV investigation. No reaction products were observed when pure isobutane was tested over a 1 hour reaction period. It appears that self-alkylation of isobutane cannot be initiated in the absence of an olefin, in agreement with other studies in the literature (Simpson et al, 1996).

### 6.6.1 Effect of 1-$C_4^=$ WHSV on Butene Disappearance

The Useful Catalyst Lifetime period was maintained for a longer duration on Y zeolite under conditions of low olefin WHSV (see Table 6.8). A reduction in the olefin WHSV from 2.57 (I/O=11) to 0.51 $h^{-1}$ (I/O=58) extended the Useful Catalyst Lifetime from 4.5 minutes to 50 minutes, illustrating the positive influence of diluting the feed with excess isobutane.

**Table 6.8:** Effect of Butene WHSV on the Number of Successful Catalyst Cycles Achieved during Useful Catalyst Lifetime Period on Y Zeolite ($T_{calc}$=540°C; $T_{rxn}$=80°C; P=382psig; $m_{cat}$=2.78g)

| Run | F11Y, F13Y, F15Y(first 40 min) | F21Y |
|---|---|---|
| $C_4^=$ WHSV [$h^{-1}$] | 0.51 | 2.57 |
| I/O | 58 | 11 |
| Useful Catalyst Lifetime [min] | ~ 50 | 4.5 |
| # Successful Cycles per Acid Site During Useful Catalyst Lifetime | 55 | 22 |

The number of successful catalyst cycles (turn-over number) can be calculated by dividing the Useful Catalyst Lifetime period by the time required to adsorb one butene molecule on all active sites. Since acidity measurements are not available, published data for Y zeolite will be used. Pyridine desorption on Y zeolite with a Si/Al ratio of 5.4 detect 151 μmol acid sites/g catalyst (Corma et al, 1994b). The time required to provide sufficient butene to fully saturate all of the active acid sites can be approximated from the butene flow rate (see Appendix A3.2.4).

Decreasing the olefin WHSV from 2.57 to 0.51 $h^{-1}$, augmented the number of successful catalyst cycles achieved per acid site from 22 to 55, representing an increase of 150 % (see Table 6.8). The modest improvement in the turn-over number, emphasizes the strong control dictated by the preferential adsorption of the olefin over the paraffin. Deactivation appears inevitable regardless of the feed concentration in the olefin, but simply proceeds at a reduced rate under conditions of high I/O ratio.

### 6.6.2 Effect of 1-$C_4^=$ WHSV on $C_5^+$ Product Distribution

No significant change in cracking activity was observed with variation in the olefin WHSV, during the Useful Catalyst Lifetime (see Figure 6.20). However, high cracking was sustained for a longer duration under conditions of low olefin WHSV. Polymerization activity was greatly suppressed under conditions of low olefin WHSV (see Figure 6.20). This is expected, as a low concentration of butene (low olefin WHSV) diminishes the probability that two butene molecules will react with one another, enhancing the opportunity for isobutane participation in the reaction. As the olefin WHSV is increased, butene concentration is elevated, increasing the favourability of oligomerization and polymerization reactions.

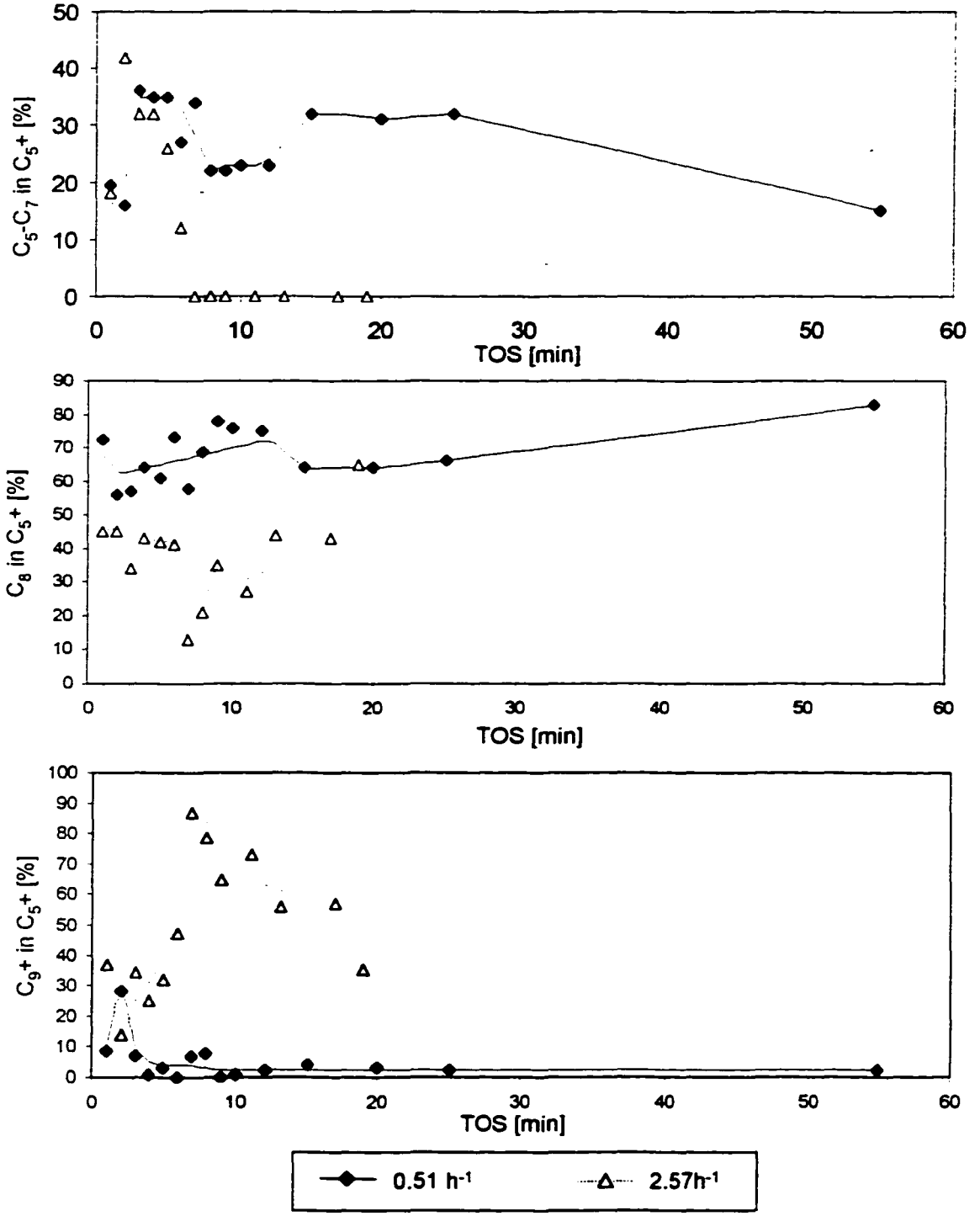



**Figure 6.20:** Effect of Butene WHSV on $C_5$+ Product Distribution on Y Zeolite ($T_{rxn}$=80°C; $T_{calc}$=540°C; P=382psig; $m_{cat}$=2.78g)

The content of $C_8$ in the $C_5$+ product increased as the olefin WHSV decreased (see Figure 6.20). It appears that a low concentration of butene enhanced the probability of alkylation reactions, leading to elevated levels of $C_8$ in the $C_5^+$ liquid. Although dimerization of the olefin will also increase the levels of $C_8$ in the $C_5^+$ liquid, adsorbed oligomers are more susceptible to secondary reactions (i.e. polymerize to higher molecular weight compounds). This explains the lower $C_8$ levels observed for higher olefin WHSV experiments.

### 6.6.3 Effect of 1-$C_4^=$ WHSV on $C_8$ Selectivity

The levels of TMP in the $C_8$ fraction decreased, with increasing olefin WHSV. In addition, high levels of TMP were sustained for longer TOS under conditions of low olefin WHSV (see Figure 6.21). It appears that the sites responsible for TMP production are deactivated rapidly, under conditions of high olefin concentration in the feed mixture. A low olefin WHSV suppresses the rate of this deactivation process, allowing these acid sites to remain active for TMP production for a longer duration.

The production of DMH and $C_8^=$ were enhanced by increasing the olefin WHSV (see Figure 6.21). It appears that the initial hydride transfer step to generate *tert*-$C_4^+$ is adversely affected by high concentrations of olefin in the feed mixture, leading to elevated DMH production levels. In addition, hydride transfer to adsorbed $C_8^+$ species is also hindered by high olefin levels in the feed, favouring desorption of an olefin product.

These results agree with those observed by Chu & Chester (1986) in which the concentration of TMPs decreased and DMHs increased, with increasing olefin WHSV. It is preferable to operate at a lower WHSV in order to maximize TMP production and maintain high catalyst activity.

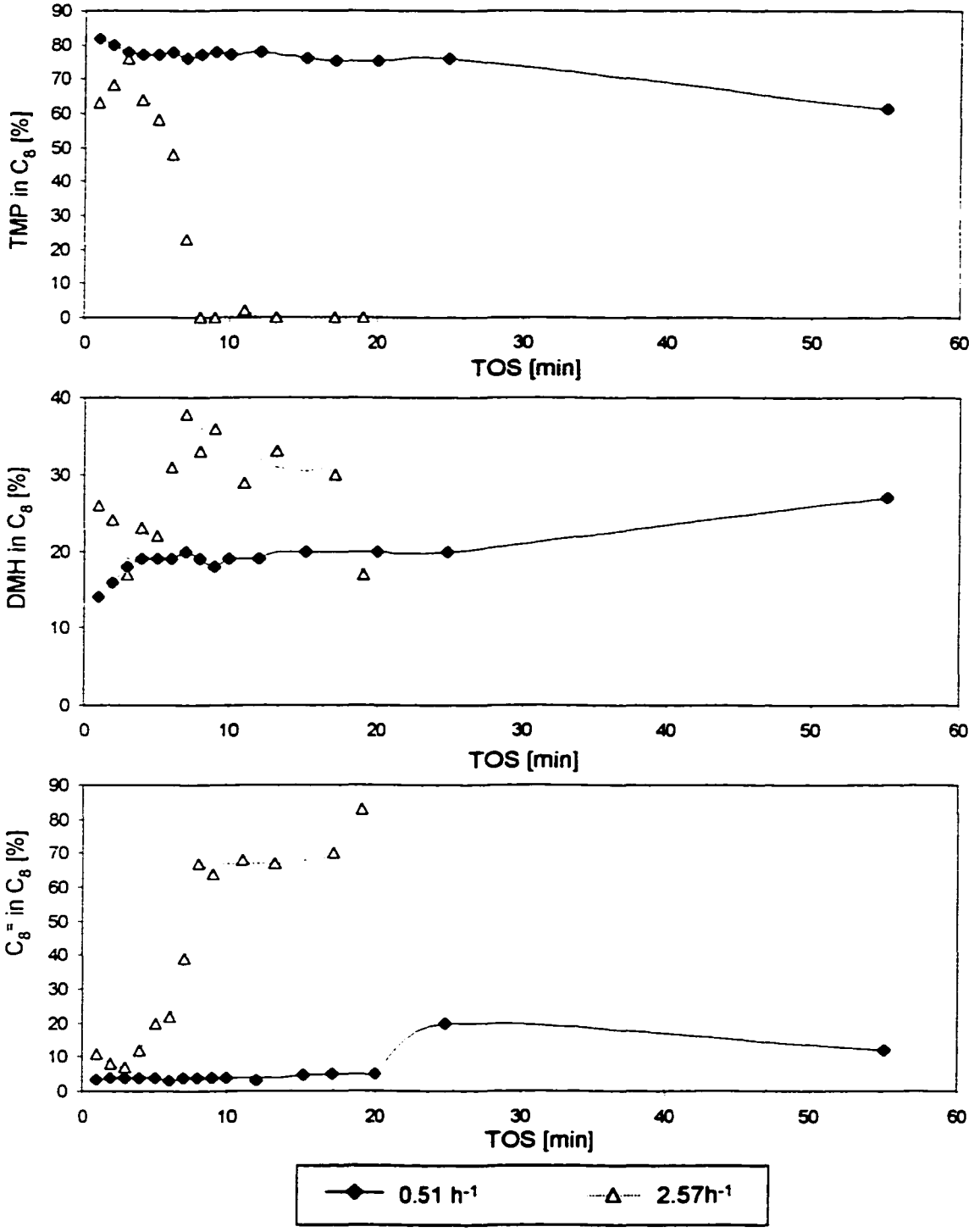



**Figure 6.21:** Effect of Butene WHSV on $C_8$ Selectivity on Y Zeolite ($T_{rxn}$=80°C; $T_{calc}$=540°C; P=382psig; $m_{cat}$=2.78g)

Catalyst activity was found to be relatively constant when operating at a low olefin WHSV, as indicated by stable product distributions. This contrasts with rapid catalyst deactivation at short TOS under conditions of high olefin WHSV. Clearly, a compromise must be made between extending catalyst lifetime through operation at low olefin WHSV, and maximizing alkylate production (g $C_5^+$ liquid collected per hour), which is compromised by utilization of a low olefin WHSV.

### 6.6.4 Effect of 1-$C_4^=$ WHSV on TMP Selectivity

The maximum 2,2,4-TMP levels achieved in the TMP fraction, were similar for both WHSV (see Figure 6.22). However, a high concentration of olefin in the feedstock accelerated the rate of deactivation, causing 2,2,4-TMP production to decline at earlier TOS. The selectivity of TMP isomers was not altered significantly by changes in olefin WHSV (see Table 6.9). Levels of 2,2,4-TMP and 2,2,3-TMP were enhanced slightly and amounts of 2,3,4-TMP were reduced, when operating at a low olefin WHSV.

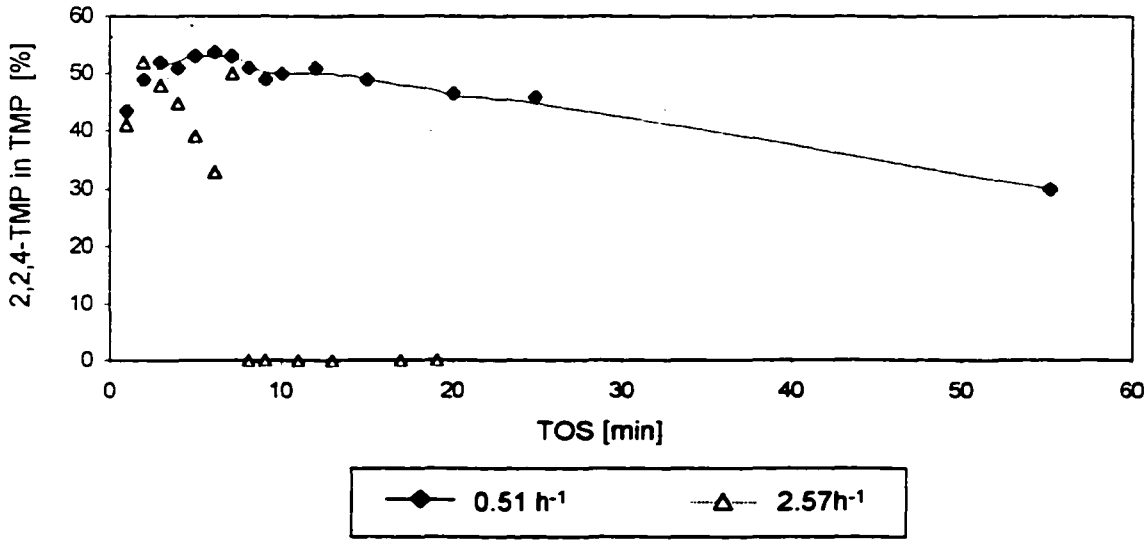



**Figure 6.22:** Effect of Butene WHSV on 2,2,4-TMP Level in TMP Fraction on Y Zeolite ($T_{rxn}$=80°C; $T_{calc}$=540°C; P=382psig; $m_{cat}$=2.78g)

**Table 6.9:** Effect of Butene WHSV on Catalyst Performance on Y Zeolite ($T_{rxn}$=80°C; $T_{calc}$=540°C; P=382psig; $m_{cat}$=2.78g)

| Run | F11Y, F13Y, F15Y(first 40 min) | F21Y |
|---|---|---|
| $C_4^=$ WHSV [$h^{-1}$] | 0.51 | 2.57 |
| I/O | 58 | 11 |
| Useful Catalyst Lifetime [min] | ~ 50 | 4.5 |
| # Successful Cycles per Acid Site During Useful Catalyst Lifetime | 55 | 22 |
| Time Period Employed for Estimating Average $C_5$+ Analysis | Initial 25 min TOS | initial 5 min TOS |
| $C_5^+$ Liquid [mass %] | | |
| $C_5$-$C_7$ | 28 | 30 |
| $C_8$ | 67 | 42 |
| $C_9^+$ | 5 | 28 |
| *$C_8$ Distribution [mass %]* | | |
| TMP | 77 | 66 |
| DMH | 19 | 22 |
| $C_8^=$ | 4 | 12 |
| *TMP Distribution [%]* | | |
| 2,2,4-TMP | 50 | 45 |
| 2,2,3-TMP | 10 | 5 |
| 2,3,4-TMP | 15 | 22 |
| 2,3,3-TMP | 25 | 28 |
| *Indicators [mass fraction]* | | |
| $\frac{\text{TMP}}{\text{DMH}}$ | 4.10 | 3.03 |
| $\frac{\text{TMP + DMH}}{C_8^= + C_9+}$ | 12.5 | 1.26 |
| $\frac{\text{2,2,3-TMP + 2,2,4-TMP}}{\text{2,3,3-TMP + 2,3,4-TMP}}$ | 1.51 | 1.01 |

The isomer, 2,2,3-TMP, is a direct product of alkylation of 2-butene with isobutane, whereas, 2,2,4-TMP is the primary product of self-alkylation of isobutane. From a structural perspective, 2,3,4- and 2,3,3-TMP cannot be formed from $C_4$ fragments, and are presumably formed through isomerization of $TMP^+$ cations. Hydride transfer to a tertiary carbenium ion is notably faster that to a secondary one. Therefore, the TMP isomers, which are most favoured from a mechanistic standpoint,

are 2,3,4-TMP and 2,3,3-TMP. The former species involves hydride transfer to a tertiary carbenium ion, and the latter can be formed through a methyl shift (Cardona et al, 1995). Considering all of these factors, it appears that a low olefin WHSV promotes formation of the thermodynamically favoured isomers. In contrast, a high olefin WHSV encourages production of the kinetically preferred isomers.

The product selectivity achieved over Y zeolite at high olefin WHSV differed significantly from that catalysed by HF and $H_2SO_4$ (see Table 6.10). However, as the olefin WHSV is decreased, the TMP isomer distribution approached that obtained over $H_2SO_4$, but deviated considerably from equilibrium predictions. The concentration effect, inherent in zeolitic catalysts, in conjunction with the steric restrictions imposed by the microporous network, are most likely responsible for the differences observed.

**Table 6.10:** Comparison of TMP Selectivity using different Catalyst Systems with Thermal Equilibrium Values

| Catalyst System | Y[1], WHSV= 0.51$h^{-1}$ | Y[2], WHSV= 2.57$h^{-1}$ | HF[3] | $H_2SO_4$[3] | Thermal Equilibrium | | |
|---|---|---|---|---|---|---|---|
| Temperature [°C] | 80 | 80 | 20 | 10 | 24[3] | 50[4] | 127[3] |
| 2,3,4-TMP/2,3,3-TMP | 0.6 | 0.8 | 1.2 | 0.6 | 1.0 | 0.9 | 0.8 |
| 2,2,3-TMP/2,2,4-TMP | 0.2 | 0.1 | <0.01 | 0.1 | 0.3 | 0.3 | 0.3 |
| 2,2,4-TMP + 2,2,3-TMP / 2,3,3-TMP + 2,3,4-TMP | 1.6 | 1.0 | 1.7 | 1.4 | 5.2 | 4.3 | 3.1 |

1 average of 1-10 min T.O.S.
2 average of 1-5 min. T.O.S.
3 data from Chu & Chester, 1986
4 data from Cardona et al, 1995

### 6.6.5 Synopsis of Effect of 1-$C_4^=$ WHSV

Employing a lower olefin WHSV suppressed the rate of catalyst deactivation in a flow reactor. However, the loss in catalyst activity appears inevitable, due to

preferential adsorption of the olefin over the paraffin. This hypothesis can be tested, by examining the surface area measurements of the spent catalyst. A "Butene Exposure Index" can be calculated by multiplying the olefin WHSV by the duration of the experiment. In this manner, the magnitude of olefin WHSV and duration and be encompassed into a single dimensionless quantity, allowing experiments using different conditions to be compared. A distinctive trend in loss of SA is observed with increasing Butene Exposure Index, regardless of the operating conditions (see Figure 6.23). These results support the conjecture that deactivation is unavoidable, regardless of how dilute the feed is with the olefin. The same final outcome will result, but will simply require a longer time period to reach.

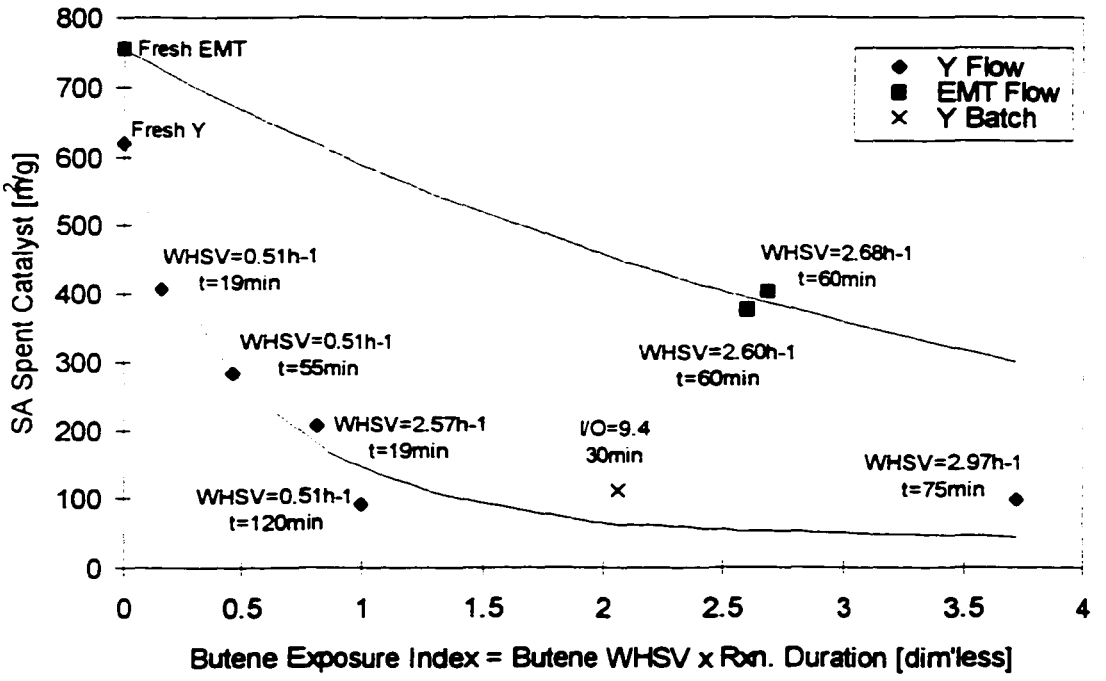



**Figure 6.23:** Effect of Butene Exposure on Surface Area of Spent Catalyst ($T_{calc}$=540°C, $T_{rxn}$=80°C; P=382psig, $m_{cat}$=2.78g)

This hypothesis is further validated by TGA/DTA measurements on the spent catalyst. Notable levels of adsorbed species were detected on the spent catalyst, which employed an olefin WHSV of 0.51 $h^{-1}$ for a 20 min reaction period. A significant loss in active surface area was also measured for this experiment (see Table 6.11). Increasing the reaction duration to 60 min at the same olefin WHSV, resulted in additional deposition of higher molecular weight species ($T_{desorp}$>200°C), incurring a further loss in surface area. No change in the amounts of lighter compounds ($T_{desorp}$<200°C) was evidenced, after longer exposure to the feed mixture. Increasing the olefin WHSV to 2.57 $h^{-1}$, augmented the amounts of higher molecular weight compounds ($T_{desorp}$>200°C) retained on the catalyst causing a significant surface area loss after only 20 min of exposure to the feed stream.

This suggests that the rate of the reactions generating higher molecular weight species are greatly enhanced by elevated olefin WHSV conditions. Hence, the loss in surface area appears to be primarily a result of oligomerization and polymerization reactions, leading to elevated levels of high molecular weight compounds which are retained on the catalyst surface.

**Table 6.11:** Effect of Butene WHSV on Properties of Spent Catalyst ($T_{calc}$=540°C, $T_{rxn}$=80°C)

| Butene WHSV [$h^{-1}$] | Run | Reaction Duration [min] | Exposure Index | TGA [mass %] Desorption Temperature [°C] | | | | SA Spent Catalyst [$m^2/g$] |
|---|---|---|---|---|---|---|---|---|
| | | | | < 200 | 200-300 | > 300 | Total | |
| 0.51 | F11Y | 20 | 0.17 | 1.2 | 0.8 | 1.7 | 3.7 | 407 |
| 0.51 | F13Y | 60 | 0.51 | 1.2 | 1.2 | 2.2 | 4.6 | 284 |
| 2.57 | F21Y | 20 | 2.57 | 1.3 | 2.5 | 3.1 | 6.9 | 205 |

Although the effect of olefin WHSV was not investigated in detail on EMT, this catalyst appears to demonstrate superior ability in preserving active surface area upon exposure to butene, relative to the behaviour shown by Y zeolite. It is possible that EMT is more carbophylic than Y zeolite, enhancing isobutane adsorption

capabilities and improving resistance to deactivation. Alternatively, it is also possible that the unique arrangement of acid sites on EMT suppresses the extent undesirable side-reactions (i.e. oligomerization), which promote deactivation processes.

## 6.7 EFFECT OF CYCLICAL FEED OPERATION USING Y ZEOLITE

Hydride transfer can be improved by choosing calcination conditions which promote Bronsted acidity. Reaction temperature can be judiciously selected to enhance selectivity to alkylation. The feed mixture can be prepared with a high I/O, and flow rates operated to achieve a low olefin WHSV, to delay the onset of deactivation. However, optimization of all operating conditions cannot prevent deactivation from ensuing, due to the preferential adsorption of the olefin over the paraffin.

For this reason, cyclical feed operation was investigated as an alternative strategy to maintain high catalyst activity. The study evaluated Y zeolite calcined at 540°C, and employed operating conditions of 80°C and 382 psig. A feed mixture with an I/O ratio of 59 (1-$C_4^=$ WHSV = 0.51 $h^{-1}$) was delivered to the catalyst bed for a period of 40 minutes. This was followed by a 30 minute isobutane flush (I/O=3000 based on impurity butene in the isobutane cylinder), after which butene/isobutane feed (I/O=59) delivery to the catalyst was resumed for a period of 30 minutes. The experiment was concluded with a final 20 min isobutane flush.

Catalyst deactivation was apparent during the first mixture delivery period (see Figure 6.24). A loss in cracking activity was observed, and a significant elevation in polymerization products detected in the effluent at longer TOS.

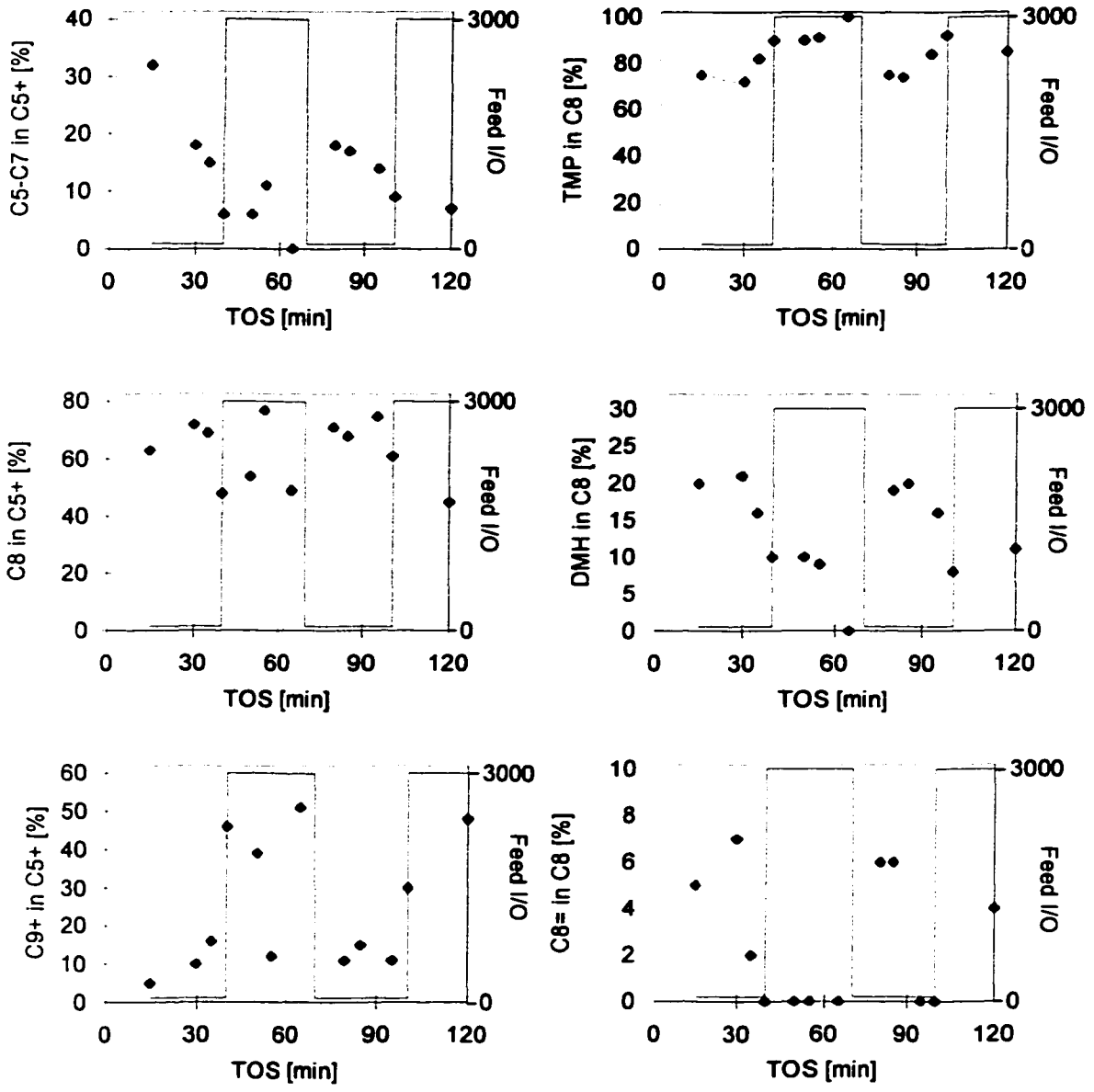



**Figure 6.24:** Effect of Cyclical Feed Operation on Catalyst Activity and Selectivity using Y Zeolite
($T_{calc}$=540°; $T_{rxn}$=80°C; P=382psig; $m_{cat}$=2.78g; Feed: $C_4^=$WHSV=0.51$h^{-1}$(40min), pure *i*-$C_4$ (30min), $C_4^=$WHSV=0.51$h^{-1}$(40min), pure *i*-$C_4$ (30min))

During the isobutane flush period, notable levels of polymerization products, as well as $C_8$ compounds, were removed from the catalyst surface. Catalyst activity was restored upon resumption of the feed mixture to the catalyst bed. High cracking activity level was recovered and polymerization function suppressed, during the second feed delivery period. At longer TOS, a loss in catalyst activity recurred, mimicking the behaviour of the first feed delivery period.

Product selectivity can provide further insight into the events leading up to deactivation. During the first period of feed delivery, the content of TMP in the $C_8$ fraction increased with longer TOS. This is a reflection of the Induction Period, in which DMH formation and oligomerization products are favoured until a sufficient population of *tert*-$C_4^+{}_{(surf)}$ species has developed on the catalyst surface. Once this is established, alkylation activity is favoured, resulting in elevated amounts of TMP in the effluent.

During the isobutane flush, TMP content increased with further TOS. It may be that hydride transfer to $TMP^+$ cations by isobutane is facilitated in the early stages of the flush period. As spatial constraints are relieved with removal of $C_8$ product, it is possible that self-alkylation of isobutane is promoted, through hydride transfer to bulkier polymeric species retained on the catalyst surface. This produces elevated levels of $C_9$+ species, as well as increased amounts of TMP, in agreement with the experimental data.

The restoration of catalyst activity and selectivity after the isobutane flush period, is remarkable. These results suggest that the onset of deactivation is a consequence of the preferential adsorption of the olefin over the paraffin. The ability of isobutane to facilitate hydride tranfer to desorb product is limited, favouring oligomerization and polymerization reactions. Upon exposure to the feed mixture, the catalyst surface becomes saturated with oligomers of butene, stifling further activity. These oligomers can be removed in a non-competitive environment with pure isobutane, restoring catalyst activity to fresh performance levels.

Loss in active catalyst SA is suppressed in the cyclical operation. After 60 min of continuous exposure to the feed stream (1-$C_4^=$ WHSV = 0.51 $h^{-1}$), the surface area of the spent catalyst measured 284 $m^2/g$, representing 54% loss in active surface area. In contrast, the spent catalyst from the cyclical feed operation, with a cumulative feed exposure of 60 min, measured 396 $m^2/g$ accounting for a 36 % reduction in active surface area. Clearly, benefits can be gained through cyclical operation where the isobutane serves to cleanse the catalyst surface of retained hydrocarbons and restore catalyst activity.

Catalytic distillation is a process, which combines reaction and distillation into one unit operation. This reactor geometry may offer some potential to this difficult reaction. By placing the catalyst bed near the top of the distillation tower, and operating under total reflux, isobutane will be continuously returned to the reaction section providing the positive cleansing benefits noted in the cyclical operation. The distillation action of the process will naturally remove product (i.e. TMP) from the reaction section on the basis of boiling point differences. In this manner, consecutive reactions are discouraged. The TMPs will concentrate in the reboiler and can be removed in the product stream. This mode of reactor geometry could be studied in subsequent investigations on this topic.

## 6.8 EFFECT OF CATALYST

The modest geometrical differences in the structural properties of EMT relative to Y, are hypothesized to produce positive benefits on alkylation. It is believed that the larger space available for reaction in the hypercages, will reduce steric restrictions during the formation of the bulky TMP isomers. The improvement in accessibility to the hypercages of EMT, via straight channels, is expected to reduce diffusional resistance during product transport.

Secondly, the nature, strength and distribution of acid sites on EMT and Y zeolite are subtly different. Although Bronsted acidity dominates on both catalyst systems, published acidity measurements suggest that Lewis acidity may be slightly greater on Y zeolite relative to EMT (see Table 2.5). The effect of calcination temperature (see Section 6.4) concluded that Lewis acidity favoured undesirable side reactions, compromising catalyst selectivity and accelerating deactivation. In addition, the data estimates a higher proportion of strong acid sites on EMT relative to Y zeolite (see Table 2.5). This is expected to exercise a favourable effect on the catalyst performance, as strong acid sites are believed to be necessary for facilitating alkylation.

Finally the distribution of acid sites on Y zeolite follows Lowenstein's rule, whereby no Al atoms are located in adjacent positions in the zeolite framework. The catalyst EMT, does not adhere to this rule, a contradiction that is not shared by any other zeolite. This is a direct consequence of the strong influences imposed by the crown ether during synthesis, which directs the Al arrangement in a unique pattern. This results in regions of high density of acid sites, separated by predominantly siliceous regions. The combined effects of these factors will be examined. The responses of EMT and Y zeolite to changes in pre-treatment and operating conditions will be compared.

### 6.8.1 Comparison of Calcination Temperature Effects on EMT and Y Zeolites

It was established that an increase in calcination temperature from 425 to 540°C, produced similar effects on alkylation activity on both EMT and Y zeolites, at an I/O ratio of 11 (see Section 6.4). A calcination temperature of 540°C suppressed cracking activity, causing polymerization products to accumulate in the effluent, thus abbreviating the Useful Catalyst Lifetime period (see Table 6.3). This behaviour was demonstrated on EMT between 55 and 100°C (see Figures 6.5 and 6.6), although the

effect was less significant above 77°C. Similar behaviour was also observed on Y zeolite between 70 and 100°C (see Figure 6.7).

The $C_8$ selectivity was modestly affected by calcination treatment on both zeolites, but the influence was dependent upon reaction temperature. Overall, catalysts calcined at 540°C produced less DMHs and favoured increased levels of $C_8^=$. This behaviour was demonstrated on EMT at 55°C (see Figure 6.8) and Y zeolite between 70 and 100°C (see Figure 6.10). However, the effect was not detected above 77°C on EMT (see Figure 6.9).

The calcination temperature exerted an influence on the distribution of the TMP isomers produced (see Table 6.3). A calcination temperature of 540°C favoured the least sterically hindered isomers, 2,3,3-TMP and 2,3,4-TMP, on EMT at 55°C and Y zeolite between 70 and 100°C. No significant effect of calcination temperature was noted on EMT above 77°C. The isomer 2,2,4-TMP predominated on all catalyst systems, regardless of the calcination temperature or reaction temperature. The levels of 2,2,4-TMP in the TMP fraction ranged from 34 % on EMT, calcined at 540°C using a reaction temperature of 56°C, to 58 % on Y, calcined at 425°C employing a reaction temperature of 70°C.

### 6.8.2 Comparison of Reaction Temperature Effects on EMT and Y Zeolites

Similar behaviour was demonstrated by both catalysts (calcined at 425°C) when reaction temperature was varied between 30 to 100°C, at an I/O ratio of 11 (see Section 6.5). The rate of cracking was reduced at 30°C, elevating polymerization product levels in the effluent on EMT (see Figure 6.14) and Y (see Figure 6.15). Production of TMPs was highest at the low reaction temperatures for both catalysts (see Figure 6.16 for EMT and Figure 6.17 for Y), which may be attributable to increased isomerization to 2-butene (Simpson et al, 1996). The Useful Catalyst Lifetimes of EMT and Y were brief, at a reaction temperature of 30°C (see Figure 6.13). This is primarily a consequence of the high polymerization rates (see Figures

6.14 and 6.15), which leads to notable amounts of hydrocarbon species retained on the catalyst surface (see Table 6.7).

A reaction temperature of 100°C promoted high cracking activity, reducing levels of $C_8$ and polymerization products in the effluent from both EMT (see Figure 6.14) and Y (see Figure 6.15). Levels of TMPs were lowered and DMHs elevated under this operating condition. This suggests that the stability of alkylate precursors was jeopardized by high reaction temperatures on both of these catalysts. The distribution of TMP isomers was also affected by reaction temperature on EMT and Y. The thermodynamically favoured isomers, 2,2,4-TMP and 2,2,3-TMP, predominated at high reaction temperatures, whereas the least sterically hindered isomers prevailed at low reaction temperatures (see Table 6.6). Overall, EMT demonstrated superior resistance to deactivation processes at 100°C relative to Y, achieving a longer Useful Catalyst Lifetime period (see Figure 6.13).

The optimal reaction temperature on both EMT and Y represents a compromise between achieving adequate cracking activity to suppress polymerization function, without encouraging excessive cracking activity leading to degradation of alkylate precursors. The former necessitates a high temperature and the latter demands a low temperature. The optimal temperature represents the balance between these opposing requirements. The best temperature was identified as 55°C for EMT and 70°C for Y, with respect to the temperature levels considered in the present investigation (see Figure 6.13).

### 6.8.3 Comparison of EMT and Y Control Experiments for Pt Study

The Pt study control experiments were investigated at 55°C and 382 psig employing an I/O ratio of 15 ($C_4^=$ WHSV=2.0 $h^{-1}$). Both EMT and Y were calcined *in situ* at 325°C for 3 h in flowing nitrogen, followed by 425°C in a flowing mixture of 10 % hydrogen in argon for 3 h (see Appendix A3.1.3). This pretreatment approach differs from that discussed previously in Chapter 6, as the Pt study control

experiments provide a baseline for Pt effects discussed in Chapter 7. The Pt supported catalysts require calcination and Pt reduction, and hence demand hydrogen in the pre-treatment stream for the reduction step. For this reason, the control experiments for this study involve pre-treating EMT and Y in a hydrogen mixture, to mimic the approach used for the Pt supported catalysts. The experiments were performed at approximately 53°C and 382 psig, employing an I/O ratio of 15 ($C_4^=$ WHSV = 2.0 $h^{-1}$) in a 12 sccm flowing stream of nitrogen.

#### *6.8.3.1 Comparison of Control Experiments (for Pt Study) with respect to Butene Disappearance*

Complete butene conversion was sustained for a longer duration on EMT relative to Y, translating into a 41 % increase in the Useful Catalyst (see Figure 6.25, Table 6.12). Another notable difference between the two solid acids, was the ability to suppress the decline in catalyst activity during the Rapid Deactivation Period. The rate of deactivation appears to proceed at a much slower rate on EMT, as indicated by the gentler slope on the butene conversion versus TOS curve.

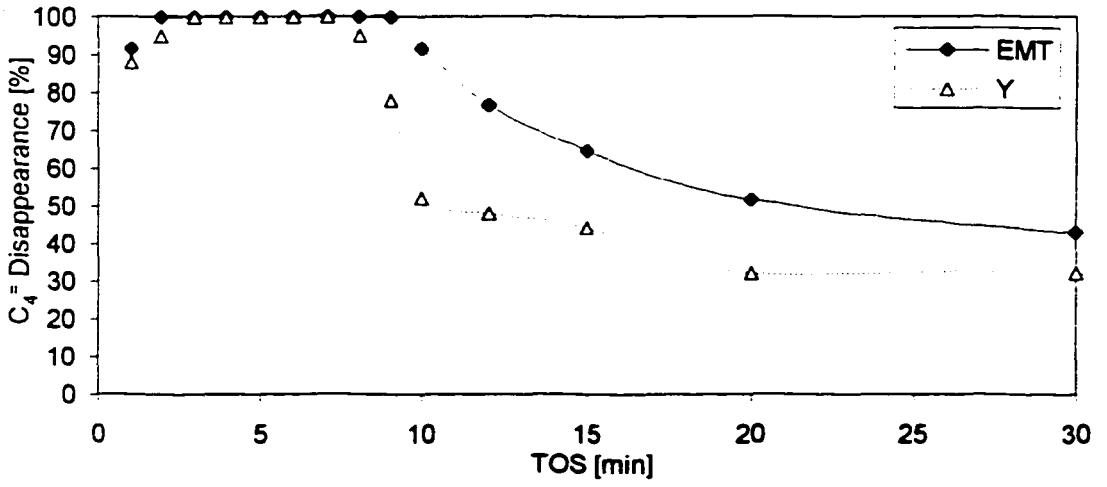



**Figure 6.25:** Effect of Catalyst Support on Butene Disappearance ($T_{rxn}$=53°C; P=382psig; $T_{calc}$=425°C, I/O=15; $C_4^=$WHSV=2.0$h^{-1}$; $m_{cat}$=2.78g)

Collectively, these observations suggest that the properties of EMT make it better suited to sustain high catalyst activity and maintain maximum butene conversion for a longer duration. It also implies that the structure of EMT is better equipped to combat the sequence of events responsible for deactivation.

#### *6.8.3.2 Comparison of Control Experiments (for Pt Study) with respect to $C_5^+$ Product Distribution*

The differences in physical structure and acidity between EMT and Y, did not effect a notable change on the $C_5$+ product distribution during the Useful Catalyst Lifetime period (see Figure 6.26). The cracking rate of EMT was slightly lower and $C_8$ production levels modestly increased, relative to those demonstrated by Y zeolite. It is interesting that the reduced cracking function of EMT did not appear to accelerate the onset of deactivation.

#### *6.8.3.3 Comparison of Control Experiments (for Pt Study) with respect to $C_8$ Selectivity*

No significant change in $C_8$ selectivity was observed between the two catalyst systems, during the Useful Catalyst Lifetime period (see Figure 6.27). However, EMT sustained TMP production for a longer duration and maintained higher levels during the deactivation period. Oligomerization function was notably suppressed during the deactivation period, suggesting that EMT was superior in sustaining hydride transfer. This ability is expected promote high butene conversion ability for a longer duration, as deactivation rates would be suppressed. This behaviour was observed on EMT (see Figure 6.25), providing further support for this hypothesis. Possible reasons for the improved hydride transfer ability of EMT, will be discussed in the Synopsis (Section 6.8.3.5).

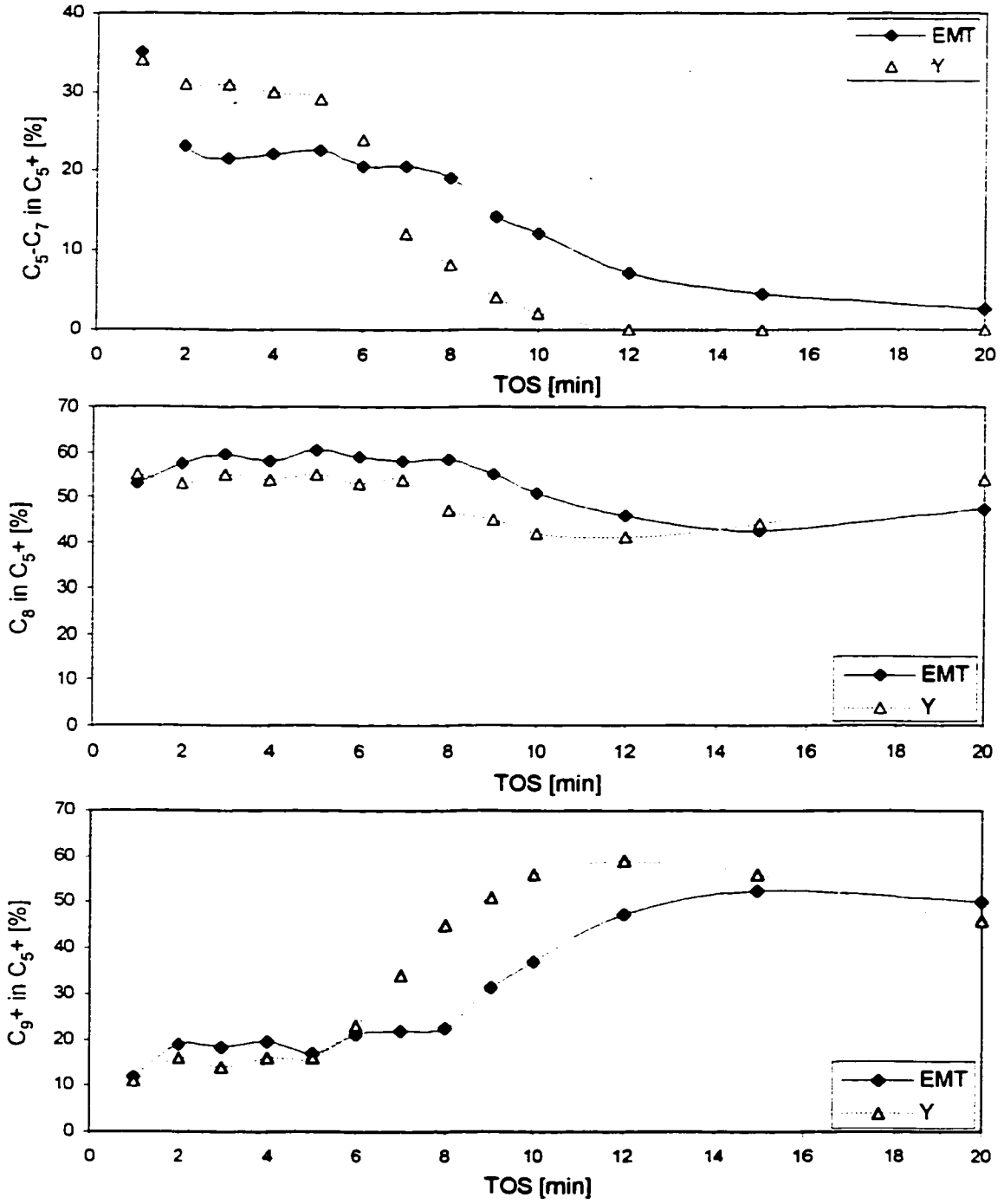



**Figure 6.26:** Effect of Catalyst Support on $C_5^+$ Product Distribution ($T_{rxn}$=53°C; P=382psig; $T_{calc}$=425°C, I/O=15; $C_4^=$WHSV=2.0$h^{-1}$; $m_{cat}$=2.78g)

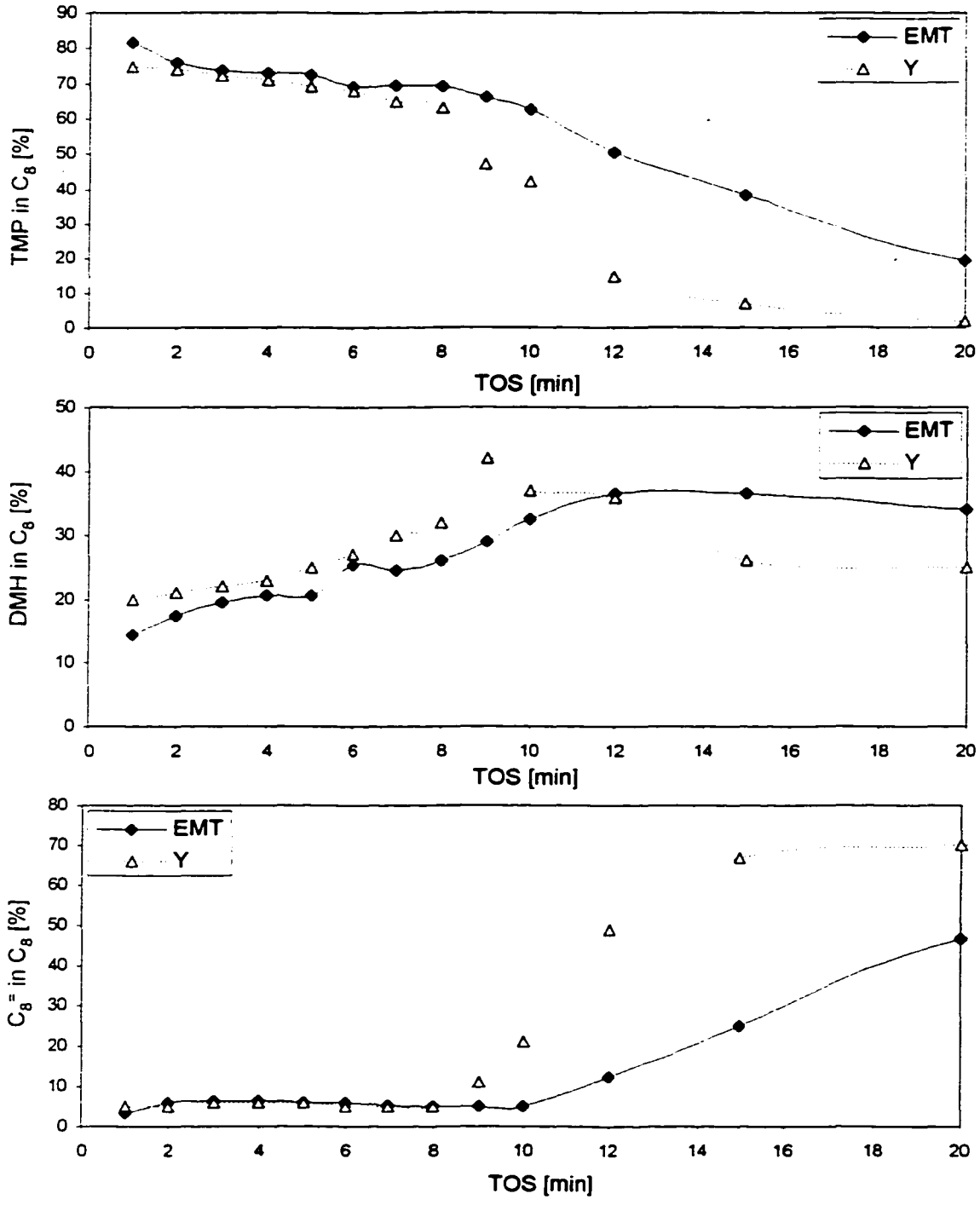



**Figure 6.27:** Effect of Catalyst Support on $C_8$ Selectivity
($T_{rxn}$=53°C; P=382psig; $T_{calc}$=425°C, I/O=15; $C_4^=$WHSV=2.0$h^{-1}$; $m_{cat}$=2.78g)

### *6.8.3.4 Comparison of Control Experiments (for Pt Study) with respect to TMP Selectivity*

Distinctive differences in the average composition of the TMP distribution produced during the Useful Catalyst Lifetime were detected (see Table 6.12). Both catalysts favoured the production of 2,2,4-TMP (see Figure 6.28). Although levels on Y were slightly higher during the Useful Catalyst Lifetime period, elevated 2.2,4-TMP levels were maintained on EMT during the Rapid Deactivation period. This is indicative of the superior ability of EMT to resist deactivation processes and sustain alkylation activity.

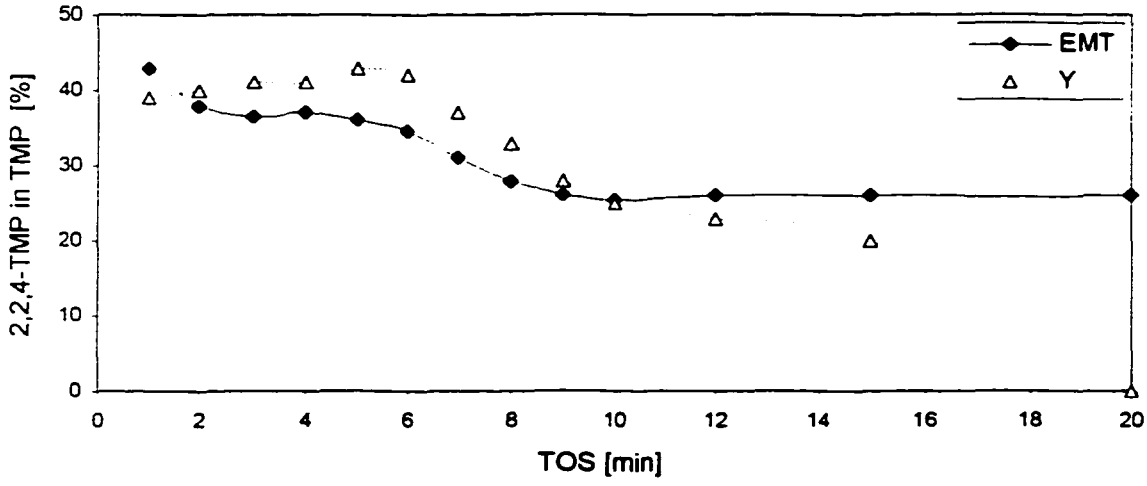



**Figure 6.28:** Effect of Catalyst Support on 2,2,4-TMP Level in TMP Fraction ($T_{rxn}$=53°C; P=382psig; $T_{calc}$=425°C, I/O=15; $C_4^=$WHSV=2.0$h^{-1}$; $m_{cat}$=2.78g)

**Table 6.12:** Comparison of Average Catalyst Performance (during first 5 min of Useful Catalyst Lifetime period) on EMT and Y Zeolites ($T_{rxn}$=53°C; P=382psig; $T_{calc}$=425°C, I/O=15; $C_4^=$ WHSV=2.0$h^{-1}$; $m_{cat}$=2.78g)

| Run(s) | F66EMT, F68EMT | F54Y |
|---|---|---|
| Catalyst | EMT | Y |
| Useful Catalyst Lifetime [min] | 10.6 | 7.9 |
| Yield [g $C_5$+/g cat/g 1-$C_4^=$ fed] | 0.083 | 0.068 |
| $C_5^+$ Liquid [mass %] | | |
| $C_5$-$C_7$ | 25 | 31 |
| $C_8$ | 58 | 55 |
| $C_9^+$ | 17 | 14 |
| *$C_8$ Distribution [mass %]* | | |
| TMP | 75 | 72 |
| DMH | 19 | 22 |
| $C_8^=$ | 6 | 6 |
| *TMP Distribution [%]* | | |
| 2,2,4-TMP | 38 | 41 |
| 2,2,3-TMP | 18 | 7 |
| 2,3,4-TMP | 17 | 21 |
| 2,3,3-TMP | 27 | 31 |
| *Indicators [mass fraction]* | | |
| $\frac{\text{TMP}}{\text{DMH}}$ | 4.2 | 3.3 |
| $\frac{\text{TMP + DMH}}{C_8^= + C_9+}$ | 2.78 | 3.03 |
| $\frac{\text{2,2,3-TMP + 2,2,4-TMP}}{\text{2,3,3-TMP + 2,3,4-TMP}}$ | 1.28 | 0.91 |

Recall that 2,2,4-TMP is claimed to be correlated to cracking activity (Corma & Martinez, 1993). Although comparable levels of 2,2,4-TMP were observed on both catalysts, cracking activity was higher on Y. It is possible that this isomer may be formed via alternative routes on EMT, such as self-alkylation of isobutane, for which 2,2,4-TMP is a direct product. This was suspected to be important in an investigation employing EMT applied to butene/isobutane alkylation (Rorvik, 1996) and will be discussed further in the Synopsis section. Evidence of self-alkylation of isobutane

on Y zeolite is difficult to ascertain, as no direct evidence can be provided by the current investigation.

The direct product of butene/isobutane alkylation isomer is 2,2,3-TMP. However, this isomer was found to be produced in the least amounts on both catalyst systems, suggesting that rapid isomerization of 2,2,3-TMP$^+$ was being facilitated under reaction conditions. It is interesting to note that EMT produced higher levels of 2,2,3-TMP, suggesting isomerization of 2,2,3-TMP$^+$ did not occur as extensively on this catalyst. Levels of the fastest diffusing isomers, 2,3,3-TMP and 2,3,4-TMP, were notably greater than thermodynamic predictions on both EMT and Y, suggesting that restrictions imposed by the pore cavities make the least sterically hindered isomers more favourable. The thermodynamically favourable isomers are bulkier and slower to diffuse, imposing an additional barrier to their formation in the zeolite cages. The catalyst EMT revealed superior ability in producing the thermodynamically favoured isomers relative to the fastest diffusing isomers ([2,2,3-TMP+2,2,4-TMP]/[2,3,3-TMP+2,3,4-TMP] ratio), which may be a direct consequence of the larger hypercages and improved accessibility to these cages.

#### *6.8.3.5 Synopsis of Control Experiments (for Pt Study) Comparison*

Similar product distributions were observed on EMT and Y for a reaction temperature of 53°C and an I/O ratio of 15 (see Table 6.12). Cracking activity was reduced on EMT and $C_8$ production levels were elevated. Although composition of the product was not significantly different, alkylation activity was sustained for a longer duration on EMT. A 40 % improvement in the Useful Catalyst Lifetime was observed on EMT relative to Y. In addition, yield was enhanced by 16 % on EMT. It was expected that a more active catalyst would increase the concentration of products in the catalyst pores, accelerating the onset of deactivation. However, EMT did not deactivate in a shorter period of time or at a faster rate.

These results lead to the hypothesis that perhaps adsorption/desorption phenomenon was exercising a significant influence on the product distribution, as was observed at higher olefin WHSV (see Section 6.6). It was found that the loss in surface area upon exposure to butene was more significant on Y, as compared to EMT. This suggests that the following are dictating catalyst activity:

- Y zeolite adsorbs butene more readily than EMT

  or

- The ability of EMT to involve isobutane, is superior to Y zeolite, enhancing hydride transfer to desorb $C_8$ product

The adsorption ability of EMT, with respect to butene, is not believed to be grossly inferior to that of Y zeolite. Complete butene disappearance was observed at similar TOS for both catalysts (see Figure 6.25). In addition, the product yield for EMT was superior to that obtained on Y zeolite (see Table 6.12). Therefore, it is suspected that EMT demonstrated superior ability in adsorbing isobutane and enhancing hydride transfer.

Published acidity measurements predict that EMT possesses a greater proportion of Bronsted acid sites relative to Y zeolite, particularly in the strong range (see Table 2.5). Spectroscopic studies on La-Y zeolite found only weak interaction, or physisorption, between isobutane and zeolite acid sites (Flego et al, 1995). It may be that the superior Bronsted acidity of EMT enhances the strength of this interaction.

The effects of WHSV (see Section 6.6) and cyclical feed delivery (see Section 6.7), suggest that many of the $C_8^+$ species adsorbed on Y zeolite grow in size, from subsequent reaction. It is possible that the close proximity of acid sites and higher content of Lewis acidity in Y favour these processes. This results in bulky oligomers populating the catalyst surface, restricting access to acid sites in the interior of the granule. Some of the larger $C_9^+$ adsorbed species on Y zeolite, will undergo cracking reactions, leading to elevated 2,2,4-TMP levels and an increase in the $C_5$-$C_7$ content in the $C_5^+$ liquid. Others will be retained on the catalyst surface blocking pores,

leading to significant surface area loss. This agrees with the experimental results reported.

TGA/DTA analysis of the spent catalyst detected a greater mass % of adsorbed species on EMT relative to Y zeolite (see Table 6.13). Although the amounts of adsorbed heavier compounds ($T_{desorp}$>300°C) is greater on EMT, it also revealed a significantly larger population of lighter adsorbed hydrocarbons ($T_{desorp}$>300°C). This suggests that EMT is able to adsorb more species without becoming deactivated. The improved accessibility to cages, nature of acid site and arrangement of acid sites potentially contribute to this behaviour.

The effect of granule size was not studied in detail in the flow reactor. However, a preliminary batch reactor experiment, employing Y catalyst pellets (1/8 " extrudate), revealed limited catalyst activity. The granule size employed for the flow reactor represents the smallest size that could safely be used, without concern for entrainment of catalyst particles in the reactor effluent.

**Table 6.13:** Effect of Catalyst Support ($T_{rxn}$ = 50°C, I/O =15, $T_{calc}$ = 425°C)

| Catalyst | SA Spent Catalyst [$m^2/g$] | TGA of Spent Catalyst [mass%] Desorption Temperature [°C] <200 | 200-300 | >300 | Total | Yield [$gC_5^+/gcat/g1\text{-}C_4^=fed$] |
|---|---|---|---|---|---|---|
| EMT | 377 | 3.5 | 2.5 | 3.0 | 9.3 | 0.083 |
| Y | 372 | 2.0 | 2.5 | 2.5 | 7.0 | 0.068 |

## 6.9 COMPARISON OF EMT AND Y ZEOLITES TO LITERATURE RESULTS

Experimental results for EMT and Y zeolite are compared to those published in the literature (see Table 6.14). Note the difference in the reactor system applied in the literature study investigating EMT. Stocker et al (Stocker et al, 1996), employed a

semi-batch reactor, in which all of the isobutane was delivered to prior to reaction and then heated to 80°C. At this point, the butene was pumped to the reactor at a WHSV of 2 $h^{-1}$ over a 2 h duration, resulting in an overall I/O ratio of 10. This mode of operation inherently provides a much higher local I/O ratio during the initial stages of the reaction.

Differences in reactor geometry and reaction temperature between the Stocker work and the present investigation, make direct comparisons impossible. It is difficult to predict the combined influence of all of these factors on the complex network of reactions that are being facilitated on these catalysts. However, knowledge of the effect of the I/O ratio and reaction temperature, can provide some insight into the estimated differences that may be imparted on product distributions.

It was found that a decrease in the olefin WHSV enhanced TMP formation and suppressed oligomerization and polymerization activities (see Section 6.6). Thermodynamic TMP isomers (2,2,3-TMP and 2,2,4-TMP) were favoured, over the least sterically hindered varieties (2,3,3-TMP and 2,3,4-TMP). An increase in reaction temperature favoured higher cracking activity, enhancing 2,2,4-TMP levels. An overall decrease in TMP production occurred at higher temperatures and a slight increase in DMH levels were noted.

Similar trends between the EMT experiments in the present work and the literature results are found. Both systems favoured high $C_8$ product levels to predominantly alkylation products. A higher TMP/DMH ratio is expected for the Stocker study, considering the mode of butene addition and lower olefin WHSV.

It is expected that the higher reaction temperature employed by the Stocker study would favour increased cracking activity, contrary to the results reported. It is possible that the method of sample collection used in the Stocker study does not provide a representative sample of the reaction products, due to dissolved (excess) isobutane. Evaporation of isobutane in the sample compromises the accuracy of the $C_5$ to $C_7$ fraction, as was found in batch experiments of the present study. The flow experiments of the present work are not vulnerable to this problem, due to the 16-loop Multiposition Trapping Valve in the on-line sampling system.

**Table 6.14: Comparison of Experimental EMT and Y Alkylation Data with Literature Results**

| | | EMT Stocker[1] | EMT[3] | Y-Corma[2] | Y[3] | Thermodynamic Equilibrium @50°C[4] |
|---|---|---|---|---|---|---|
| Run | | parent H-EMT | F66EMT F68EMT | USY-1 | F54Y | |
| Si/Al | | 3.5 | 6.9 | 5.4 | 6.3 | |
| Calcination Temperature [°C] | | 540 | 425 | 500 | 425 | |
| Reaction Temperature [°C] | | 80 | 50 | 50 | 50 | |
| Pressure [psig] | | n.a. | 382 | 382 | 382 | |
| I/O | | 10 | 15 | 15 | 15 | |
| $C_4^=$ WHSV [$h^{-1}$] | | 1.2 | 2 | 1 - 2 | 2 | |
| reactor | | semi-batch | flow | flow | flow | |
| *$C_5^+$ Dist.* | $C_5$-$C_7$ | 10 | 25 | 24 | 31 | |
| | $C_8$ | 82 | 58 | 59 | 55 | |
| | $C_9^+$ | 8 | 17 | 17 | 14 | |
| *$C_8$ Dist.* | TMP | 83 | 75 | 70 | 72 | |
| | DMH | 16 | 19 | 23 | 22 | |
| | $C_8^=$ | 1 | 6 | 7 | 6 | |
| *TMP Dist.* | 2,2,4-TMP | 29 | 38 | 34 | 41 | 63.5 |
| | 2,2,3-TMP | 9 | 18 | 7 | 7 | 17.5 |
| | 2,3,4-TMP | 27 | 17 | 28 | 21 | 9.0 |
| | 2,3,3-TMP | 35 | 27 | 31 | 31 | 10.0 |
| *Indicator* | $\frac{TMP}{DMH}$ | 5.2 | 4.2 | 3.0 | 3.3 | |

*1* bulk liquid sample after 3 h reaction, Stocker et al, 1996
*2* instantaneous liquid sample (TOS=1min), Corma et al, 1994b
*3* average alkylate quality during initial 5 min of Useful Catalyst Lifetime period
*4* thermal equilibrium composition, Cardona et al, 1995

The high *local* I/O ratio inherent in the semi-batch reactor system, can explain the remainder of the differences noted between the Stocker study and the present work. A high *local* I/O ratio is expected to reduce polymerization content in the product and enhance TMP levels in the $C_8$ fraction. This agrees with the data presented in Table 6.14.

An increase in reaction temperature, combined with a high I/O, favour high 2,2,4-TMP levels. However, the work of Stocker et al (1996) detected significantly lower 2,2,4-TMP levels than those obtained in the present work. It was suggested that 2,2,4-TMP was formed via self-alkylation of isobutane on EMT (Stocker et al, 1996). It is possible that a flow reactor design, favours self-alkylation of isobutane to a more significant extent than the semi-batch reactor, where residence time of butene is significantly longer.

The literature results for Y zeolite (Corma et al, 1994b) employed a similar reactor system, method of product collection and analysis, as those applied in the present work. The Corma study revealed a lower cracking activity and higher $C_8$ production levels, as compared to those reported by the present study. This is a direct reflection of the method of reporting catalyst activity. The Corma study reported instantaneous catalyst activity in the absence of deactivation (TOS = 1 min), where maximum alkylation activity occurs. The present work reports an arithmetic average of catalyst activity, during the initial 5 min of the Useful Catalyst Lifetime period.

A higher calcination temperature has been found to suppress cracking activity and elevate polymerization function, with little significant effect on the distribution of components in the $C_8$ fraction. Comparison of the Corma study, which applied a higher calcination temperature than the present work, supports this behaviour. Cracking activity was reduced and polymerization product levels were slightly higher, in agreement with the predictions. The distribution of components in the $C_8$ in the Corma study, match closely with those obtained in the present work.

Slight differences in the TMP isomer distribution are observed with higher levels of 2,2,4-TMP reported for the present work. Lower 2,3,4-TMP levels were

found in the present study, with all other TMP isomer levels being comparable to Corma's work. This is consistent with the effect of calcination temperature previously established, in that more severe calcination conditions favour the least sterically hindered isomers of 2,3,3-TMP and 2,3,4-TMP.

# Chapter 7

# Preliminary Studies on the Effect of Pt on the Performance of EMT and Y Zeolites

It is hypothesized that the presence of Pt in the zeolite pores can activate spillover. Hydrogen spillover will increase the amount of available reactive hydrogen in the vicinity of the acid sites. Hydride transfer will be improved and the Useful Catalyst Lifetime period extended. The effect of Pt on fresh catalyst performance will be discussed in Section 7.1.

Pt can also activate oxygen during regeneration. This would enhance the removal of carbonaceous deposits on the spent catalyst, improving the efficacy of regeneration. The effect of Pt on regenerated catalyst performance will be discussed in Section 7.2.

## 7.1 EFFECT OF Pt ON FRESH CATALYST PERFORMANCE OF EMT AND Y ZEOLITES

The primary objective of this investigation was to examine the effect of Pt addition on catalyst activity and selectivity. Two levels of Pt (0.1% Pt and 0.5% Pt) were considered on EMT (denoted as 0.1%Pt/EMT and 0.5%Pt/EMT respectively) and a single fixed amount (0.5%Pt) on Y zeolite (denoted as 0.5%Pt/Y). These loadings represent typical amounts employed in hydrogen spillover research. Preparation details are described in Section 3.5.1. Catalyst properties for Pt/EMT and Pt/Y systems are summarized in Tables 3.4 and 3.6.

Results from the Pt/EMT and Pt/Y experiments were compared to those of parent materials, EMT and Y respectively, where no noble metal is present. In this manner it can be established whether positive benefits can be gained through Pt incorporation into the catalyst design.

Undoubtedly, a minimum amount of Pt is necessary to generate a sufficient population of spillover species to effect a significant change. However, it is expected that an excessive amount of Pt will impose steric restrictions in the catalyst pores, and the benefits of spillover will be lost to diffusional limitations. Therefore, it is reasonable to assume that a preferred Pt level exists. This provides the framework for the secondary objective of this study, which is to identify whether Pt loading is important. Results on EMT at 0.1% Pt and 0.5% Pt loadings were compared, to determine whether a preferable Pt level exists. The effect of Pt content was not investigated on Y zeolite.

All experiments were performed in a hydrogen atmosphere, at a reaction temperature of 53°C and an operating pressure of 382 psig employing an I/O ratio of 15 and a $C_4^=$ WHSV of 2.0 $h^{-1}$. Catalyst pre-treatment was performed *in situ* prior to initiation of the experiment. Calcination of Pt catalyst systems prior to the reduction step, has been reported to improve the dispersion of the noble metal. Milder calcination conditions are recommended as this reduces the risk of metal agglomeration (Gates, 1995). The Pt/zeolite systems were calcined at 325°C for 3 hours in a stream of nitrogen maintained at 50 sccm. The calcination treatment was immediately followed by the reduction step, performed at 425°C for 3 h in a flowing mixture of 10.1 wt% $H_2$ in Ar, at a combined flow rate of 2 sccm. Those catalyst systems, which do not incorporate a noble metal, were calcined in the same manner to permit comparison (see Section 6.8.3).

At the conclusion of the reduction cycle, the catalyst bed was flushed with nitrogen for 5 min and then cooled under a nitrogen blanket to the reaction temperature. Experiments for the Pt/EMT and Pt/Y catalysts were performed in a flowing stream of 1.4 wt% $H_2$ in an argon/nitrogen mixture using a combined flow rate of 12 sccm. Those reactions studying EMT and Y zeolites utilized a 12 sccm stream of nitrogen.

### 7.1.1 Effect of Pt on Butene Disappearance for Fresh Catalysts

A minor change in the Useful Catalyst Lifetime occurred with impregnation of Pt into the pore network of EMT. The lower loading of Pt (0.1%) on the EMT carrier, did not significantly affect the Useful Catalyst Lifetime period, whereas the higher Pt level (0.5%) improved the lifetime modestly by 11.3 % (see Table 7.1). It may be that the lower loading of Pt is inadequate to generate a sufficient population of reactive hydrogen to produce a positive effect on catalyst lifetime of EMT. Butene conversion was not significantly affected by impregnation of 0.5% Pt onto acidic Y zeolite (see Table 7.1).

**Table 7.1:** Effect of Pt on Useful Catalyst Lifetime of Fresh EMT and Y Systems ($T_{calc}$=325°C; $T_{red}$=425°C; $T_{rxn}$=53°C; P=382psig; I/O=15; $C_4^=$WHSV=2.0$h^{-1}$; $m_{cat}$=2.78g; 12 sccm $H_2$/Ar/$N_2$ mix with 1.4 wt%$H_2$ used for Pt runs)

| Catalyst | Useful Catalyst Lifetime period [min][1] |
|---|---|
| EMT | 10.6 |
| 0.1%Pt/EMT | 9.5 |
| 0.5%Pt/EMT | 11.8 |
| Y | 7.9 |
| 0.5%Pt/Y | 8.0 |

Sensitivity limit = ± 0.7 min

### 7.1.2 Effect of Pt on $C_5$+ Product Distribution for Fresh Catalysts

The incorporation of 0.1% Pt impregnated in the EMT pore structure, did not significantly alter catalyst performance (see Figure 7.1). A loading of 0.1% Pt cannot develop the reactive hydrogen population necessary to enhance hydride transfer and improve catalyst performance relative to EMT. Increasing the Pt loading to 0.5 % on EMT, resulted in measurable benefits. Cracking activity and $C_8$ production levels were enhanced slightly, and polymerization function suppressed, on 0.5%Pt/EMT relative to parent EMT (see Figure 7.1). It appears that a minimum amount of Pt is necessary to establish a sufficient population of reactive hydrogen, possibly hydrogen spillover, to produce detectable differences in catalytic behaviour.

A similar loading of Pt on Y zeolite (0.5%Pt/Y) did not produce significant changes in the $C_5$+ liquid, during the Useful Catalyst Lifetime period. Cracking activity was lowered slightly, with very little differences in $C_8$ and $C_9$+ levels observed. This suggests that the reactive hydrogen generated by Pt on Y zeolite, does not exert a major effect on the alkylate composition from the catalyst.

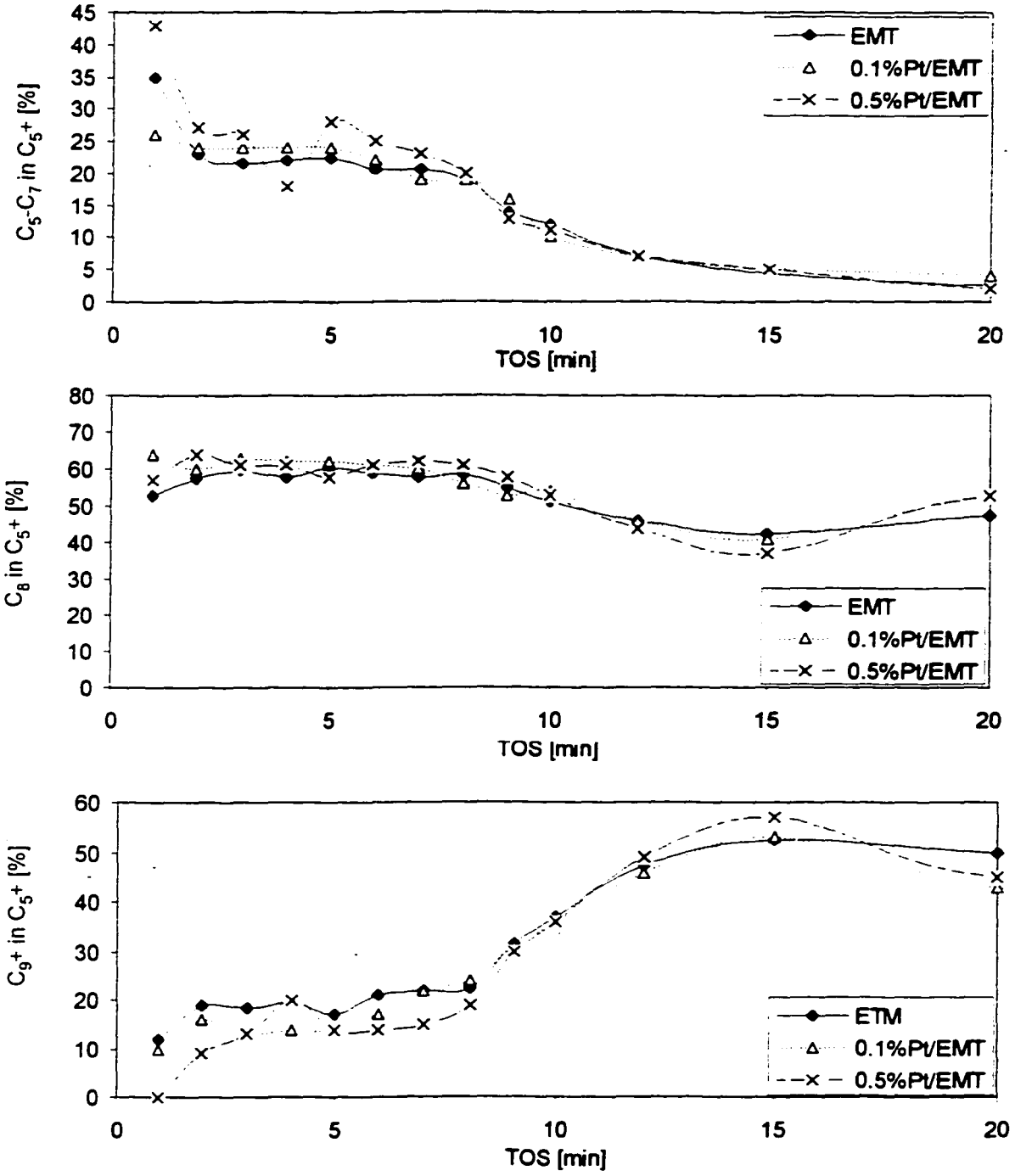



**Figure 7.1:** Effect of Pt on $C_5$+ Product Distribution of Fresh EMT Systems ($T_{calc}$=325°C; $T_{red}$=425°C; $T_{rxn}$=53°C; P=382psig; I/O=15; $C_4^=$WHSV=2.0$h^{-1}$; $m_{cat}$=2.78g; 12 sccm $H_2$/Ar,$N_2$ mix with 1.4 wt%$H_2$ used for Pt runs)

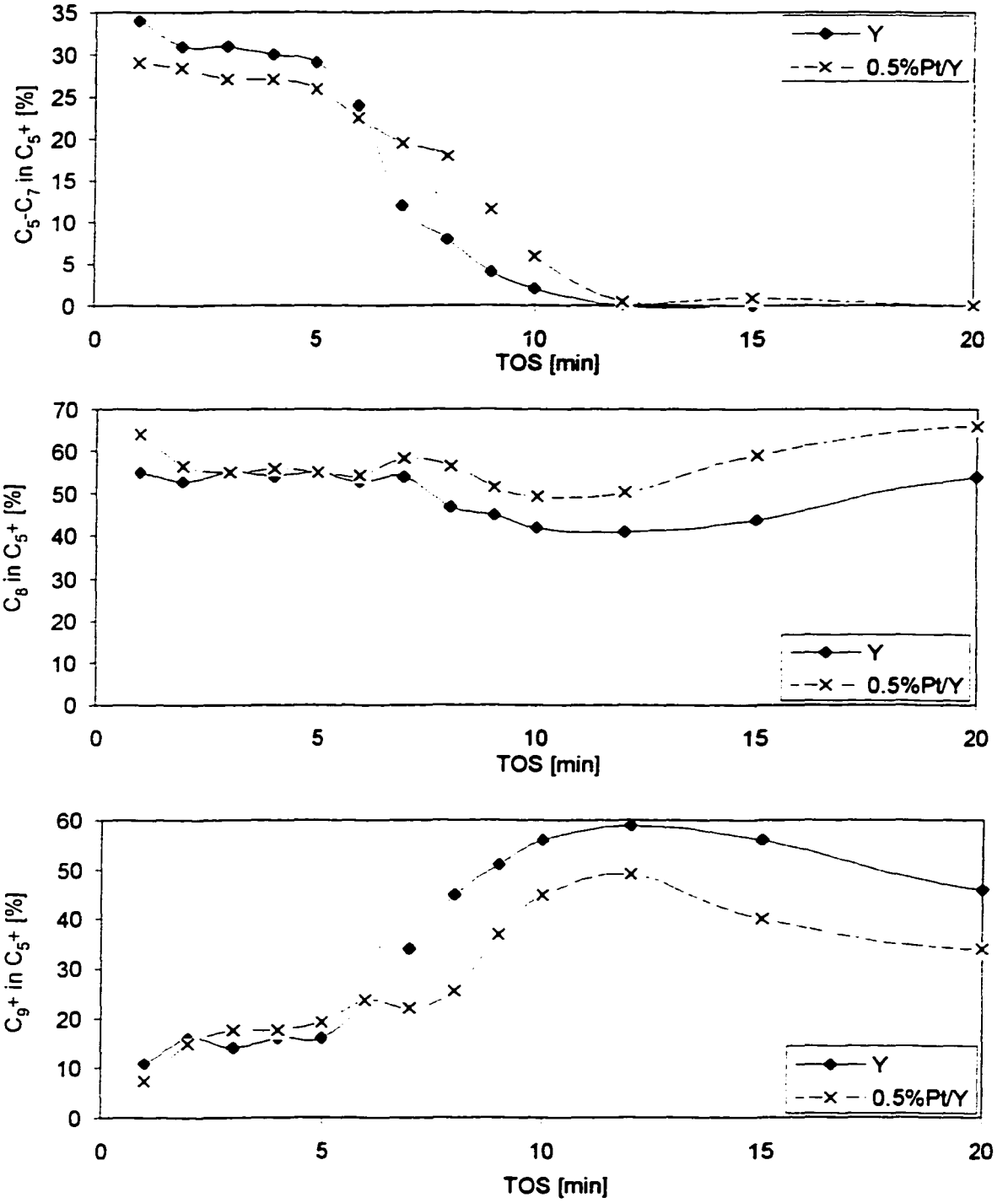



**Figure 7.2:** Effect of Pt on $C_5$+ Product Distribution of Fresh Y Systems ($T_{calc}$=325°C; $T_{red}$=425°C; $T_{rxn}$=53°C; P=382psig; I/O=15; $C_4^=$WHSV=2.0$h^{-1}$; $m_{cat}$=2.78g; 12 sccm $H_2$/Ar,$N_2$ mix with 1.4 wt%$H_2$ used for Pt runs)

### 7.1.3 Effect of Pt on $C_8$ Selectivity for Fresh Catalysts

No significant change in $C_8$ selectivity was observed for 0.1%Pt/EMT (see Figure 7.3). It appears that 0.1% Pt loading on EMT is inadequate to generate a sufficient reactive hydrogen population to exert a measurable effect on catalyst performance. Increasing the Pt loading to 0.5% on EMT caused slight changes in $C_8$ selectivity, during the Useful Catalyst Lifetime period (see Figure 7.3). Higher TMP levels were observed and reduced DMH formation noted. A modest increase in DMH levels was observed on Y zeolite using the same Pt loading of 0.5% (see Figure 7.4). The reactive hydrogen population developed by Pt on Y is not able to produce the same positive benefit of enhancing TMP levels, as noted for 0.5% Pt on EMT.

### 7.1.3 Effect of Pt on TMP Selectivity for Fresh Catalysts

TMP selectivity was not significantly altered by 0.1% Pt impregnated on EMT (see Table 7.2). This agrees with previous findings where no measurable change in the $C_5$+ product distribution and $C_8$ selectivity were observed on this catalyst.

Increasing the Pt loading to 0.5% produced a detectable change, favouring higher levels of the least sterically hindered isomers, 2,3,3-TMP and 2,3,4-TMP, and reduced amounts of 2,2,3-TMP and 2,2,4-TMP. Similar behaviour was observed for 0.5% Pt on Y zeolite, where levels of 2,3,3-TMP and 2,3,4-TMP were augmented in the presence of Pt.

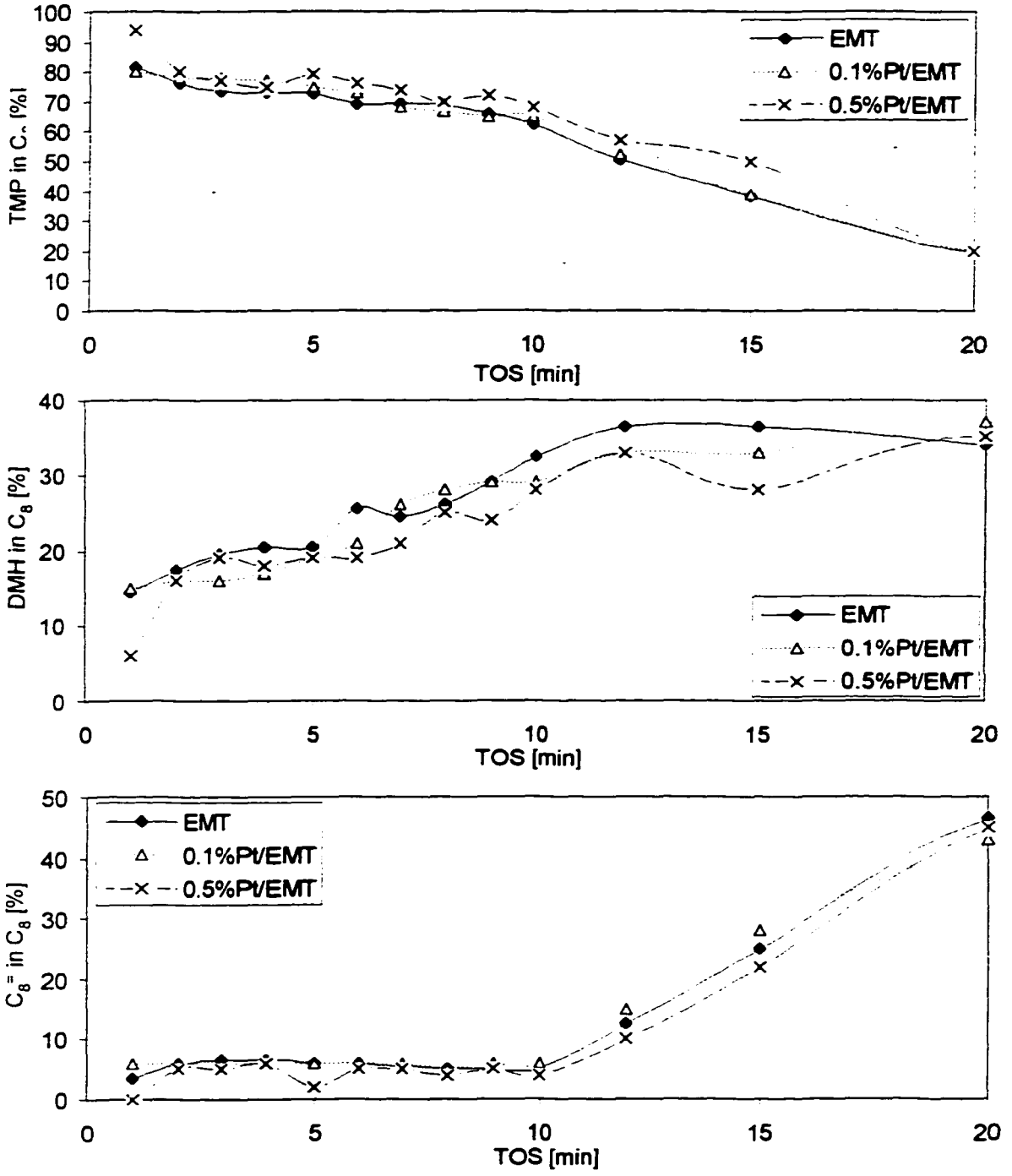



**Figure 7.3:** Effect of Pt on $C_8$ Selectivity of Fresh EMT Systems ($T_{calc}$=325°C; $T_{red}$=425°C; $T_{rxn}$=53°C; P=382psig; I/O=15; $C_4^=$WHSV=2.0$h^{-1}$; $m_{cat}$=2.78g; 12 sccm $H_2$/Ar,$N_2$ mix with 1.4 wt%$H_2$ used for Pt runs)

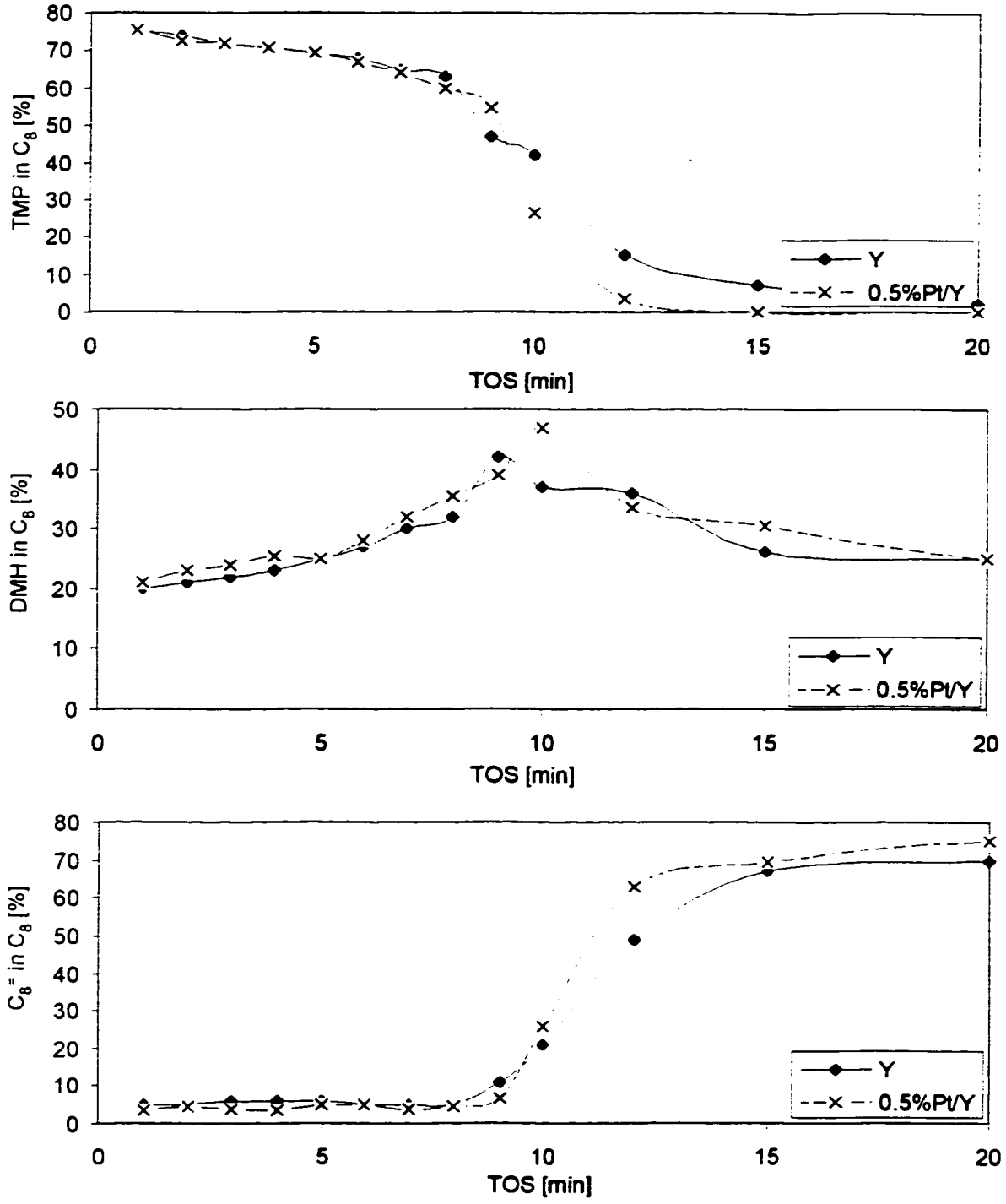



**Figure 7.4:** Effect of Pt on $C_8$ Selectivity of Fresh Y Systems ($T_{calc}$=325°C; $T_{red}$=425°C; $T_{rxn}$=53°C; P=382psig; I/O=15; $C_4^=$WHSV=2.0$h^{-1}$; $m_{cat}$=2.78g; 12 sccm $H_2$/Ar,$N_2$ mix with 1.4 wt%$H_2$ used for Pt runs)

**Table 7.2:** Comparison of Average Catalyst Activity during First 5 min of Useful Catalyst Lifetime Period for Fresh Parent and Pt Supported Catalysts ($T_{calc}$=325°C; $T_{red}$=425°C; $T_{rxn}$=53°C; P=382psig; I/O=15; $C_4^=$WHSV=2.0$h^{-1}$; $m_{cat}$=2.78g, 12 sccm $H_2$/Ar/$N_2$ mix with 1.4 wt%$H_2$ used for Pt runs)

| Run | F66EMT F68EMT | F62Pt1EMT | F49Pt5EMT | Sensitivity | F54Y | F44Pt5Y F56Pt5Y |
|---|---|---|---|---|---|---|
| Catalyst | EMT | 0.1% Pt/EMT | 0.5% Pt/EMT | | Y | 0.5% Pt/Y |
| Pt Dispersion [%] | n.a. | 74 | 76 | n.a. | n.a. | 91 |
| Useful Catalyst Lifetime [min] | 10.6 | 9.5 | 11.8 | ± 0.7 | 7.9 | 8.0 |
| Time of Deactivation [min] (80% > $C_4^=$ Conversion > 50%) | 10.4 | 12.5 | 12.6 | ± 1.6 | 1.9 | 3.2 |
| Yield [g $C_5$+/g cat/ g 1-$C_4^=$ fed] | 0.083 | 0.078 | 0.095 | ± 0.016 | 0.068 | 0.063 |
| *$C_5^+$ Dist. [mass %]* | | | | | | |
| $C_5$-$C_7$ | 25 | 24 | 28 | ± 2.3 | 31 | 28 |
| $C_8$ | 58 | 62 | 61 | ± 2.5 | 55 | 57 |
| $C_9^+$ | 17 | 14 | 11 | ± 3.7 | 14 | 15 |
| *$C_8$ Dist. [mass %]* | | | | | | |
| TMP | 75 | 77 | 81 | ± 3.3 | 72 | 71 |
| DMH | 19 | 17 | 15 | ± 2.7 | 22 | 25 |
| $C_8^=$ | 6 | 6 | 4 | ± 0.8 | 6 | 4 |
| *TMP Dist. [%]* | | | | | | |
| 2,2,4-TMP | 38 | 36 | 33 | ± 2.5 | 41 | 35 |
| 2,2,3-TMP | 18 | 18 | 14 | ± 2.1 | 7 | 4 |
| 2,3,4-TMP | 17 | 18 | 20 | ± 2.1 | 21 | 28 |
| 2,3,3-TMP | 27 | 28 | 33 | ± 2.4 | 31 | 33 |
| *Indicators [mass fraction]:* | | | | | | |
| $\frac{\text{TMP}}{\text{DMH}}$ | 4.2 | 4.7 | 6.6 | ± 0.57 | 3.3 | 2.9 |
| $\frac{\text{TMP + DMH}}{C_8^= + C_9+}$ | 2.78 | 3.47 | 3.73 | ± 0.63 | 3.03 | 3.35 |
| $\frac{\text{2,2,4-TMP + 2,2,3-TMP}}{\text{2,3,3-TMP + 2,3,4-TMP}}$ | 1.28 | 1.17 | 0.90 | ± 0.20 | 0.91 | 0.63 |

### 7.1.5 Synopsis of Pt Effects for Fresh Catalysts

The stages of catalyst activity and selectivity that were observed for EMT and Y zeolites (see Section 6.2), are also demonstrated on Pt/EMT (see Figures 7.5 to 7.8) and Pt/Y (see Figures 7.9 to 7.10) systems. Supporting Pt on the zeolite support does not alter the Useful Catalyst Lifetime period, with the exception of 0.5%Pt/EMT where a modest improvement was noted.

No significant change in alkylate composition or yield, were observed on 0.1%Pt/EMT. This loading of Pt appeared to be insufficient to develop an adequate reactive hydrogen population to enhance hydride transfer. TGA/DTA data for 0.1%Pt/EMT was similar to EMT for all desorption temperatures, except $T_d$>300°C, where the mass retained was slightly higher on 0.1%Pt/EMT (see Table 7.2). It is possible that the Pt inside the catalyst pores of EMT, imposed steric constraints, increasing the likelihood of larger molecular weight species being retained on the surface. The formation of these polymeric species cannot be suppressed by reactive hydrogen, as the population is insufficiently developed at a Pt loading of 0.1%.

Increasing the Pt loading to 0.5 % on EMT, resulted in measurable benefits being demonstrated. It appears that this loading is equal to, or exceeds, the minimum amount of Pt necessary to establish a sufficient population of reactive hydrogen. Production of $C_8$ compounds was elevated on 0.5%Pt/EMT, relative to parent EMT (see Table 7.2), with TMP isomers favoured. Hence, a notable increase in the octane value of the alkylate, as measured by the TMP/DMH ratio, was observed on 0.5%Pt/EMT. Although alkylation activity was enhanced on 0.5%Pt/EMT, the distribution of TMP isomers was altered, favouring the less sterically hindered isomers of 2,3,3-TMP and 2,3,4-TMP. This is not unexpected, as these isomers will diffuse most efficiently out of the pore network, under conditions of increased TMP production.

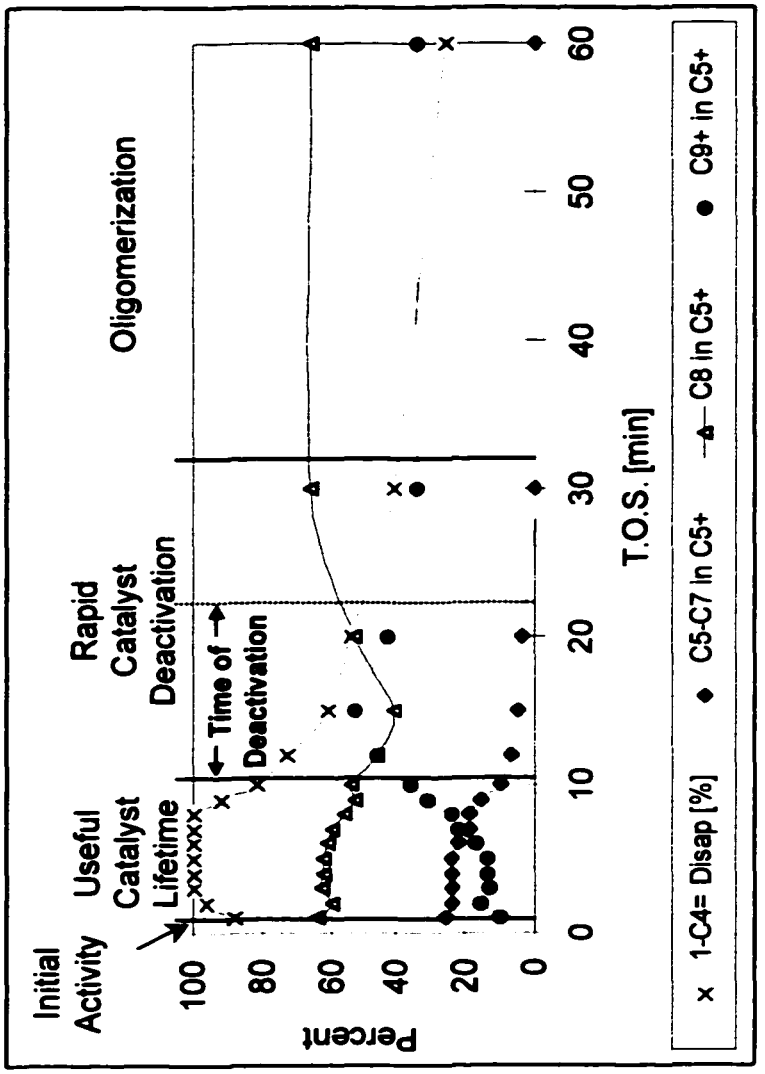



**Figure 7.5:** Stages of Catalyst Activity on 0.1%Pt/EMT with respect to $C_5$+ Product Distribution (F62Pt1EMT; $T_{rxn}$=53°C; $T_{calc}$=325°C; $T_{red}$=325°C; P=382psig; I/O=15; t=1h; $C_4^=$ WHSV=2.0$h^{-1}$; $m_{cat}$=2.78g; 12sccm $H_2$/Ar,$N_2$ with 1.4wt% $H_2$)

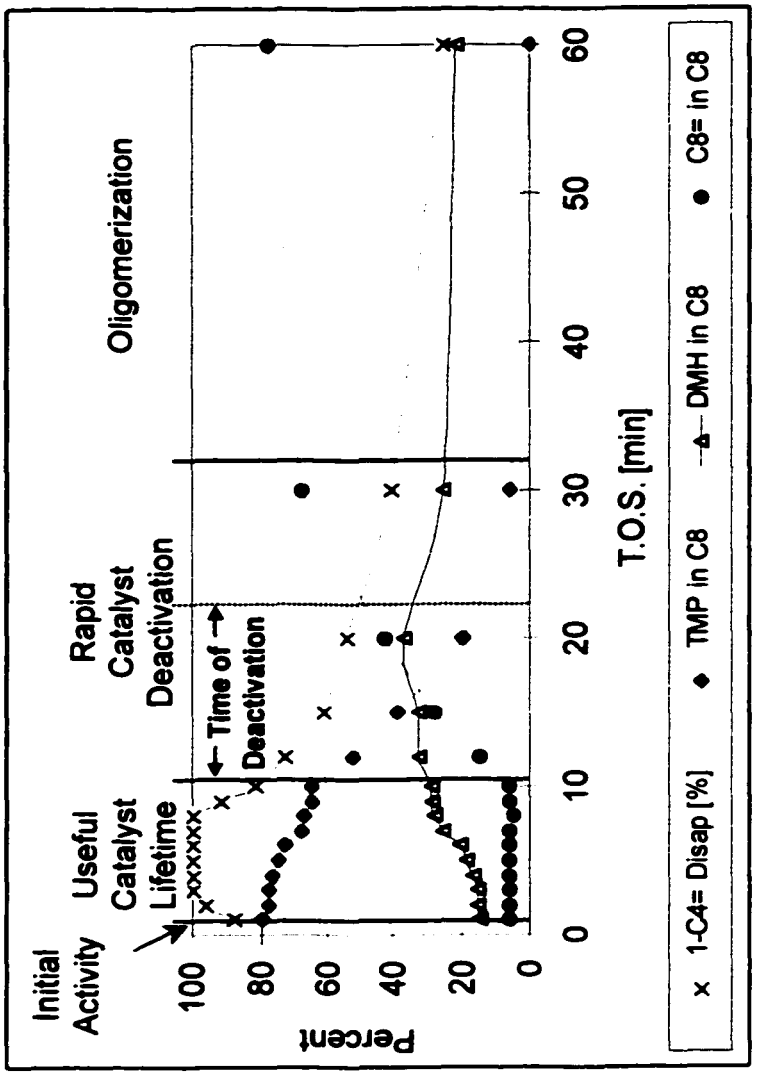



**Figure 7.6:** Stages of Catalyst Activity on 0.1%Pt/EMT with respect to $C_8$ Fraction Distribution (F62Pt1EMT; $T_{rxn}$=53°C; $T_{calc}$=325°C; $T_{red}$=325°C; P=382psig; I/O=15; t=1h; $C_4^=$ WHSV=2.0$h^{-1}$; $m_{cat}$=2.78g; 12sccm $H_2$/Ar,$N_2$ with 1.4wt% $H_2$)

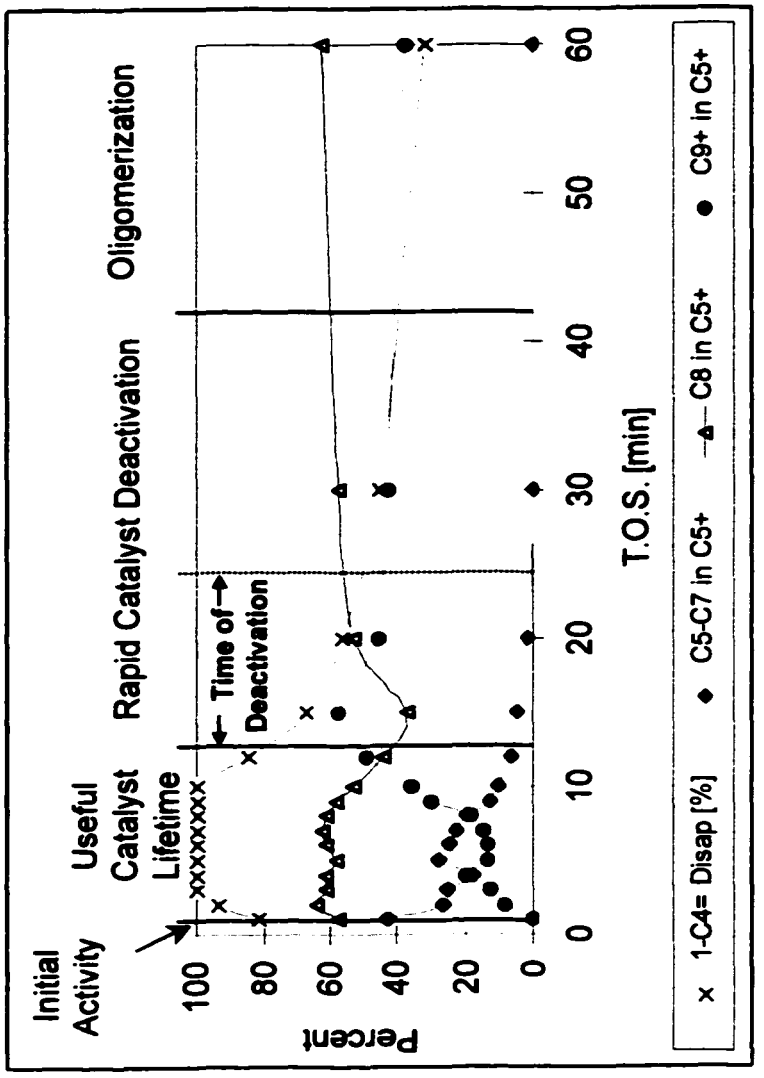



**Figure 7.7:** Stages of Catalyst Activity on 0.5%Pt/EMT with respect to $C_5$+ Product Distribution (F49Pt5EMT; $T_{nn}$=53°C; $T_{calc}$=325°C; $T_{red}$=325°C; P=382psig; I/O=15; t=1h; $C_4^=$ WHSV=2.0$h^{-1}$; $m_{cat}$=2.78g; 12sccm $H_2$/Ar,$N_2$ with 1.4wt% $H_2$)

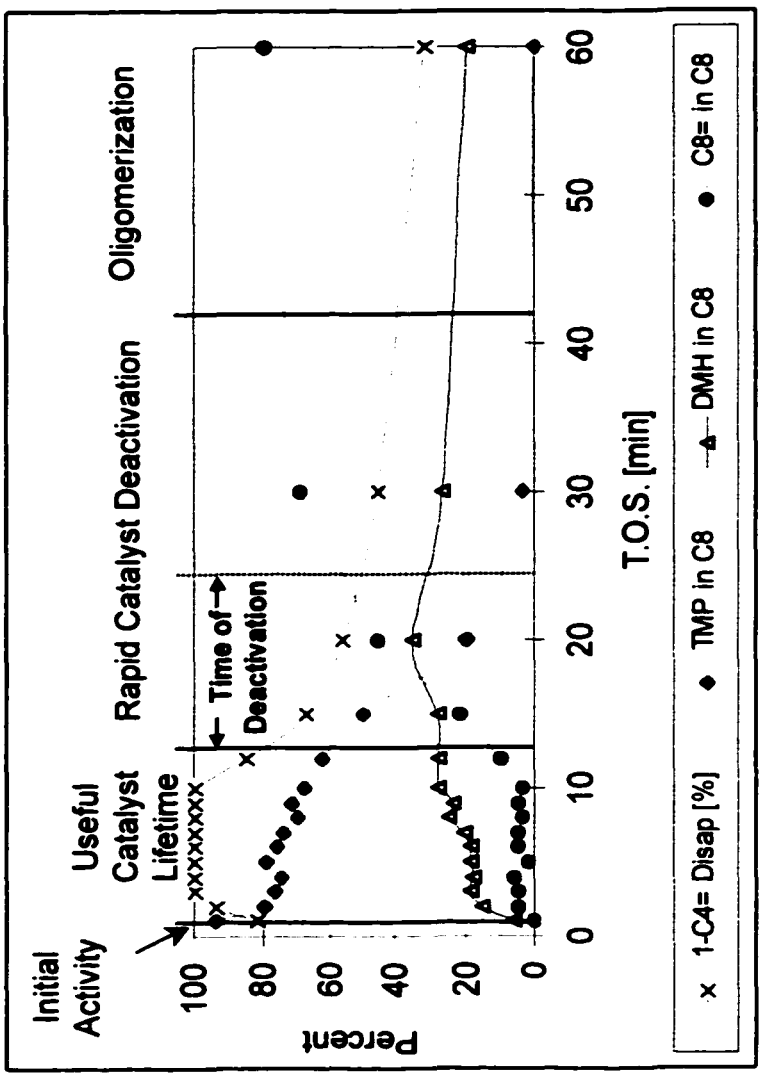



**Figure 7.8:** Stages of Catalyst Activity on 0.5%Pt/EMT with respect to $C_8$ Fraction Distribution (F49Pt5EMT; $T_{rxn}$=53°C; $T_{calc}$=325°C; $T_{red}$=325°C; P=382psig; I/O=15; t=1h; $C_4^=$ WHSV=2.0$h^{-1}$; $m_{cat}$=2.78g; 12sccm $H_2$/Ar,$N_2$ with 1.4wt% $H_2$)

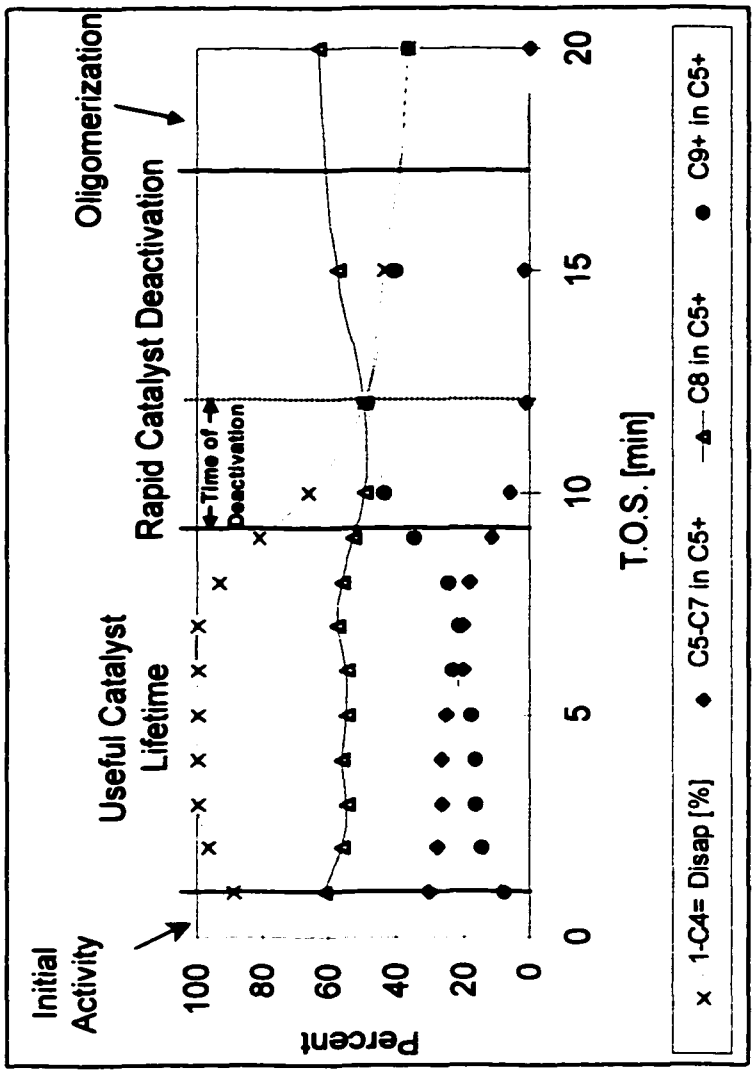



**Figure 7.9:** Stages of Catalyst Activity on 0.5%Pt/Y with respect to $C_5$+ Product Distribution (Average F44Pt5Y, F56Pt5Y; $T_{rxn}$=53°C; $T_{calc}$=325°C; $T_{red}$=325°C; P=382psig; I/O=15; t=1h; $C_4^=$ WHSV=2.0$h^{-1}$; $m_{cat}$=2.78g; 12sccm $H_2$/Ar,$N_2$ with 1.4wt% $H_2$)

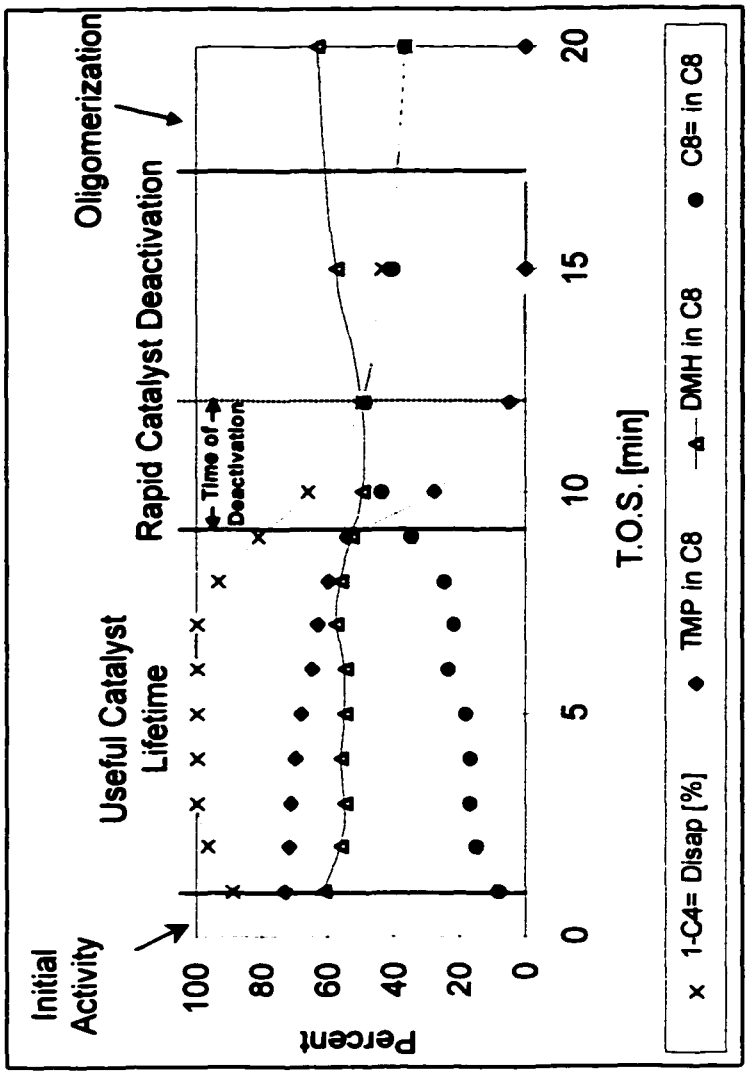



**Figure 7.10:** Stages of Catalyst Activity on 0.5%Pt/Y with respect to $C_8$ Fraction Distribution (Average F44Pt5Y, F56Pt5Y; $T_{rxn}$=53°C; $T_{calc}$=325°C; $T_{red}$=325°C; P=382psig; I/O=15; t=1h; $C_4^=$ WHSV=2.0$h^{-1}$; $m_{cat}$=2.78g; 12sccm $H_2$/Ar,$N_2$ with 1.4wt% $H_2$)

Evidence of hydride transfer is estimated by the proportion of branched saturated products in the alkylate. A loading of 0.5% Pt on EMT improved hydride transfer (see (TMP + DMH)/($C_8^=$ + $C_9$+) indicator of Table 7.2), producing higher levels of saturated, branched $C_8$ products and suppressing the formation of coke precursors ($C_8^=$ and $C_9$).

The increase in the concentration of reactive hydrogen in close proximity to the acid sites as a result of Pt presence, could enhance desorption of TMP products. This would suppress the opportunity for continued reaction of $TMP^+$ carbenium ions to higher molecular weight compounds, which are known to encourage deactivation. The rate of deactivation would be suppressed, allowing the acid sites to sustain activity for an extended duration.

The sampling frequency during the deactivation phase was inadequate to accurately estimate the duration of the Deactivation Period. Therefore, the "Time of Deactivation" was defined as the time period for butene conversion to decrease from 80% to 50% levels, where sufficient data was available. The presence of Pt on EMT, increased the Time of Deactivation, independent of the Pt loading (see Table 7.2, Figures 6.1, 6.2, 7.5 to 7.8). Active participation of reactive hydrogen could suppress the rate of deactivation by reducing hydride transfer contributions from adsorbed polymeric species, which lead to coke. Although 0.1% Pt/EMT did not develop an adequate reactive hydrogen population to effect a significant change during the Useful Catalyst Lifetime period, it appears that this loading was sufficient to suppress the rate of deactivation processes.

The positive benefits of Pt could also be related to butene hydrogenation, which would inflate the local I/O ratio in the vicinity of the acid site. It has been previously concluded (see Section 6.6) that a higher I/O ratio favoured increased $C_8$ production, particularly TMPs, and suppressed oligomerization and polymerization activity. These trends are consistent with the behaviour of 0.5%Pt/EMT. If butene hydrogenation was extensive, a significant increase in *n*-butane levels in the reactor effluent would be expected. In addition, a reduction in yield (g $C_5$+/g cat/g $C_4^=$ fed) is anticipated, as less butene is available for alkylation reaction. Levels of *n*-butane in

the product were not significantly higher for 0.5%Pt/EMT, although sensitivity to *n*-butane changes is poor in the experimental set-up. In addition, yield was not compromised on 0.5%Pt/EMT, relative to that achieved by EMT (see Table 7.2). Although butene hydrogenation cannot be excluded as a potential explanation for improved catalyst performance on 0.5%Pt/EMT, these contradictions suggest that other factors, such as hydrogen spillover, which may be responsible for the positive benefits observed.

The presence of Pt on Y zeolite did not produce the same benefits noted on EMT. No significant change in the Useful Catalyst Lifetime period or Time of Deactivation were noted (see Table 7.2, Figures 6.3, 6.4, 7.9, 7.10). The levels of DMH increased modestly on 0.5%Pt/Y, contradicting the trend of elevated TMP levels observed on EMT. A review of the alkylation mechanism presents a possible explanation for this behaviour. Under conditions of a well developed reactive hydrogen population, the $TMP^+$ cation can desorb via two mechanisms: hydride transfer from isobutane or reactive hydrogen, such as hydrogen spillover, which is facilitated by Pt (see Figure 7.11).

If hydride transfer is provided by isobutane, the *tert*-$C_4^+$ cation is regenerated eliminating the need for supplying this species via other reactions. However, if reactive hydrogen facilitates hydride transfer to desorb TMP, the *tert*-$C_4^+$ cation is not replenished, necessitating a re-establishment the *tert*-$C_4^+$ cation population through the "Induction Period" reactions. Under conditions of excessive involvement of reactive hydrogen, the *tert*-$C_4^+$ cation population becomes notably depleted. The population of *sec*-$C_4^+$ cation grows, favouring production of DMH through reaction with butene (see Figure 7.11), which was observed on 0.5%Pt/Y.

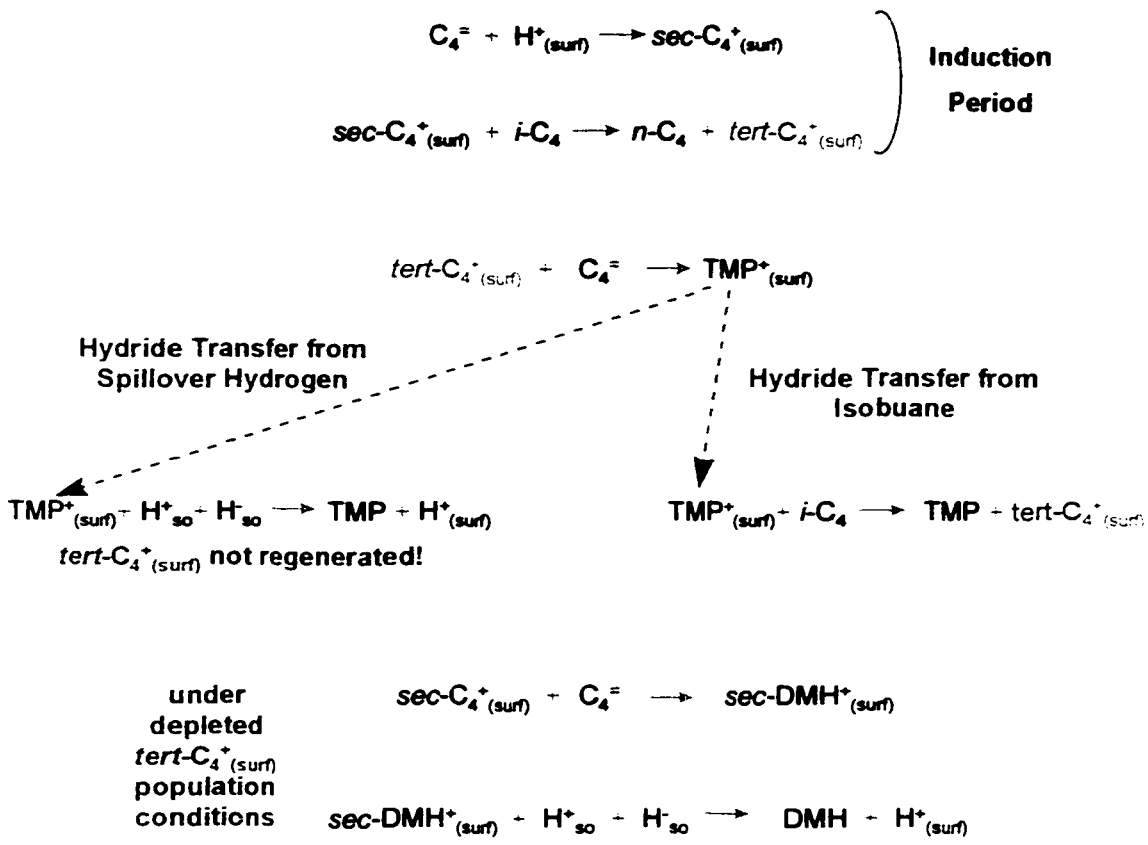



**Figure 7.11:** Proposed Effect of Excessive Hydrogen Spillover Participation

It is possible that reactive hydrogen population was developed too extensively on 0.5%Pt/Y, compromising the size of the *tert*-$C_4^+$ cation population and favouring DMH formation. Hydride transfer to a *sec*-$C_8^+$ cation is slower to than to a *tert*-$C_8^+$ cation (Cardona et al, 1995), increasing the lifetime of reactive oligomers on the catalyst surface under conditions of excessive reactive hydrogen involvement. This promotes the development of high molecular weight species on these catalysts, which is supported by TGA/DTA data for 0.5%Pt/Y relative to Y (see Table 7.3).

**Table 7.3:** Effect of Pt Presence on TGA/DTA Measurements of Spent Catalysts ($T_{calc}$ = 425°C, $T_{rxn}$ = 50°C, I/O =15, $C_4^=$ WHSV=2.0$h^{-1}$; 12 sccm $H_2$/Ar/$N_2$ mix with 1.4 wt%$H_2$ used for Pt runs)

| Catalyst | TGA of Spent Catalyst [mass%] Desorption Temperature [°C] | | | |
|---|---|---|---|---|
| | <200 | 200-300 | >300 | Total |
| EMT | 3.5 | 2.5 | 3.0 | 9.0 |
| 0.1%Pt/EMT | 3.3 | 2.2 | 3.5 | 9.0 |
| Y | 2.0 | 2.5 | 2.5 | 7.0 |
| 0.5%Pt/Y | 1.5 | 2.5 | 3.2 | 7.2 |

EMT and Y zeolites both possess a similar Si/Al ratio (see Tables 3.4 and 3.5) but differ slightly in the size of cages, accessibility to the cages and nature / distribution of acid sites. The dependency of the Pt effects on acidic support, emphasizes the sensitivity of catalyst activity to subtle changes in the local acidic environment. It is possible that Al-enriched and Al-depleted regions of EMT, relative to the random Al arrangement on Y zeolite, make EMT less effective at transporting reactive hydrogen.

Alternatively, the dispersion of Pt may be a contributing factor. Pt dispersion on Y zeolite was improved relative to the Pt/EMT systems (see Table 7.2). This could potentially explain why 0.5%Pt/Y would be more effective at facilitating the transport of hydrogen spillover, relative to 0.1%Pt/EMT and 0.5%Pt/EMT and could account for the negative effects imposed by Pt on Y zeolite.

These results suggest that the optimal extent of reactive hydrogen participation (possibly through spillover), represents a fine balance between promoting desorption of the product before consecutive reactions can occur. An adequate population of reactive hydrogen will increase the production of TMP improving alkylate quality. However, excessive amounts of reactive hydrogen, deplete the *tert*-$C_4^+$ poplulation, encouraging DMH formation and polymerization reactions. This compromises the octane value of the alkylate and expedites the onset of deactivation.

## 7.2 EFFECT OF Pt ON THE EFFICACY OF REGENERATION

Solid acid catalysts deactivate upon exposure to butene during butene/isobutane alkylation. Efficient regeneration is critical for a successful solid acid catalyst. Measures to improve the efficiency of regeneration are of paramount importance. As mentioned previously, Pt incorporation into the catalyst design could serve a dual purpose. Aside from promoting hydrogen spillover to enhance hydride transfer during butene/isobutane alkylation, Pt can also facilitate oxygen spillover and improve the efficacy of recalcination (Conner & Falconer, 1995). During the regeneration step, spillover oxygen can react with surface carbon, retained in the catalyst pores, and remove it as $CH_4$ or $CO_2$. An increase in the amount of reactive oxygen through the spillover, is expected to improve the efficacy of regeneration.

The spent catalysts from the fresh experiments were recalcined *in situ* for the regeneration runs. All spent catalysts (with or without Pt) were retreated in the same manner. Recalcination was performed *in situ* at 325°C for 3 h in 25 sccm of flowing air. This was immediately followed by a re-reduction cycle in which the catalyst bed was maintained at 425°C for 3 h in a flowing mixture of 10.1 % $H_2$ in Ar at a total flow rate of 2 sccm. Upon completion of the re-reduction step, the experimental procedure and reaction conditions outlined in Section 7.1 were followed.

All experiments employed a reaction temperature of 53°C and an operating pressure of 382 psig, with an I/O ratio of 15 and a $C_4^=$ WHSV of 2.0 $h^{-1}$. Experiments involving Pt catalysts employed a flowing stream of 1.4 wt% $H_2$ in an argon/nitrogen mixture, using a combined flow rate of 12 sccm. Those reactions investigating regenerated EMT and Y zeolites utilized a nitrogen stream maintained at 12 sccm.

### 7.2.1 Effect of Pt on Butene Disappearance for Regenerated Catalysts

The activity of EMT and Y zeolites was not fully recovered by the recalcination treatment. The Useful Catalyst Lifetime periods of regenerated EMT and Y were

notably reduced after retreatment (see Table 7.4). It is possible that residual material was not removed by the reconditioning step and is clogging the catalyst pores, preventing access to all catalytic sites in the subsequent experiment. No attempts were made to optimize the air flow rate or calcination conditions. Optimization of these parameters may improve the efficacy of the regeneration process.

The incorporation of Pt into the pore network improves the efficiency of the regeneration step. The Useful Catalyst Lifetime periods of regenerated 0.1%Pt/EMT and regenerated 0.5%Pt/EMT were comparable to their fresh performance levels (see Table 7.4). Although regenerated 0.5%Pt/Y did not demonstrate the same ability as Pt/EMT systems with respect to recovering the Useful Catalyst Lifetime period, it did exhibit superior regeneration efficacy over Y zeolite.

**Table 7.4:** Effect of Pt on Useful Catalyst Lifetime of Fresh and Regenerated EMT and Y Systems ($T_{calc}$=325°C; $T_{red}$=425°C; $T_{rxn}$=53°C; P=382psig; I/O=15; $C_4^=$WHSV=2.0$h^{-1}$; $m_{cat}$=2.78g; 12 sccm $H_2$/Ar/$N_2$ mix with 1.4 wt%$H_2$ used for Pt runs)

| Catalyst | Useful Catalyst Lifetime Period [min] | |
|---|---|---|
| | Fresh | Regenerated |
| EMT | 10.6 | 6.8 |
| 0.1%Pt/EMT | 9.5 | 10.1 |
| 0.5%Pt/EMT | 11.8 | 10.3 |
| Y | 7.9 | 5.5 |
| 0.5%Pt/Y | 8.0 | 6.2 |

### 7.2.2 Effect of Pt on $C_5$+ Product Distribution of Regenerated Catalysts

Cracking activity of regenerated EMT was suppressed during the Useful Catalyst Lifetime period resulting in accumulation of polymerization products in the alkylate (see Figure 7.12). Similar behaviour was observed on Y zeolite, although regeneration appeared more efficient on Y, in terms of recovery of fresh catalyst activity (see Figure 7.13).

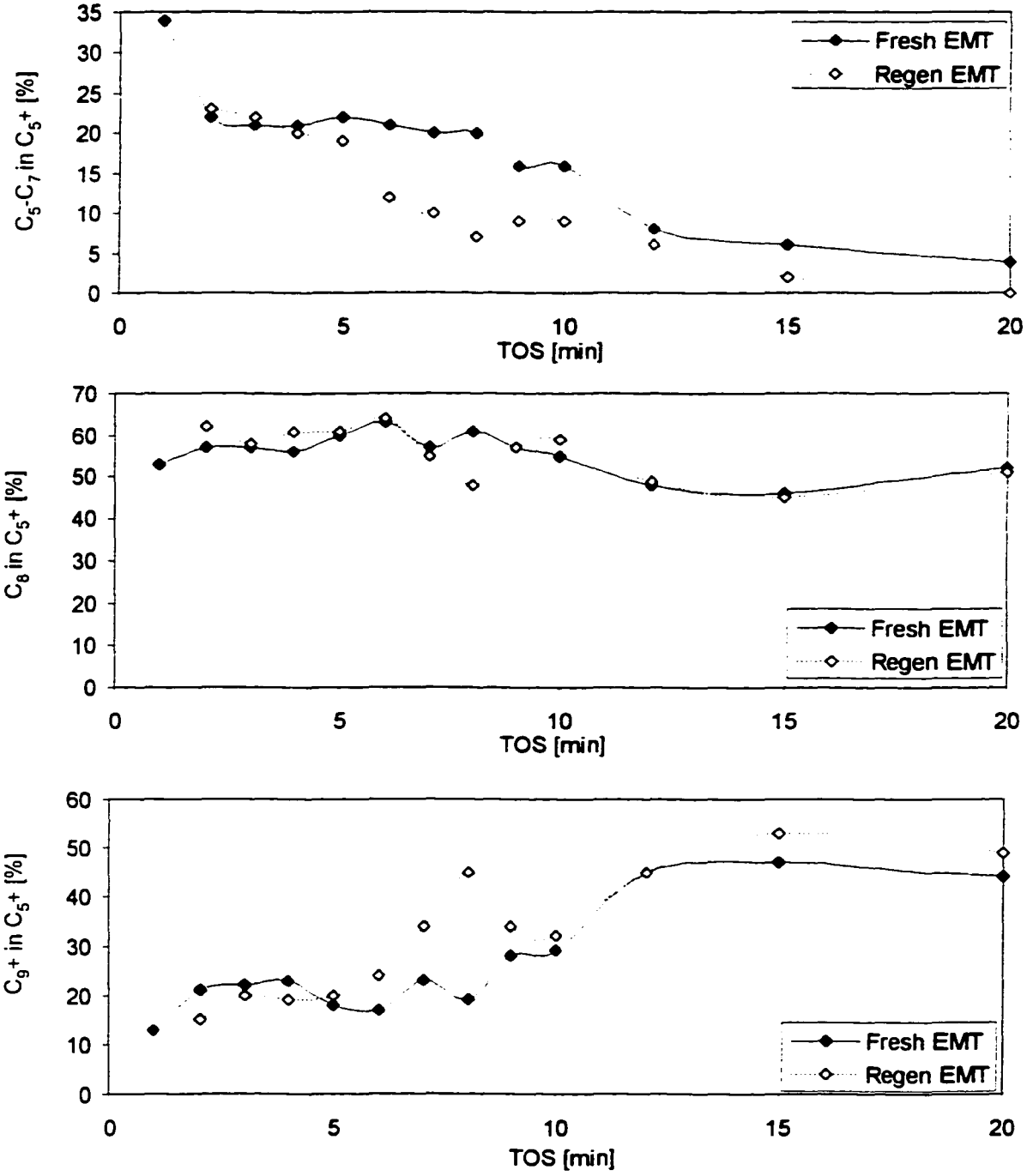



**Figure 7.12:** Effect of Regeneration on $C_5$+ Product Distribution of EMT ($T_{calc}$=425°C; $T_{rxn}$=53°C; P=382psig; I/O=15; $C_4^=$WHSV=2.0$h^{-1}$; $m_{cat}$=2.78g)

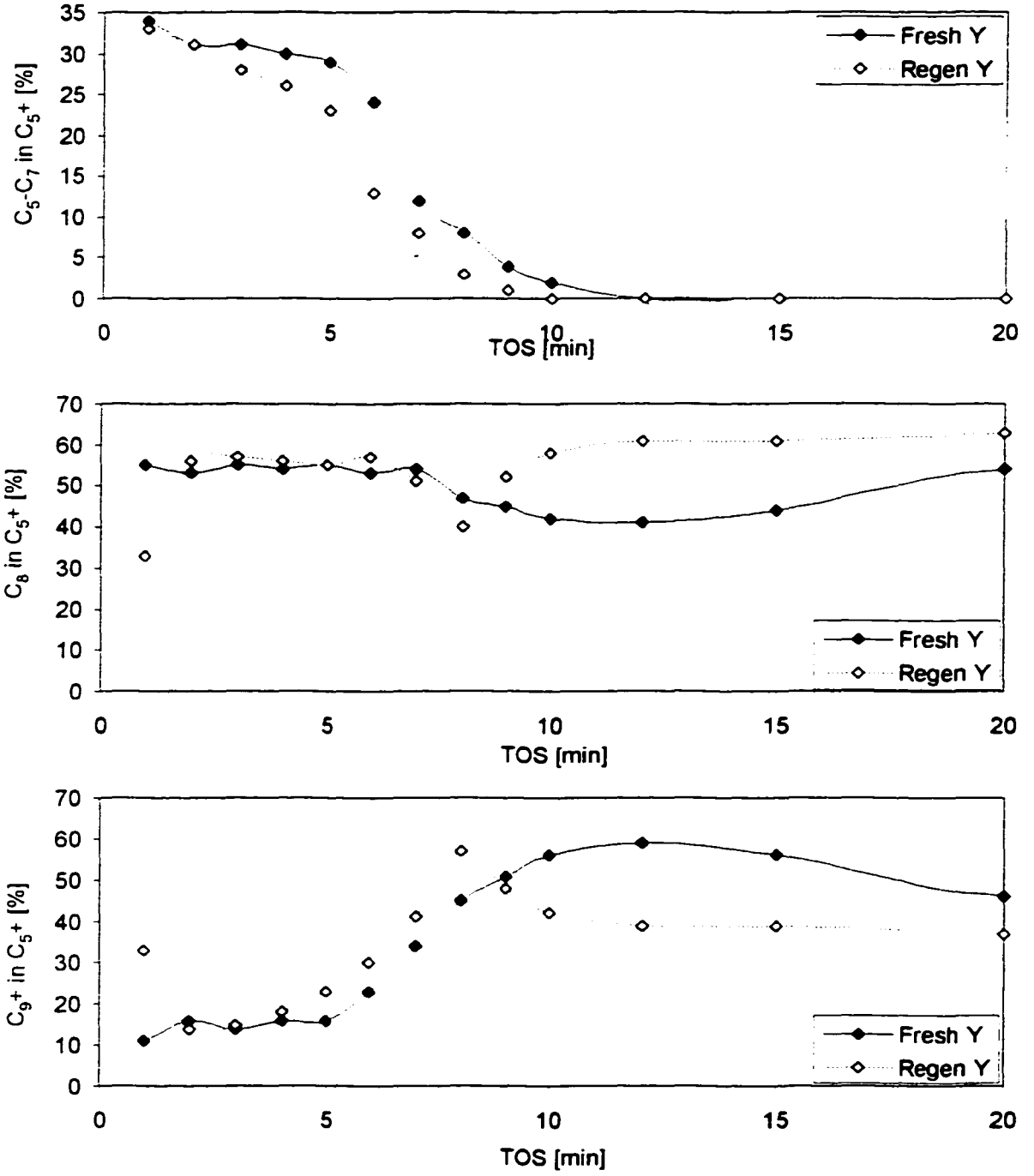



**Figure 7.13:** Effect of Regeneration on $C_5$+ Product Distribution of Y
($T_{calc}$=425°C; $T_{rxn}$=53°C; P=382psig; I/O=15; $C_4^=$WHSV=2.0$h^{-1}$; $m_{cat}$=2.78g)

Alkylation of butene with isobutane demands acid sites of similar strength to those required for cracking reactions (Corma et al, 1994b; Corma & Wojciechowski, 1982; Corma et al, 1994a; O'Young et al, 1994; Corma et al, 1996a). In contrast DMH production, oligomerization and polymerization reactions are facilitated by weaker acid sites. It appears that some strong acid sites are not reclaimed by the regeneration step, and rather promote less demanding reactions such as polymerization.

Impregnation of Pt into the pore network of EMT improved the efficacy of regeneration at both 0.1% (see Figure 7.14) and 0.5 % (see Figure 7.15) Pt loading. High cracking activity was recovered on regenerated Pt/EMT systems irrespective of the Pt loading, matching levels achieved by fresh catalysts. The levels of $C_8$ and polymerization product levels, were comparable to those obtained by fresh Pt/EMT catalyst systems. This behaviour contradicts regenerated EMT, where enhanced polymerization activity accelerated deactivation processes, abbreviating the Useful Catalyst Lifetime period. This suggests that Pt activates reactive oxygen on Pt/EMT systems during the reconditioning step, improving the extent of removal of retained hydrocarbons on the spent catalyst surface. The activity of strong acid sites on Pt/EMT is recovered more efficiently in the presence of Pt.

The benefits of Pt were not apparent on Y zeolite (see Figure 7.16). Cracking activity was lost at an earlier TOS on regenerated 0.5%Pt/Y relative to fresh performance levels, causing polymerization products to accumulate. The behaviour of Y and 0.5%Pt/Y, in terms of the efficacy of regeneration, is similar with no improvement in catalyst recovery demonstrated by Pt. This contradicts the behaviour of Pt on EMT systems where an improvement in regeneration efficiency was observed.

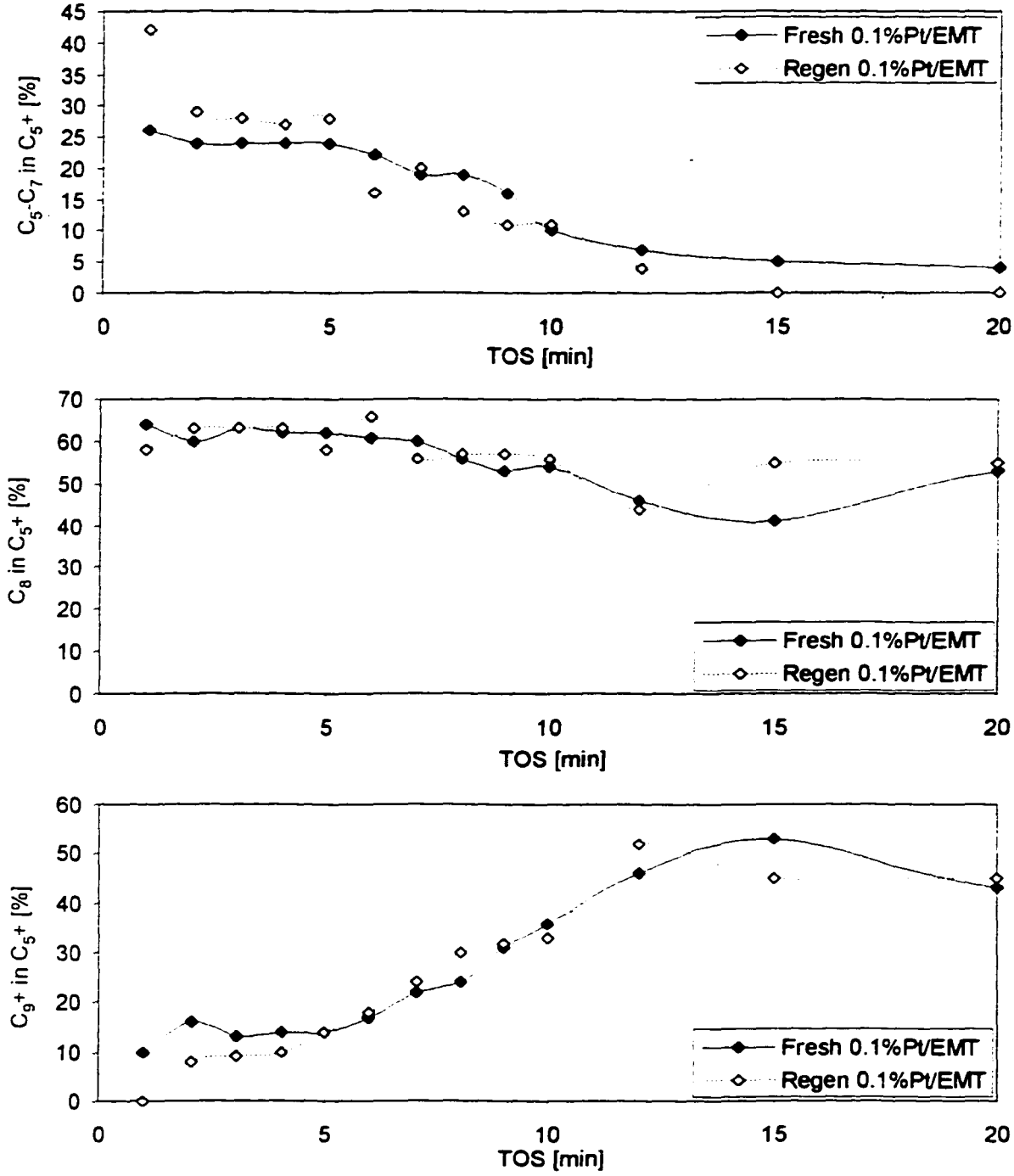



**Figure 7.14:** Effect of 0.1%Pt Loading on Regeneration of EMT with respect to $C_5$+ Product Distribution
($T_{calc}$=325°C; $T_{red}$=425°C; $T_{rxn}$=53°C; P=382psig; I/O=15; $C_4^=$WHSV=2.0$h^{-1}$; $m_{cat}$=2.78g; 12 sccm $H_2$/Ar/$N_2$ mix with 1.4 wt%$H_2$ used for Pt runs)

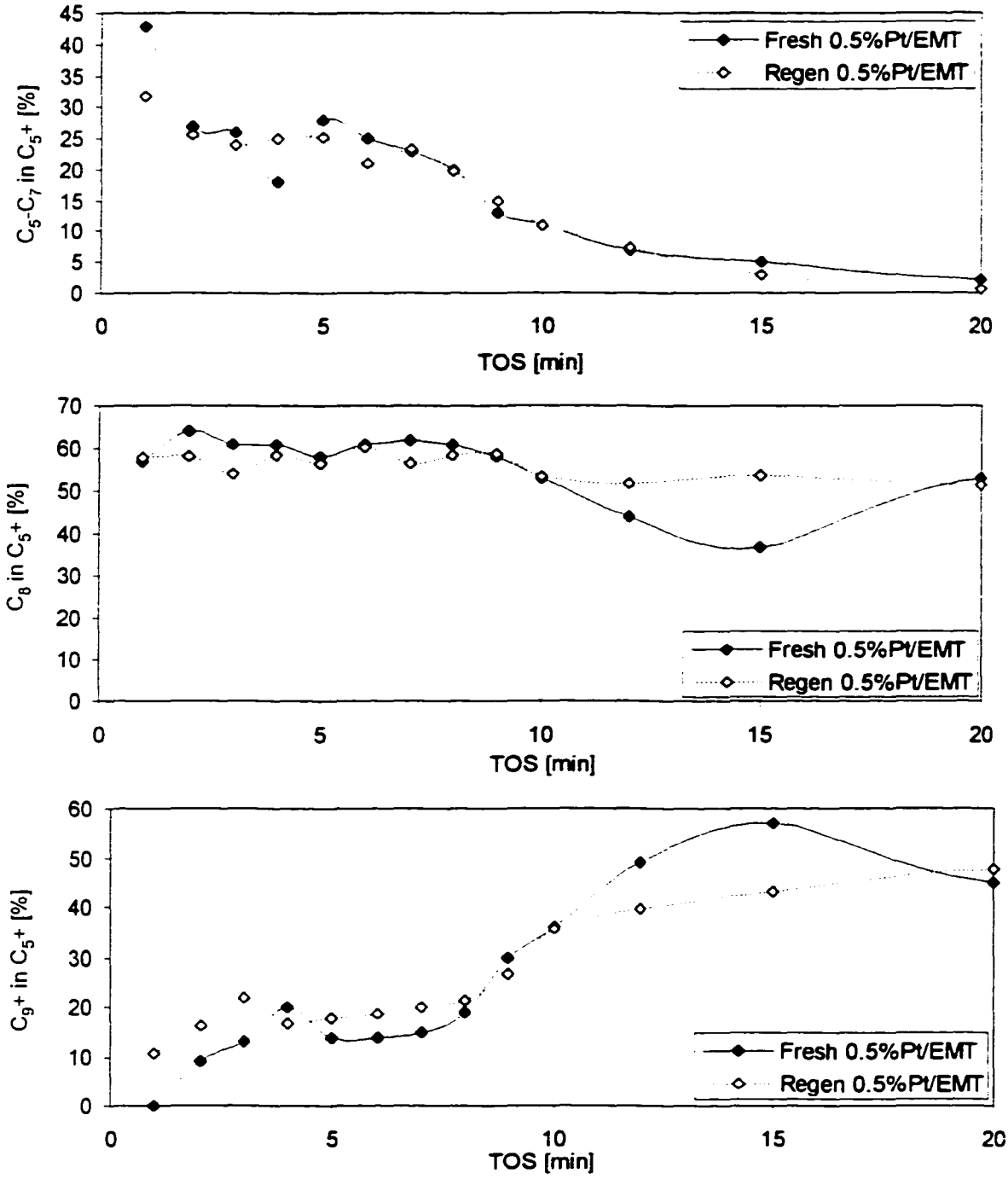



**Figure 7.15:** Effect of 0.5%Pt Loading on Regeneration of EMT with respect to $C_5$+ Product Distribution
($T_{calc}$=325°C; $T_{red}$=425°C; $T_{rxn}$=53°C; P=382psig; I/O=15; $C_4^=$WHSV=2.0$h^{-1}$; $m_{cat}$=2.78g; 12 sccm $H_2$/Ar/$N_2$ mix with 1.4 wt%$H_2$ used for Pt runs)

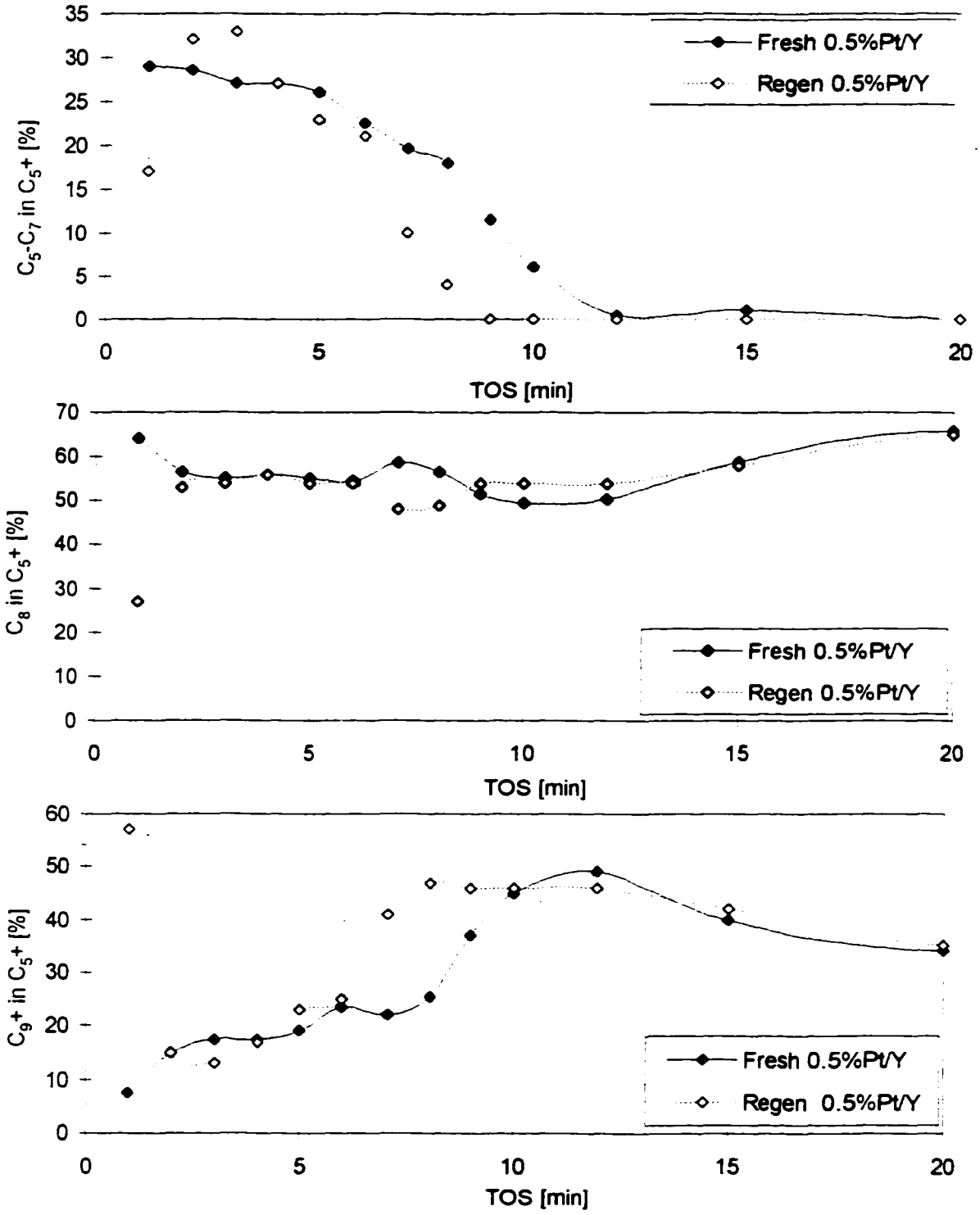



**Figure 7.16:** Effect of 0.5%Pt Loading on Regeneration of Y with respect to $C_5$+ Product Distribution
($T_{calc}$=325°C; $T_{red}$=425°C; $T_{rxn}$=53°C; P=382psig; I/O=15; $C_4^=$WHSV=2.0$h^{-1}$; $m_{cat}$=2.78g; 12 sccm $H_2$/Ar/$N_2$ mix with 1.4 wt%$H_2$ used for Pt runs)

### 7.2.3 Effect of Pt on $C_8$ Selectivity for Regenerated Catalysts

The content of TMP declined at shorter TOS on regenerated EMT, relative to fresh performance levels (see Figure 7.17). The Useful Catalyst Lifetime period of the retreated catalyst was characterized by declining levels of TMP in the $C_8$ fraction, creating a larger disparity between fresh EMT and regenerated EMT activity. Initially, lost TMP ability was compensated by elevated DMH production, but as this capability was lost, oligomerization functions became increasingly important.

Note that regenerated EMT still sustained significant DMH production ability while undergoing rapid deactivation. It can be concluded that EMT, in both the fresh and regenerated state, is able to maintain a measurable degree of hydride transfer while deactivating. Unfortunately, it was not able to facilitate this hydride transfer to form TMP products, but rather favoured DMH formation. This is most likely a consequence of lost activity due to incomplete regeneration.

The catalyst Y zeolite revealed slightly different behavior. The regenerated catalyst rapidly lost the ability to produce TMPs from the onset of the reaction (see Figure 7.18). These results are consistent with the explanations discussed for the $C_5^+$ distribution on Y zeolite. The strong acid sites active for cracking reactions on fresh Y were not completely restored on regenerated Y. As alkylation and cracking reactions demand similar acid strength, it appears that some of the strong acid sites active for alkylation are not reconditioned as well. Instead, these sites become active for DMH production, a reaction that demands a lower acid strength. As this function becomes deactivated with additional exposure to butene, these sites become active for oligomerization activities. Recalcined Y zeolite was not able to sustain DMH production to the same extent observed on recalcined EMT, during the deactivation phase. Rather, retreated Y promoted higher oligomerization activity during this period.

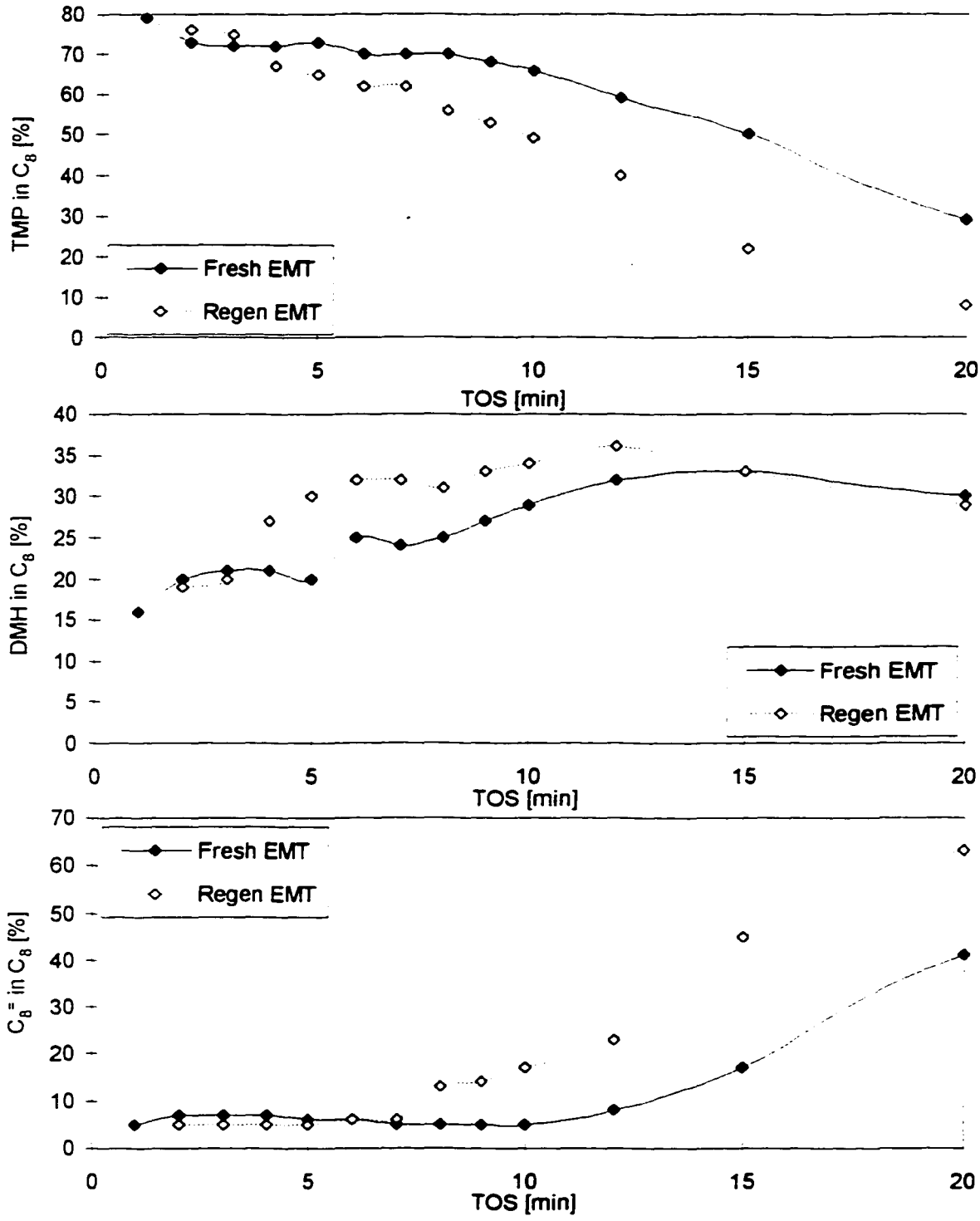



**Figure 7.17:** Effect of Regeneration on $C_8$ Selectivity of EMT
($T_{calc}$=425°C; $T_{rxn}$=53°C; P=382psig; I/O=15; $C_4^=$WHSV=2.0$h^{-1}$; $m_{cat}$=2.78g)

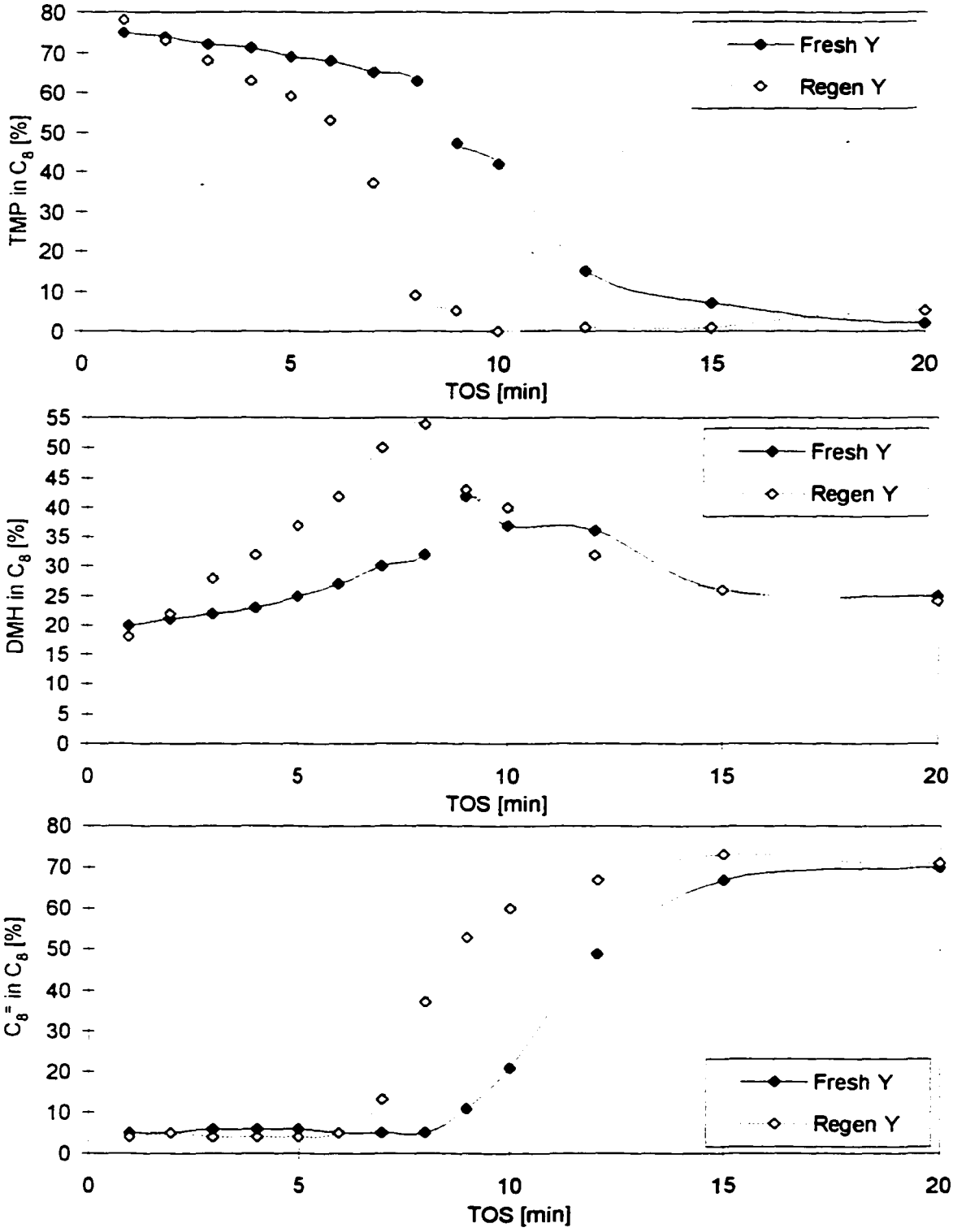



**Figure 7.18:** Effect of Regeneration on $C_8$ Selectivity of Y
($T_{calc}$=425°C; $T_{rxn}$=53°C; P=382psig; I/O=15; $C_4^=$WHSV=2.0$h^{-1}$; $m_{cat}$=2.78g)

Plateaus regions in the product distributions established on fresh catalysts, were not observed on the regenerated materials when no noble metal was present (see Figures 7.17 and 7.18). The ability to sustain stable catalyst performance appears to be hampered after the regeneration treatment. This suggests that the distribution of acid strength had been altered from the original state in fresh materials.

Catalyst activity was completely restored on regenerated Pt/EMT systems, regardless of the Pt loading. Comparable levels of TMP, DMH and $C_8^=$ were observed on fresh and regenerated 0.1%Pt/EMT (see Figure 7.19) during the Useful Catalyst Lifetime period. Similarly, regenerated 0.5%Pt/EMT produced identical $C_8$ selectivity levels observed on fresh material (see Figure 7.20).

Although catalyst activity was restored during the Useful Catalyst Lifetime period on regenerated 0.1%Pt/EMT systems, hydride transfer ability was suppressed during the Deactivation period. This resulted in higher $C_8^=$ levels during this phase. This behaviour was not observed on regenerated 0.5%Pt/EMT, suggesting that the reactive hydrogen population was reduced on regenerated 0.1%Pt/EMT.

Regenerated 0.5%Pt/Y did not recover alkylation capacity, with TMP levels declining from the onset of the reaction in favour of increased DMH formation (see Figure 7.21). This imitates the behaviour of regenerated Y zeolite in the absence of the noble metal, suggesting that TMP activity is attributable to Y zeolite with no contribution made by Pt. The benefits of Pt are absent on Y zeolite in the regenerated state, similar to the behviour observed in the fresh state.

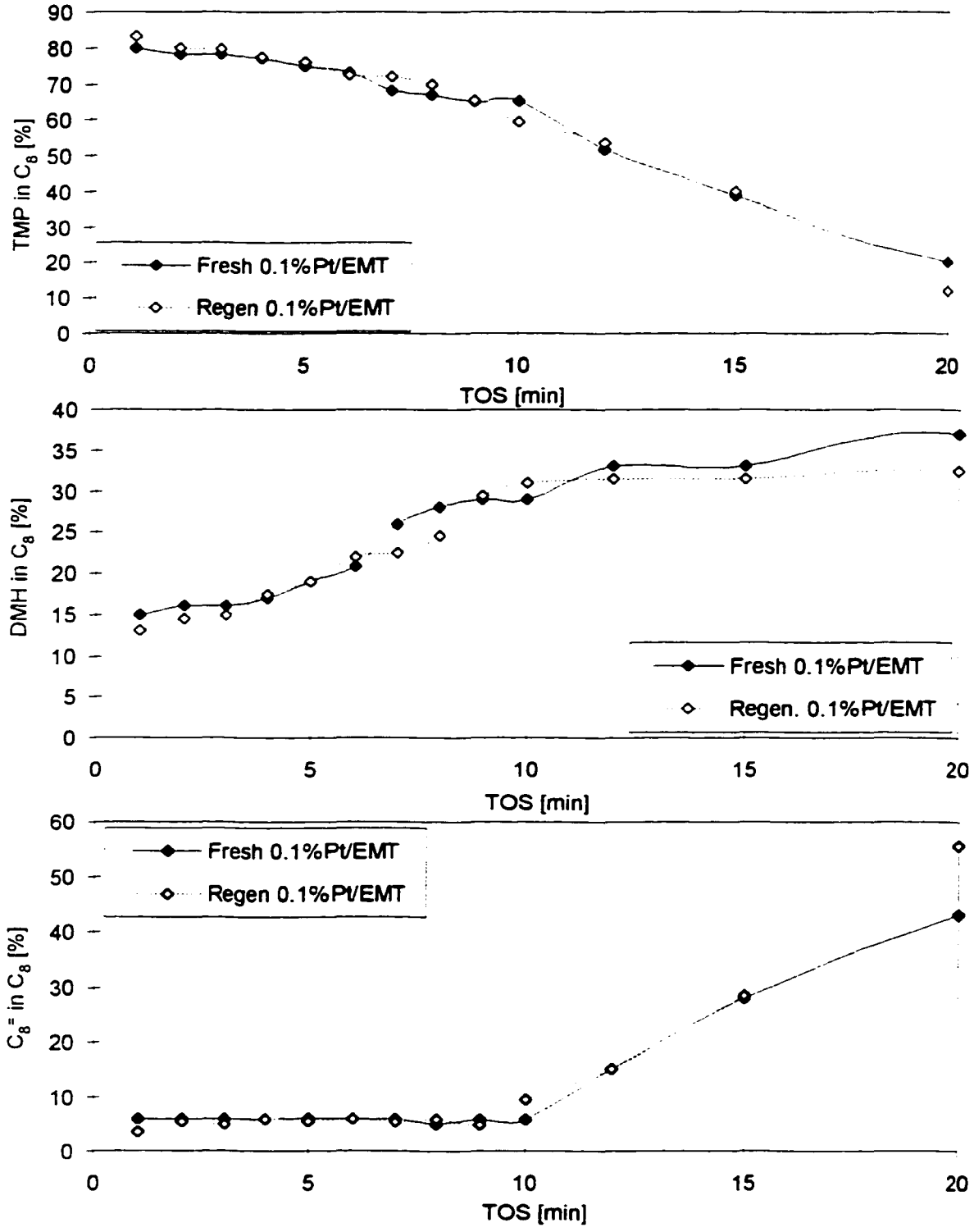



**Figure 7.19:** Effect of 0.1%Pt Loading on Regeneration of EMT with respect to $C_8$ Selectivity ($T_{calc}$=325°C; $T_{red}$=425°C; $T_{rxn}$=53°C; P=382psig; I/O=15; $C_4^=$WHSV=2.0$h^{-1}$; $m_{cat}$=2.78g; 12 sccm $H_2$/Ar/$N_2$ mix with 1.4 wt%$H_2$ used for Pt runs)

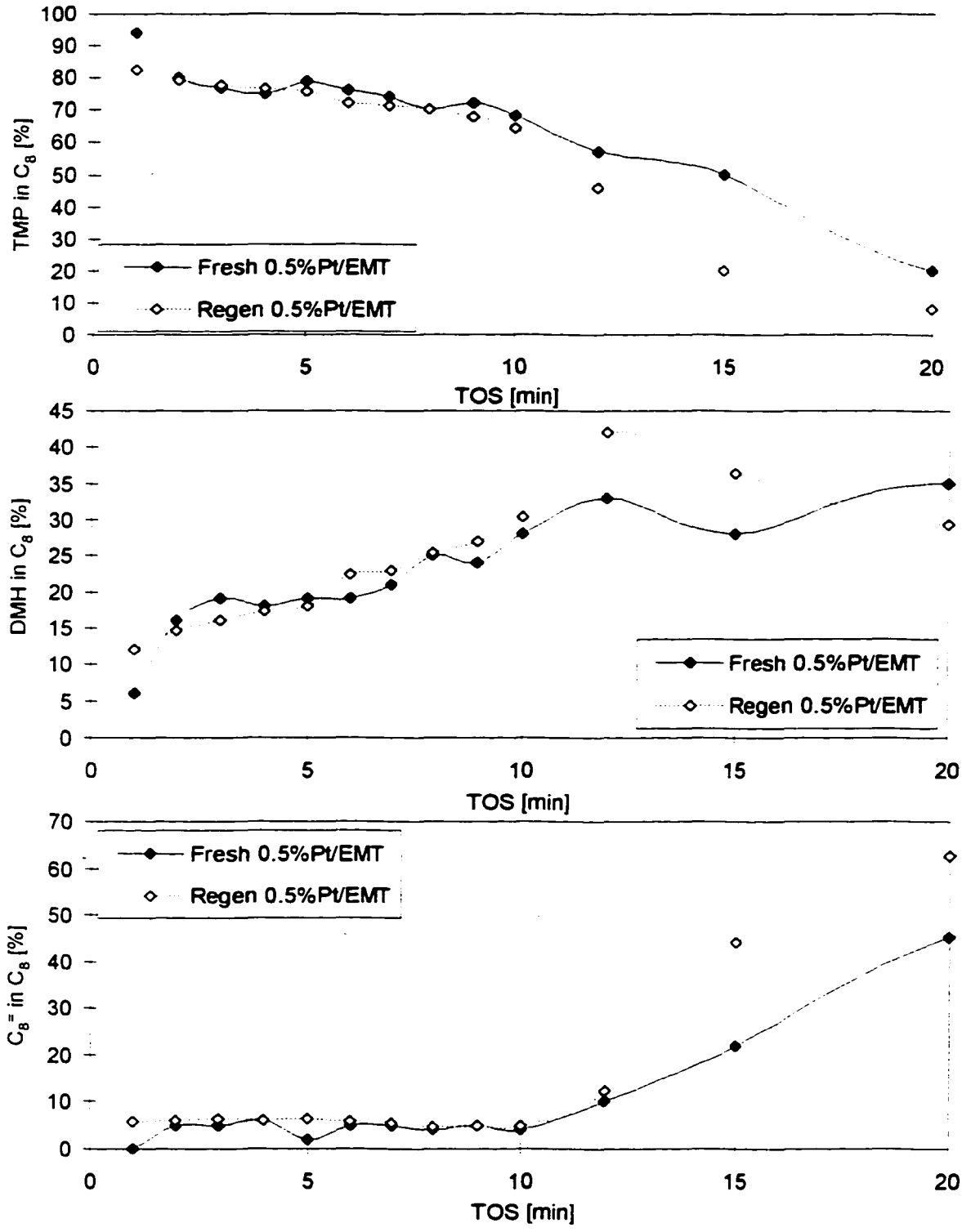



**Figure 7.20:** Effect of 0.5%Pt Loading on Regeneration of EMT with respect to $C_8$ Selectivity ($T_{calc}$=325°C; $T_{red}$=425°C; $T_{rxn}$=53°C; P=382psig; I/O=15; $C_4^=$WHSV=2.0$h^{-1}$; $m_{cat}$=2.78g; 12 sccm $H_2$/Ar/$N_2$ mix with 1.4 wt%$H_2$ used for Pt runs)

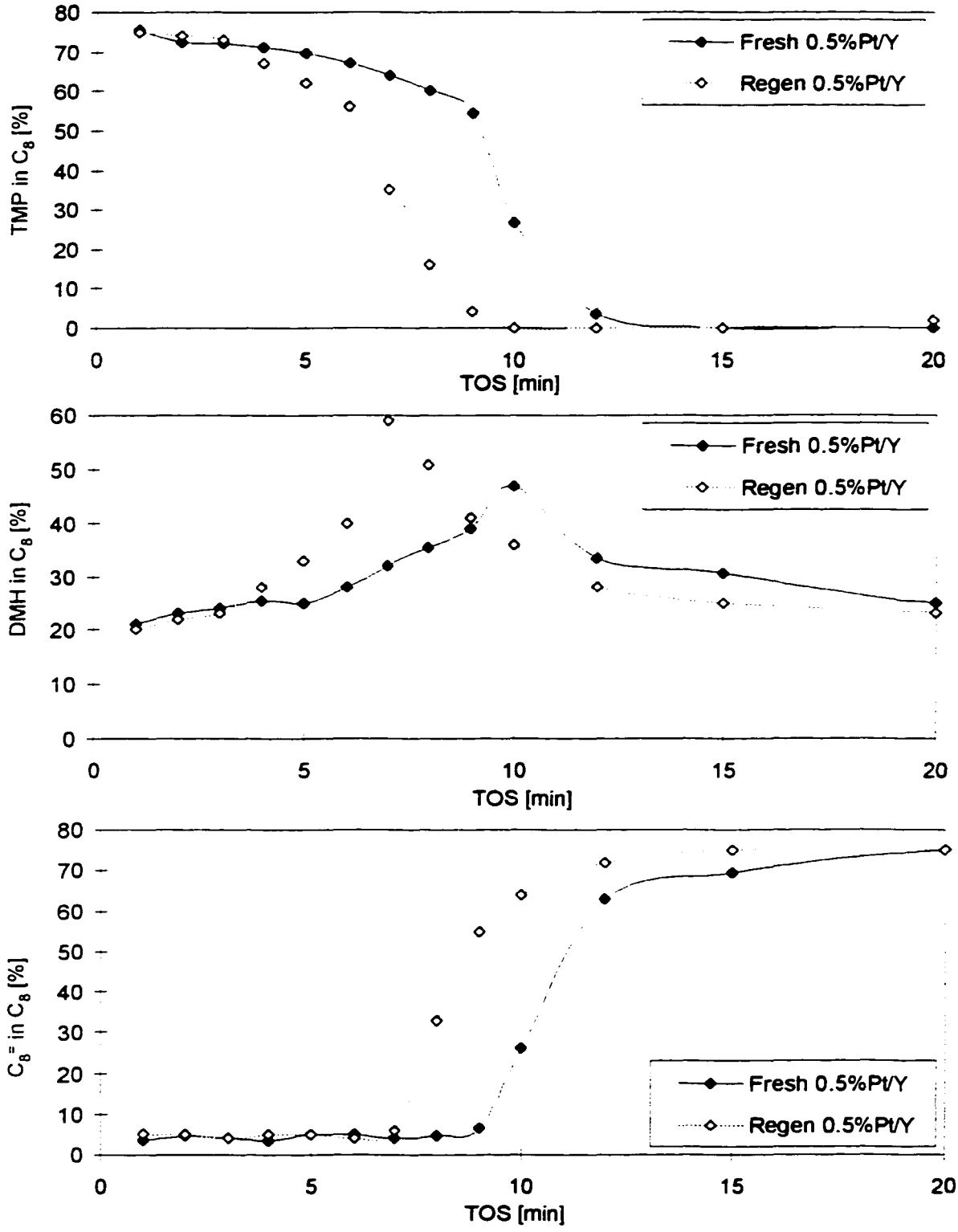



**Figure 7.21:** Effect of 0.5%Pt Loading on Regeneration of Y with respect to $C_8$ Selectivity ($T_{calc}$=325°C; $T_{red}$=425°C; $T_{rxn}$=53°C; P=382psig; I/O=15; $C_4^=$WHSV=2.0$h^{-1}$; $m_{cat}$=2.78g; 12 sccm $H_2$/Ar/$N_2$ mix with 1.4 wt%$H_2$ used for Pt runs)

### 7.2.5 Effect of Pt on TMP Selectivity for Regenerated Catalysts

The least sterically hindered isomers, 2,3,3-TMP and 2,3,4-TMP were favoured on recalcined EMT and Y zeolites, in comparison to fresh catalyst performance (see Table 7.5). These effects were not observed in the presence of Pt. Comparable TMP distributions were observed on regenerated and fresh Pt/EMT and Pt/Y systems. The benefits of Pt in improving the efficacy of regeneration hold true, in that the TMP selectivity is recovered more efficiently on regenerated catalysts that incorporate Pt into their design.

### 7.2.5 Synopsis of Pt Effects for Regenerated Catalysts

Regeneration of EMT and Y zeolites was incomplete in the absence of a noble metal. The Useful Catalyst Lifetime and yield were both reduced on recalcined EMT and Y (see Table 7.5). Some of the strong acid sites responsible for cracking activity and TMP formation in the fresh materials, were not reactivated by the reconditioning treatment. Instead, the regenerated zeolites favoured less demanding reactions, such as DMH production and polymerization activity. The distribution of TMP isomers was altered on recalcined materials relative to fresh material performance, favouring the less sterically hindered isomers, 2,3,4-TMP and 2,3,3-TMP.

Although the hydride transfer was not significantly different on regenerated materials (see (TMP + DMH)/($C_8^=$ + $C_9$+) ratio in Table 7.3), TGA/DTA data suggest that a greater proportion of hydride transfer was being provided by adsorbed species retained on the catalyst surface (see Table 7.6). High molecular weight, polymeric species, demanding high temperatures to desorb ($T_d$>300°C in TGA analysis) were detected. These are formed when extensive hydride transfer is provided by hydrocarbons trapped inside the catalyst pores.

**Table 7.5:** Comparison of Average Catalyst Activity during First 5 min of Useful Catalyst Lifetime Period for Regenerated Parent and Supported Catalysts ($T_{calc}$=325°C; $T_{red}$=425°C; $T_{rxn}$=53°C; P=382psig; I/O=15; $C_4^=$WHSV=2.0$h^{-1}$; $m_{cat}$=2.78g; 12 sccm $H_2$/Ar/$N_2$ mix with 1.4 wt%$H_2$ used for Pt runs)

| Run | F66EMT F68EMT F67EMTr | | F62Pt1EMT F45Pt1EMTr F63Pt1EMTr | | F49Pt5EMT F48Pt5EMTr F60Pt5EMTr | | | F54Y F55Yr | | F44Pt5Y F56Pt5Y F58Pt5Yr | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Catalyst System | EMT | | 0.1% Pt/EMT | | 0.5% Pt/EMT | | Sensitivity | Y | | 0.5 % Pt/Y | |
| | Frsh. | Reg. | Frsh. | Reg. | Frsh. | Reg. | | Frsh. | Reg. | Frsh. | Reg. |
| Pt Dispersion [%] | n.a. | | 74 | | 76 | | | n.a. | | 91 | |
| Useful Catalyst Lifetime Period ($C_4^=$ Conv > 80%) [min] | 10.6 | 6.8 | 9.5 | 10.1 | 11.8 | 10.3 | ± 0.7 | 7.9 | 5.5 | 8.0 | 6.2 |
| Yield [$gC_5^+$/gcat/$gC_4^=$fed] | .083 | .062 | .078 | .079 | .095 | .092 | ± 0.016 | .068 | .050 | .063 | .051 |
| *$C_5^+$ Dist. [mass %]* | | | | | | | | | | | |
| $C_5$-$C_7$ | 25 | 21 | 24 | 25 | 28 | 24 | ± 2.3 | 31 | 28 | 28 | 26 |
| $C_8$ | 58 | 61 | 62 | 62 | 61 | 57 | ± 2.5 | 55 | 52 | 57 | 49 |
| $C_9^+$ | 17 | 18 | 14 | 13 | 11 | 19 | ± 3.7 | 14 | 20 | 15 | 25 |
| *$C_8$ Dist. [mass %]* | | | | | | | | | | | |
| TMP | 75 | 71 | 77 | 77 | 81 | 75 | ± 3.3 | 72 | 68 | 71 | 70 |
| DMH | 19 | 24 | 17 | 18 | 15 | 19 | ± 2.7 | 22 | 28 | 25 | 25 |
| $C_8^=$ | 6 | 5 | 6 | 5 | 4 | 6 | ± 0.8 | 6 | 4 | 4 | 5 |
| *TMP Dist. [%]* | | | | | | | | | | | |
| 2,2,4-TMP | 38 | 31 | 36 | 38 | 33 | 41 | ± 2.5 | 41 | 37 | 35 | 38 |
| 2,2,3-TMP | 18 | 10 | 17 | 17 | 14 | 16 | ± 2.1 | 7 | 5 | 4 | 5 |
| 2,3,4-TMP | 17 | 27 | 18 | 18 | 20 | 16 | ± 2.1 | 21 | 25 | 28 | 25 |
| 2,3,3-TMP | 27 | 32 | 28 | 27 | 33 | 27 | ± 2.4 | 31 | 33 | 33 | 32 |
| *Indicators [mass fract.]* | | | | | | | | | | | |
| $\frac{\text{TMP}}{\text{DMH}}$ | 4.2 | 3.08 | 4.7 | 4.5 | 6.6 | 4.1 | ± 0.57 | 3.3 | 2.7 | 2.9 | 2.9 |
| $\frac{\text{TMP + DMH}}{C_8^= + C_9+}$ | 2.78 | 2.68 | 3.47 | 4.74 | 3.73 | 2.87 | ± 0.63 | 3.03 | 2.43 | 3.35 | 2.29 |
| $\frac{\text{2,2,4-TMP + 2,2,3-TMP}}{\text{2,3,3-TMP + 2,3,4-TMP}}$ | 1.28 | 0.70 | 1.17 | 1.34 | 0.90 | 1.32 | ± 0.20 | 0.91 | 0.73 | 0.63 | 0.75 |

### 7.2.5 Effect of Pt on TMP Selectivity for Regenerated Catalysts

The least sterically hindered isomers, 2,3,3-TMP and 2,3,4-TMP were favoured on recalcined EMT and Y zeolites, in comparison to fresh catalyst performance (see Table 7.5). These effects were not observed in the presence of Pt. Comparable TMP distributions were observed on regenerated and fresh Pt/EMT and Pt/Y systems. The benefits of Pt in improving the efficacy of regeneration hold true, in that the TMP selectivity is recovered more efficiently on regenerated catalysts that incorporate Pt into their design.

### 7.2.5 Synopsis of Pt Effects for Regenerated Catalysts

Regeneration of EMT and Y zeolites was incomplete in the absence of a noble metal. The Useful Catalyst Lifetime and yield were both reduced on recalcined EMT and Y (see Table 7.5). Some of the strong acid sites responsible for cracking activity and TMP formation in the fresh materials, were not reactivated by the reconditioning treatment. Instead, the regenerated zeolites favoured less demanding reactions, such as DMH production and polymerization activity. The distribution of TMP isomers was altered on recalcined materials relative to fresh material performance, favouring the less sterically hindered isomers, 2,3,4-TMP and 2,3,3-TMP.

Although the hydride transfer was not significantly different on regenerated materials (see (TMP + DMH)/($C_8^=$ + $C_9$+) ratio in Table 7.3), TGA/DTA data suggest that a greater proportion of hydride transfer was being provided by adsorbed species retained on the catalyst surface (see Table 7.6). High molecular weight, polymeric species, demanding high temperatures to desorb ($T_d$>300°C in TGA analysis) were detected. These are formed when extensive hydride transfer is provided by hydrocarbons trapped inside the catalyst pores. The quantity of high molecular weight ($T_d$>300°C) material was augmented on the regenerated parent materials (see Table 7.6). These species act as coke precursors and are expected to abbreviate the

Useful Catalyst Lifetime and reduce the active surface area, in agreement with the experimental results for regenerated EMT and Y.

Pt, incorporated into the pore network of EMT, notably improved the efficacy of regeneration, independent of Pt loading. Similar Useful Catalyst Periods and yields were observed for all recalcined Pt/EMT systems, relative to their fresh performance levels (see Table 7.5). It is believed that the noble metal activates reactive oxygen, thus improving the removal of byproduct coke.

**Table 7.6:** Effect of Pt on TGA/DTA Measurements of Regenerated Catalysts ($T_{calc}$=325°C; $T_{red}$=425°C; $T_{rxn}$=53°C; P=382psig; I/O=15; $C_4^=$WHSV=2.0$h^{-1}$; $m_{cat}$=2.78g; 12 sccm $H_2$/Ar/$N_2$ mix with 1.4 wt%$H_2$ used for Pt runs)

| Catalyst System | Catalyst State for Expt | SA of Spent Catalyst [$m^2/g$] | TGA of Spent Catalyst [mass%] Desorption Temperature [°C] <200 | 200-300 | >300 | Total |
|---|---|---|---|---|---|---|
| EMT | Fresh | 377 | 3.5 | 2.5 | 3.0 | 9.0 |
| | Regen | 287 | 1.5 | 1.0 | 5.0 | 7.5 |
| 0.1%Pt/EMT | Fresh | 263 | 3.3 | 2.2 | 3.5 | 9.0 |
| | Regen | 243 | 3.6 | 2.9 | 3.3 | 9.8 |
| Y | Fresh | 372 | 2.0 | 2.5 | 2.5 | 7.0 |
| | Regen | n.a. | 1.0 | 0.4 | 5.5 | 6.9 |
| 0.5%Pt/Y | Fresh | 270 | 1.5 | 2.5 | 3.2 | 7.2 |
| | Regen | 280 | 1.9 | 2.3 | 3.0 | 7.2 |

The catalyst system employing a Pt loading of 0.1 % on EMT, displayed comparable results to fresh material performance. No significant differences were found in alkylate quantity or quality. TGA/DTA analysis of the spent recalcined catalyst, suggests that hydride transfer from adsorbed species in the pore network was not faciltated extensively (see Table 7.6). Similar spent surface areas were measured for fresh and regenerated 0.1%Pt/EMT, whereas a notable loss was observed between fresh and regenerated EMT.

The positive benefits of Pt on EMT were maintained at a higher Pt loading. Increasing the Pt loading to 0.5 % on EMT achieved similar results to those observed for regenerated 0.1%Pt/EMT, with respect to lifetime and yield.

The benefits of Pt, on the efficacy of EMT regeneration, were not apparent on recalcined 0.5%Pt/Y. The Useful Catalyst Lifetime period and yield were reduced on recalcined 0.5%Pt/Y relative to fresh performance levels (see Table 7.4). Polymerization levels are notably higher and $C_8$ production reduced on regenerated 0.5%Pt/Y. TGA/DTA measurements suggest that the diminished activity of the catalyst, was not a consequence of increased hydride transfer from adsorbed species, retained in the catalyst pores (see Table 7.6). Spent surface area provide additional support for this hypothesis, in that no significant difference was found between fresh versus regenerated surface area measurements for 0.5%Pt/Y experiments.

It was previously suggested that 0.5%Pt/Y may promote excessive reactive hydrogen involvement in the fresh state. Perhaps this same behaviour occurs with respect to reactive oxygen promotion. It is possible that 0.5%Pt/Y becomes sintered during regeneration, reducing Pt dispersion to low levels. This hypothesis is consistent with the behaviour of regenerated 0.5%Pt/Y, in that this catalyst appears to behave like Y zeolite in all respects. This re-emphasizes the sensitivity of the catalyst performance to Pt effects and the fine balance that must be achieved to produce beneficial results.

# Chapter 8

# Conclusions

Four distinct stages of catalyst activity and selectivity were observed for the alkylation of butene with isobutane in a flow reactor. The "Initial Activity" period was a brief phase of high catalyst activity of less than 1 min in duration. The "Useful Catalyst Lifetime" period represented the second stage of catalyst activity, and was characterized by butene conversion in excess of 80 %. Approximately half of the alkylate consisted of $C_8$ products, with TMPs accounting for approximately 60 to 80 % of the $C_8$ fraction. The isomer 2,2,4-TMP was the dominant product in the TMP

fraction. As butene conversion levels declined below 80%, the commencement of the "Rapid Deactivation" phase was marked. The loss in hydride transfer function favoured oligomerization and polymerization reactions. Cracking activity was completely lost during this phase. The final stage of catalyst activity was the "Oligomerization" phase, characterized by butene conversion levels below 40 %. The $C_5$+ liquid consisted of mainly $C_8^=$ and $C_9$+ products.

The effect of calcination temperature is consistent with the hypothesis that the alkylation mechanism is promoted by a Bronsted acid site. A calcination temperature of 425°C, which favours a higher density of Bronsted acid sites on both Y and EMT zeolites, effectively facilitated hydride transfer resulting in more saturated branched $C_8$ molecules being formed. Alkylation activity was sustained for a longer duration and the onset of deactivation was delayed, when a calcination temperature of 425°C was employed on both EMT and Y zeolites.

In contrast, a calcination temperature of 540°C, which increases Lewis acidity at the expense of reduced Bronsted acidity, had a detrimental effect on hydride transfer and favoured oligomerization and polymerization reactions over production of saturated compounds. High molecular weight species were retained on the acid sites, leading to rapid loss in catalyst surface area, accelerating the onset of deactivation. As a result, a shorter Useful Catalyst Lifetime was observed for catalysts calcined at 540°C.

Low reaction temperatures in the vicinity of 30°C, resulted in low butene conversion and favoured predominantly polymerization products. Reaction temperatures approaching 100°C promoted cracking activity, jeopardizing the stability of alkylate precursors. The optimal reaction temperature represents a compromise between cracking polymerization products without degrading alkylate quality.

No alkylate was produced when using pure isobutane as the feed, suggesting that the presence of small amounts of olefin are necessary to initiate the mechanism. A low olefin WHSV favoured alkyation reactions, and discouraged oligomerization and polymerization activities. The estimated number of successful catalyst cycles per active site was improved when the feed was less concentrated in the olefin.

Unfortunately, the preferential adsorption of the olefin over the isoparaffin made deactivation an inevitable outcome, regardless of the feed composition.

A definite trend in surface area loss with increasing Butene Exposure Index was observed. It appears that the catalyst acts as a sponge adsorbing butene from the feed, saturating the surface with oligomers. The isoparaffin acts as a diluent, rather than as a competitive reactant. Hence feed, which is more dilute in the olefin, simply takes longer to saturate all of the acid sites with oligomers of butene. This emphasizes the poor suitability of the fixed bed reactor for this reaction.

This hypothesis is consistent with the modest improvement in the number of successful catalyst cycles which was calculated for a significant decrease in the butene WHSV. Further evidence was provided by a cyclical feed study. Restoration in catalyst activity for a deactivating catalyst was remarkable after an isobutane flush period. In addition, the loss in active surface area of the catalyst was suppressed with cyclical feed operation relative to uninterrupted delivery.

The cleansing benefits of washing the catalyst with isobutane could be explored in catalytic distillation, which combines reaction and distillation in one process. Situating the reaction section near the top of the column and operating under total reflux, will increase the local I/O ratio. The distillation process will naturally remove the product from the reaction section, discouraging continued reaction of the product. This mode of reactor geometry may offer some promise for this challenging reaction, if a suitable solid acid catalyst is found.

The composition of the alkylate produced from EMT and Y zeolite was similar. However, EMT revealed superior resistance to deactivation relative to Y zeolite, in terms of extending the Useful Catalyst Lifetime by 41 % and increasing the yield by 16%. This behavior may be a consequence of the unique distribution of acid sites on EMT, which discourages deactivation processes. Alternatively, EMT may possess improved ability to adsorb isobutane relative to Y. An increase in the local I/O ratio is expected to improve catalyst lifetime as demonstrated by olefin WHSV studies.

TGA/DTA analysis revealed that the distribution of material retained on the spent EMT, was more heavily weighted toward low desorption temperatures relative to that measured on spent Y. It is speculated that the greater preference for olefin adsorption demonstrated by Y zeolite enhanced polymerization reactions, blocking access to acid sites deeper in the catalyst granule. In contrast, the uneven arrangement of acid sites in EMT may suppress the extent of this process.

A loading of 0.1 % Pt/EMT did not produce a significant effect on the Useful Catalyst Lifetime period or alkylate quality of the fresh catalyst, in the presence of hydrogen. A marginal improvement in the fraction of $C_8$ produced in $C_5$+ liquid was observed. It may be that a loading of 0.1 % Pt on EMT, was inadequate to generate a sufficient population of reactive hydrogen to produced a notable effect.

An improvement in fresh catalyst performance was achieved using a higher loading of Pt on EMT. Impregnation of 0.5 % Pt/EMT modestly extended the Useful Catalyst Lifetime period in a hydrogen containing environment, over fresh EMT. Although the product yield was not significantly altered by the presence of Pt, alkylate quality was notably enhanced. Polymerization activity and DMH production were suppressed and TMP formation promoted on 0.5 % Pt/EMT relative to EMT.

A similar loading of Pt on Y zeolite did not produce positive benefits in a hydrogen atmosphere. No significant change in the Useful Catalyst Lifetime period was detected. Although alkylate quality was not notably altered by Pt presence, a slight increase in DMH levels was observed.

The enhanced catalyst performance on Pt catalyst systems in the presence of hydrogen, does not appear to be a result of butene hydrogenation. Elevated *n*-butane levels were not detected in the effluent and catalyst yield was not compromised by Pt incorporation.

It was proposed that reactive hydrogen, such as hydrogen spillover, was responsible for the positive benefits in catalyst performance. A minimum amount of Pt was necessary, to generate an adequate population of reactive hydrogen species to effect a measurable change. A Pt loading of 0.1 % on EMT in the presence of hydrogen, was insufficient to meet the activity demands of alkylation. In contrast,

increasing the loading to 0.5 % Pt on EMT in the presence of hydrogen, developed an adequate population of reactive hydrogen species, improving the ability of the catalyst to desorb TMP product.

It is suggested that Y zeolite was more effective at transporting reactive hydrogen species than EMT. Hence, the population of reactive hydrogen species was overdeveloped for 0.5 % PT/Y. Excessive involvement of reactive hydrogen occurred, compromising the stability of the *tert*-$C_4^+$ cation population. This favoured DMH formation and accelerated deactivation. A balance between active participation of isobutane and reactive hydrogen is essential to improve alkylate quality and extend the Useful Catalyst Lifetime.

The benefits of Pt are reiterated in regenerated catalyst performance. Both EMT and Y revealed a notable loss in catalyst activity with respect to yield and alkylate quality after regeneration. Impregnation of Pt onto the catalyst surface of EMT, resulted in almost complete restoration of catalyst activity and recovery of the Useful Catalyst Lifetime period. The presence of Pt on Y zeolite, did not produce the same benefits as were observed on EMT. The yield and Useful Catalyst Lifetime period were reduced on regenerated 0.5%Pt/Y relative to those observed in the fresh state, but resembled those achieved on regenerated Y. This behaviour was attributed to excessive involvement of reactive oxygen during regeneration, which may sinter the catalyst and reduce Pt dispersion significantly.

It is concluded that Pt can serve a dual purpose in catalyst design. Firstly, regulated participation of hydrogen spillover can improve catalyst lifetime and alkylate quality. Secondly, incorporation of Pt into the catalyst system will promote oxygen spillover during the recalcination step, improving the efficacy of the regeneration treatment. The challenge for the catalyst design, is to promote reactive hydrogen involvement to improve desorption of TMP, but not encourage excessive involvement as this favours DMH formation.

# Chapter 9

# Recommendations

EMT reveals interesting behavior in terms of its ability to promote hydride transfer and suppress deactivation. An adsorption study employing FTIR measurements could compare the adsorption abilities of *i*-$C_4$ relative to $C_4^=$ on EMT and Y zeolites. These measurements would be useful in explaining catalytic behaviour towards alkylation.

Acidity estimates are largely dependent upon the method of measurement and constants (i.e. extinction coefficients of adsorbate when using TPD/FTIR technique) applied in the calculations. Comparison of acidity estimations is most reliable when the same method is applied for all materials and identical operating conditions employed for the analysis. The literature acidity measurements for EMT and Y, do not utilize the same extinction coefficients for TPD/FTIR pyridine desorption correlations. Results were re-calculated using a single set of extinction coefficients. However, this introduces a degree of uncertainty when attempting to qualify catalytic behavior in terms of differences in acidities.

A significant contribution to this study would be acidity measurements using FTIR/TPD with pyridine as the adsorbate. This will provide important information regarding the nature and strength of acid sites on EMT relative to Y zeolite. The effect of calcination temperature on Lewis and Bronsted acidity, could also be acertained using TPD/FTIR pyridine desorption measurements. This is particularly important to rationalize the catalytic differences observed with respect to product selectivity, alkylate yield and duration of Useful Catalyst Lifetime.

The hydride transfer ability of EMT and Y zeolite could be compared through characterization of the carbonaceous deposits on the spent catalysts. UV-VIS spectra of spent catalysts would provide information of the chain length of adorbed species, offering insight into the mechanism responsible for deactivation. The carbon bonding environment of adsorbed species could be investigated through $^{13}C$ CP/MAS NMR measurements to assess the degree of unsaturation of the adsorbed species. The effect of I/O ratio on the quality and quantity of the deposit could also be examined in this study, as this process variable is known to exert a positive influence on suppressing the rate of deactivation.

The positive benefits of Pt in terms of promoting hydrogen spillover, needs to be substantiated through replicated experiments. Catalyst preparation for this study should employ the exchange method for Pt incorporation, as this technique yields a more uniform distribution of Pt, relative to that achieved with the incipient wetness approach.

Performance of the exchanged materials could be assessed to confirm the distinctive differences noted with Pt incorporation into the catalyst design. The effect of hydrogen flow rate during the reduction step, as well as during the reaction, could be explored. Variation in air flow rate during recalcination could also be studied, to determine whether a preferred rate exists in terms of restoring catalyst activity on regenerated catalysts.

The equipment employed for hydrogen chemisorption measurements, reveals high variability in Pt dispersion estimations for the Pt standard sample. Undoubtedly, uncertainty in Pt dispersion measurements for prepared catalyst systems could significantly affect interpretation of results. Reliable estimates are necessary to accurately characterize the catalysts systems so that these properties can be related to catalyst activity with confidence.

Evidence of hydrogen spillover could be assessed using an approach outlined by Ohgoshi et al, 1993. Zeolite A is prepared in the presence of a cationic platinum complex (Weisz et al, 1962), trapping the platinum within the cavities during the formation of the crystalline material (Pt-A). Butene and isobutane are too large to fit through the 5 Å port dimensions of A zeolite, shielding the Pt atoms from these reactants.

The Pt-A could be physically mixed with EMT to form a hybrid catalyst. The performance of the hybrid catalyst could be compared to EMT, where no spillover activator is provided. If the results of the two experiments are similar, this suggests that hydrogen spillover is not contributing an important effect to the reaction. Note that this criteria assumes that the distance of separation between the activator (Pt in A zeolite) and the acceptor (acid sites of EMT) phases is within the mobility range of spillover hydrogen. Evidence of hydrogen spillover participation is indicated by detectable differences in catalyst performance of the hybrid catalyst with EMT.

The method of bulk liquid collection could be improved, to enhance the accuracy of yield measurements and mass balance. The separator of the BTRS system could be explored for this application. A chilled fluid could flow through the copper coil surrounding the separator, to condense liquid product for the purpose of

bulk collection. Effluent gases from the separator could be measured and collected for bulk gas analysis.

Catalytic distillation may offer some promise for this reaction. The viability of this recommendation may be questioned, as this equipment is expensive to operate and requires stable catalyst activity.

A fixed bed reactor is poorly suited to butene/isobutane alkylation. It is worthwhile to consider a CSTR for this reaction, as higher local I/O ratios can be achieved using this reactor geometry. The BTRS supports the use of an external reactor permitting connection of a CSTR with minor equipment modifications. Cyclical feed flow could be explored to assess catalyst behaviour toward deactivation in a CSTR reactor environment.

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# Appendix 1:

# Catalyst Preparation and Characterization

## A1.1 EMT SYNTHESIS

EMT is synthesized using the modified method of Feijen et al, 1994b, provided by Prof. Martens and Anne Gossens, Centre of Surface Science and Catalysis, KU Leuven. A description of the reagents employed in the synthesis is outlined in Table A1.1.

**Table A1.1**: Description of Reagents Employed for EMT Synthesis

| Reagent | Chemical Formula | Supplier | Description |
|---|---|---|---|
| 18-crown-6 ether | $C_{12}H_{24}O_6$ | Acros Organics | 99 % purity |
| double de-ionized water | $H_2O$ | U of W | |
| sodium hydroxide pellets | NaOH | BDH | 97.0 % |
| Gibbsite | $Al(OH)_3$ | Fluka | 64-66 % |
| Ludox HS-40 | Colloidal $SiO_2$ | Aldrich | 40 % $SiO_2$ in $H_2O$ |

The Feijen method is written for a 40 mL teflon lined reactor and requires approximately 60 minute time interval to complete the gel preparation. NaOH (2.56 g) is mixed with 6.59 g of water under magnetic stirring. Gibbsite (2.08 g) is added to the mixture and heated to 80°C, with magnetic stirring, until all of the Gibbsite has dissolved (approximately 10 minutes).

Water (10.28 g) was added to 20.00 g Ludox HS-40 under mechanical stirring. The 18-crown-6 ether (3.41 g) was added to this sol and stirring was continued. When all of the Gibbsite was dissolved, the heat was turned off and the solution was allowed to cool. Some of the Al may precipitate while cooling but this does not affect the synthesis. When the aqueous solution of Gibbsite and sodium hydroxide had reached room temperature, the amount of water that had evaporated was determined and added back to the solution. This solution was immediately added to the silica sol followed by 3.52 g water and stirred for 15 minutes using a mechanical stirrer. The molar composition of the final hydrogel is as follows:

10.00 $SiO_2$ : 1.00 $Al_2O_3$ : 2.40 $Na_2O$ : 140.25 $H_2O$ : 0.97 18-crown-6 ether

The resulting gel was transferred into a 40 mL teflon lined reactor, sealed and then aged at room temperature for 3 days. The crystallization period was initiated by heating the hydrogel at 100°C for 9 days. After this time period had elapsed, the product was cooled to room temperature. The crystallized material was recovered by filtration, washed with double deionized water (four times the gel volume) and dried overnight at 80°C. The resulting product was calcined in flowing air at 425°C for 5 h. The average calcined product yield was approximately 10.50 g of Na-EMT per batch. Identification was confirmed using powder X-ray diffraction.

Since our laboratory does not possess a small teflon reactor, teflon bottles were evaluated as alternative vessels for catalyst synthesis. Two sizes are commercially available in the vicinity of 40 mL. The preparation method for a 40 mL reactor was successfully scaled up for use in a 60 mL teflon bottle as well as scaled down to perform the synthesis in a 35 mL teflon bottle (see Table A1.2).

**Table A1.2:** Reagents in EMT Synthesis (masses indicated in grams)

| Reagent | Original Recipe* (40 Ml Telflon Lined Reactor) | Scale up to 60 mL Teflon Bottle | Scale down to 35 mL Teflon Bottle |
|---|---|---|---|
| Crown Ether | 3.41 | 5.12 | 2.99 |
| Water (total) | 20.39 | 30.49 | 17.83 |
| with NaOH | 6.59 | 9.87 | 5.77 |
| with Ludox HS-40 | 10.28 | 15.42 | 9.01 |
| with final sol | 3.52 | 5.20 | 3.05 |
| NaOH Pellets | 2.56 | 3.83 | 2.24 |
| Gibbsite | 2.08 | 3.12 | 1.72 |
| Ludox HS-40 | 20.00 | 29.97 | 17.52 |

* Recipe provided by Prof. Marten's group, Centrum voor Oppervlaktechemie en Katalyse, KU Leuven, Belgium

The 60 mL teflon bottle method was primarily used as it produced the highest yield of product.

## A1.2 PHASE IDENTIFICATION

A Siemens Diffractometer (laboratory of Prof. L. Nazar, Department of Chemistry, University of Waterloo) equipped with a CuK$\alpha$ source was used for powder XRD measurements to identify the phase of the zeolite. A current of 30 mA current and a voltage of 50 kV, were employed for the analysis. A step of 0.05 ° and a dwell time of 0.5 s were used for data collection.

The sample was bombarded with X-ray beams at an angle, $\theta$. A portion of the X-rays were diffracted and measured by a radiation detector. The sample was rotated through a range of angles of $2° < 2\theta < 40°$ to obtain an entire spectrum. If a sample possessed a regular crystal structure, a distinctive pattern was observed.

The spectra can be compared to the literature pattern for EMT (Delprato et al, 1990) to confirm the phase identity of the sample.

## A1.3 AMMONIUM ION EXCHANGE OF Na-EMT

The exchange process employed a 2 M solution of $NH_4NO_3$ with a concentration of 25 $cm^3$ of exchanging solution per gram of Na-EMT. Typically, the Na-EMT was exchange in batch sizes of approximately 15 g. The solid was added to the exchanging solution and heated at 70°C for 3 h. Once the exchange period had expired, the mixture was cooled to room temperature and filtered and washed thoroughly with double de-ionized water. The filter cake was heated at 80°C overnight to remove the loosely bound water. The dried material was calcined at 425°C in flowing air for 5 h. A total of three exchange cycles, followed by calcination, were employed to ensure high Na removal.

The batches of Na-EMT were combined to form two groups, G1 and G2.

G1: batches G5008 - G5013
G2: batches G5014 - G5019

Starting with G1, half of the mass from each batch (M1) were mixed together, forming set, S1 (see Figure A1.1). The first exchange process was applied to this material (G1-E1-S1). The solids were removed from the exchanging solution by filtration, heated overnight at 80°C and calcined in two separate batches (C1 and C2) at 425°C for 5 h in flowing air.

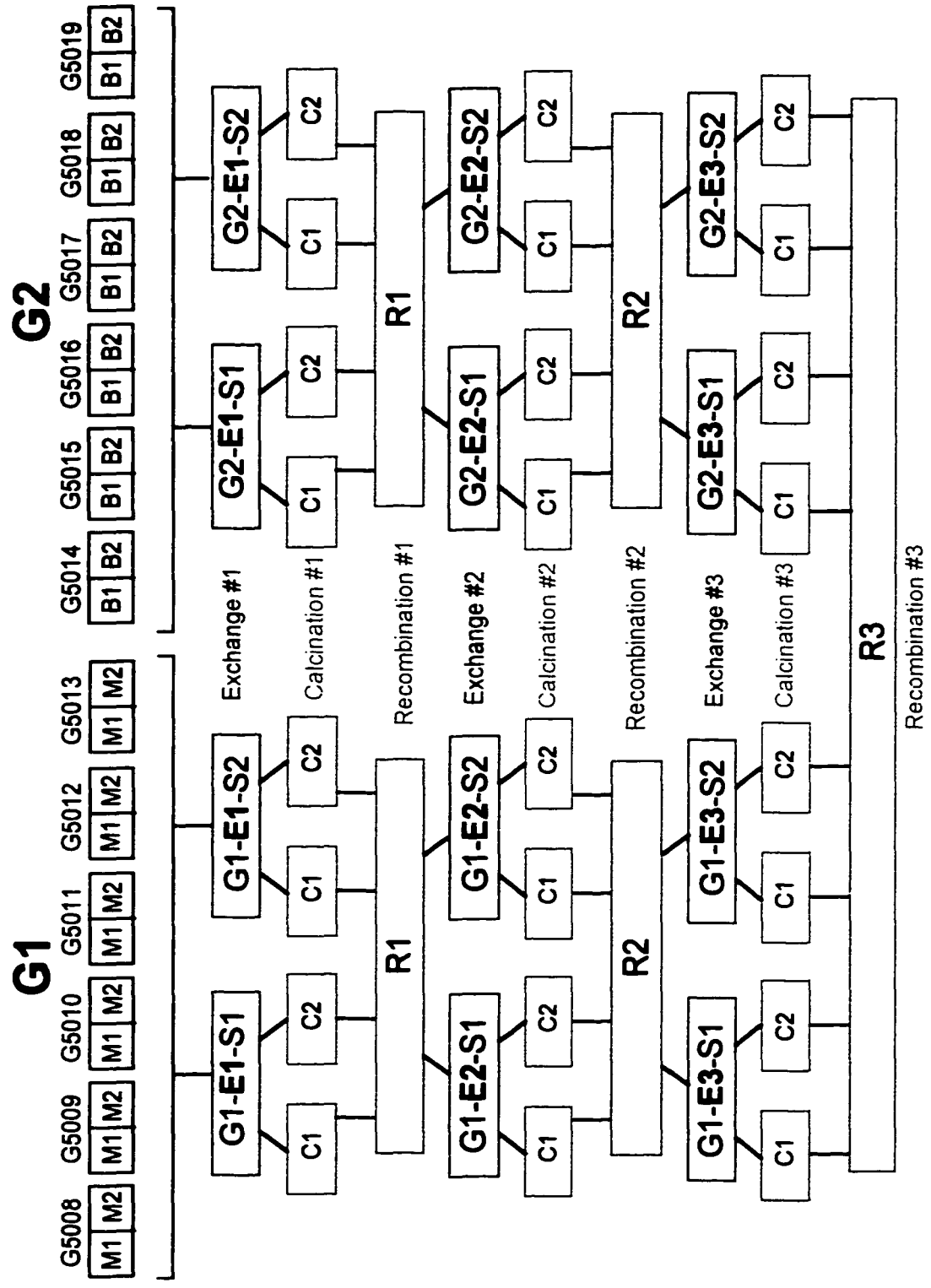



**Figure A1.1:** Methodology for Ammonium Ion Exchange of Na-EMT

The same treatment was applied to the other half of the six batches (M2) of G1. These were combined to form a second set (S2). All of the calcined material from the first exchange step was recombined and thoroughly mixed (R1). The resulting material was equally divided into two amounts, S1 and S2, for the second exchange step.

The same procedure was applied to the second and third exchange step of G1, as was adopted in the first exchange treatment. An identical approach was employed for G2. The final calcined, thrice exchanged product from G1 and G2, were recombined and mixed thoroughly for use in the catalytic study.

## A1.4 Na CONTENT

### A1.4.1 Experimental

Atomic absorption spectroscopy was used to evaluate the Na content as a measure of the ammonium ion exchange efficiency of Na-EMT. It was also used to compare the Na level of the commercial product, Y zeolite. The method of additions was employed for both materials, as this approach accounts for matrix effects in the sample analysis. The "sample mixture" was prepared by digesting 1 g zeolite in 10 mL concentrated HF and then diluting the mixture with double de-ionized water to a total of 100 g. A "standard solution" with a known amount of Na was also made.

The method of additions begins with the preparation of three separate solutions (see Figure A1-2). The Specimen solution consisted of equal volumes of diluent (double de-ionized water) and sample mixture. The A1 solution spiked the sample mixture with the standard solution and then diluted the total with diluent. The A1 solution was comprised of 50 % sample mixture, 25 % standard solution and 25 % diluent by volume. Finally, the A2 solution spiked the sample mixture more

extensively with the standard solution. It consisted of 50 % standard and 50 % sample mixture, by volume.

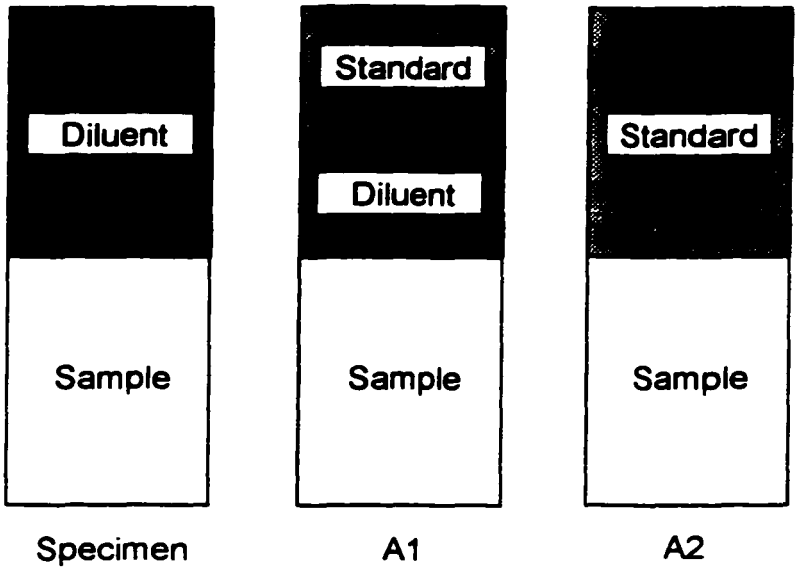



**Figure A1.2:** Solutions for Method of Additions

The sample absorbance was measured on a Perkin Elmer Atomic Absorbance Spectrometer 3100. The EMT sample mixture employed a wavelength of 589.0 nm, a slit width of 0.2 nm, a relative noise of 1.0. The Y sample mixture utilized a wavelength of 330 nm, a slit width of 0.7 nm and a relative noise of 0.63. All sample measurements utilized an ethylene flow rate of 2.0 L/min with air sustained at 9.0 L/min.

The three solutions were analysed and the absorbance plotted on an absorbance versus concentration graph. The "Specimen" absorbance was assigned a concentration of zero. The best-fit line was found through the three points, and the x-intercept determined. The concentration of the digested sample was taken as the negative value of the x-intercept for the best-fit line. The Na concentration was

calculated from the sample mixture Na level and corrected for the extent of dilution in the digestion process.

### A1.4.2 Sample Calculation

1.04886 g EMT dissolved in 127.700 g sample (EMT, HF, $H_2O$)

From the absorbance spectra for the digested mixture of EMT, the x-intercept was calculated to be -2.09 ppm Na (see Figure A1.3)

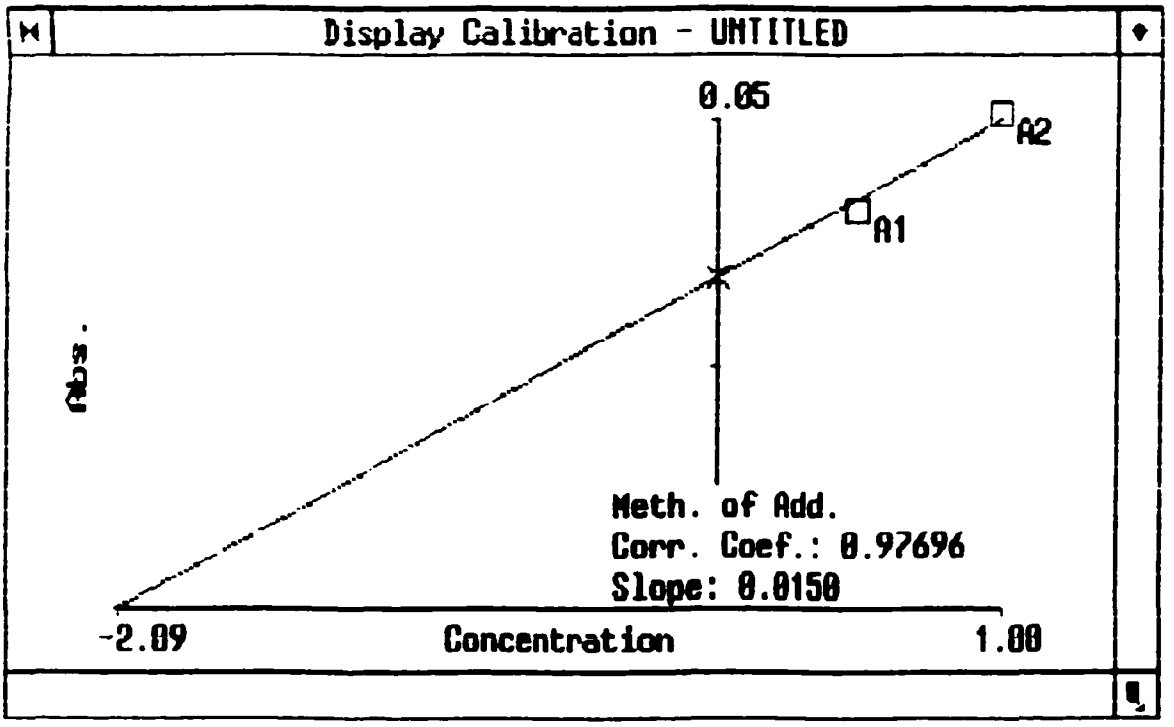



**Figure A1.3:** Absorbance Spectra for Digested EMT

The concentration of Na in the sample is calculated as follows:

$$\frac{2.09 \text{ g Na}}{10^6 \text{ g sample}} \left| \frac{127.700 \text{ g sample}}{1.04886 \text{ g EMT}} \right| \frac{10^6 \text{ g EMT}}{} = 254.5 \text{ ppm Na in EMT}$$

## A1.5 $^{29}$Si AND $^{27}$Al MAS NMR

### A1.5.1 Experimental

$^{29}$Si and $^{27}$Al MAS NMR measurements were performed on a Bruker AMX 500 Spectrometer by Chris Kirby (PhD Candidate) in the laboratory of Prof. W. Powers, Department of Chemistry, University of Waterloo. Si spectra for EMT and Y (see Figures A1.4 and A1.5 respectively) were recorded at 99.36 MHz employing a pulse length of 1.5 μs, a recycle time of 15 s and a spinning rate of 20 kHz. A minimum of 1000 scans were performed for $^{29}$Si MAS NMR data acquisition. The recording of Al spectra for EMT and Y (see Figures Al.6 and A1.7 respectively) were undertaken at 130.32 MHz using a pulse length of 1.5, a recycle time of 15 s and a spinning rate of 125 kHz. A total of 4096 scans were completed for $^{27}$Al MAS NMR data analysis. All details for data acquisition are summarized on a side bar of the spectra.

The framework Si/Al molar ratio is given by the following equation:

$$\text{Si/Al} = \frac{\sum_{n=0}^{4} \text{A Si(nAl)}}{\sum_{n=0}^{4} (n/4) \text{ A Si(nAl)}} \qquad \text{(A1-1)}$$

where A Si(nAl) is the area of the NMR signal attributed to the Si(nAl) units. The area of the intensity peak is found by multiplying the intensity by the peak width at half height.

Quantitative analysis is not readily available from $^{27}Al$ MAS NMR data due to broadening of the spectra by quadrupolar effects. The types of Al environments can be identified from the spectra but the relative amounts cannot be specified. A shift of 55 ppm is indicative of tetrahedral coordination of Al, -1.9 ppm identifies 6 coordinated Al environment and 15 ppm and 29.5 ppm representative of hybrid type of environments.

### A1.5.2 Sample Calculation for Si/Al Ratio

The peak intensity and width from the spectra of EMT are recorded in Table A1.3. The product of these two measures determines the area of the peak. The Si/Al ratio for the sample can be calculated using equation A1-1.

**Table A1.3:** Sample Calculation of Si/Al Ratio for EMT using $^{29}Si$ NMR Data (see Figure A1.3)

| Si(nAl) | n | Position [ppm] | Intensity [abs.] | Width [Hz] | Area | n/4 x Area |
|---|---|---|---|---|---|---|
| Si(0Al) | 0 | -108.0 | 897251 | 314.85 | 282499477.4 | 0 |
| Si(1Al) | 1 | -102.6 | 607851 | 497.14 | 302187046.1 | 75546761.525 |
| Si(2Al) | 2 | -96.9 | 61440 | 347.99 | 21380505.6 | 10690252.8 |
| Si(3Al) | 3 | -92.2 | 14162 | 132.57 | 1877456.34 | 1408092.255 |

$$\text{Si/Al Ratio} = \frac{607944485.44}{87645106.58} = 6.94$$

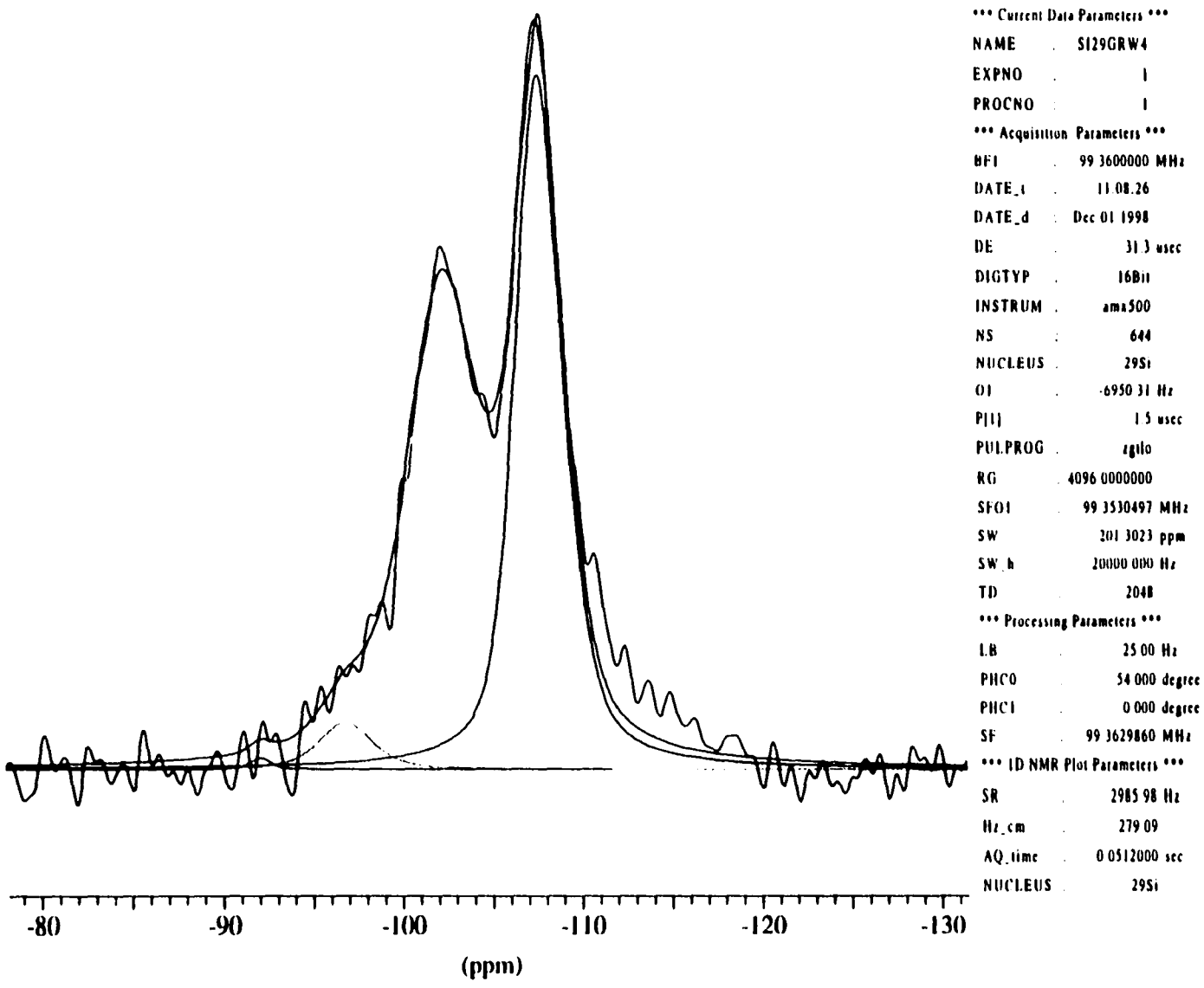



**Figure AI.4: $^{29}$Si MAS NMR for EMT Zeolite**

Y

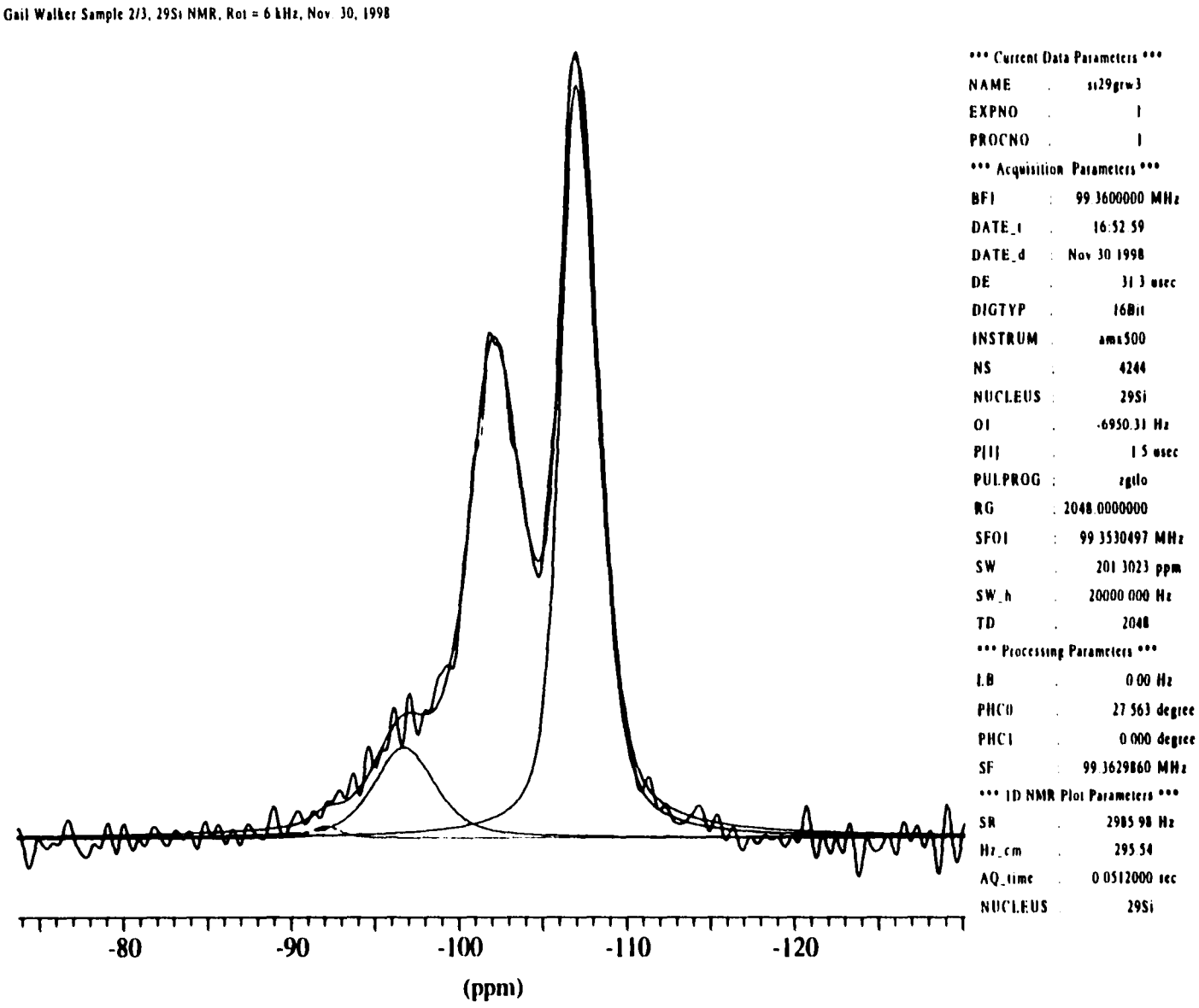



**Figure AI.5: $^{29}$Si MAS NMR for Y Zeolite**

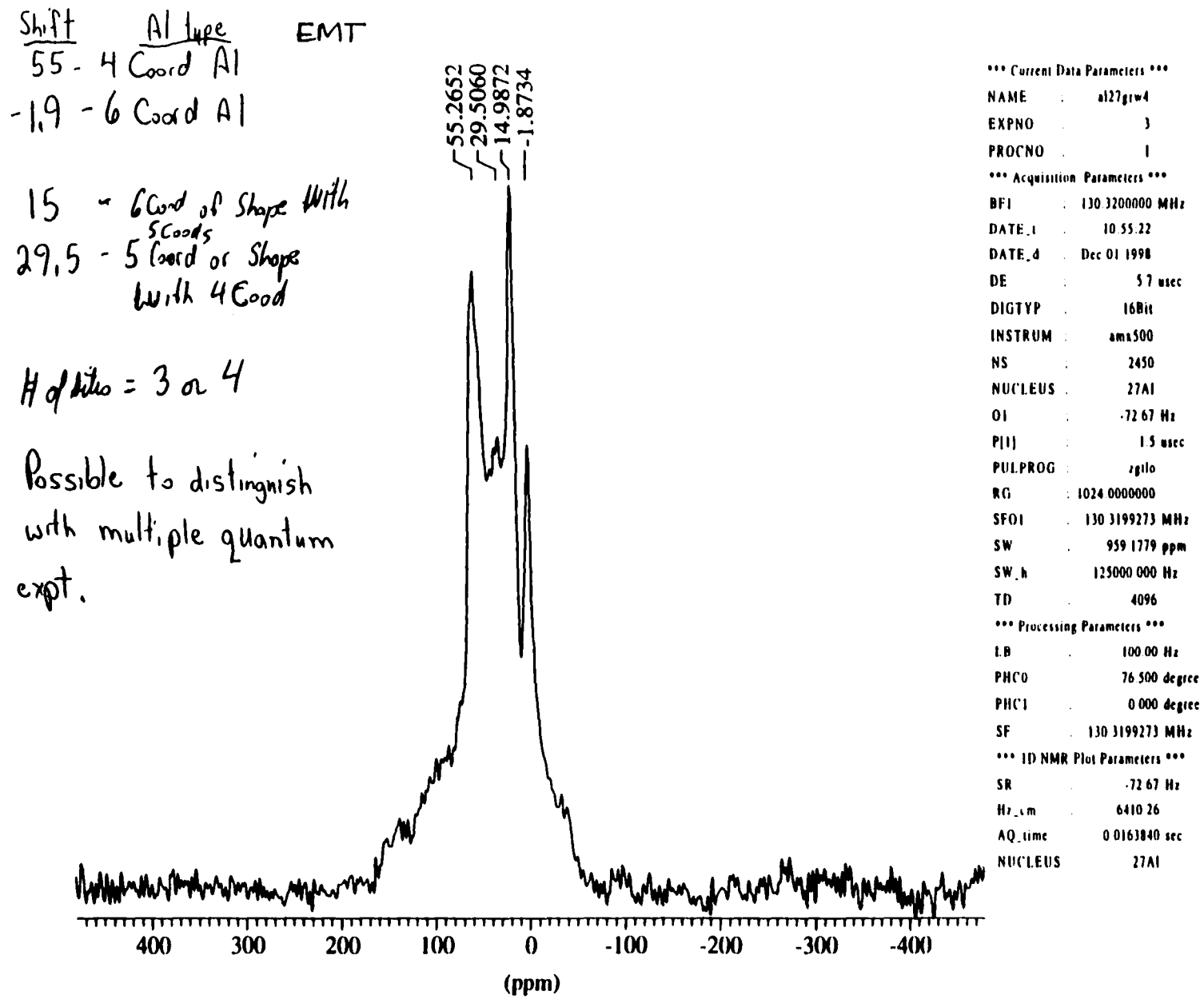



**Figure Al.6: $^{27}$Al MAS NMR for EMT Zeolite**

Y

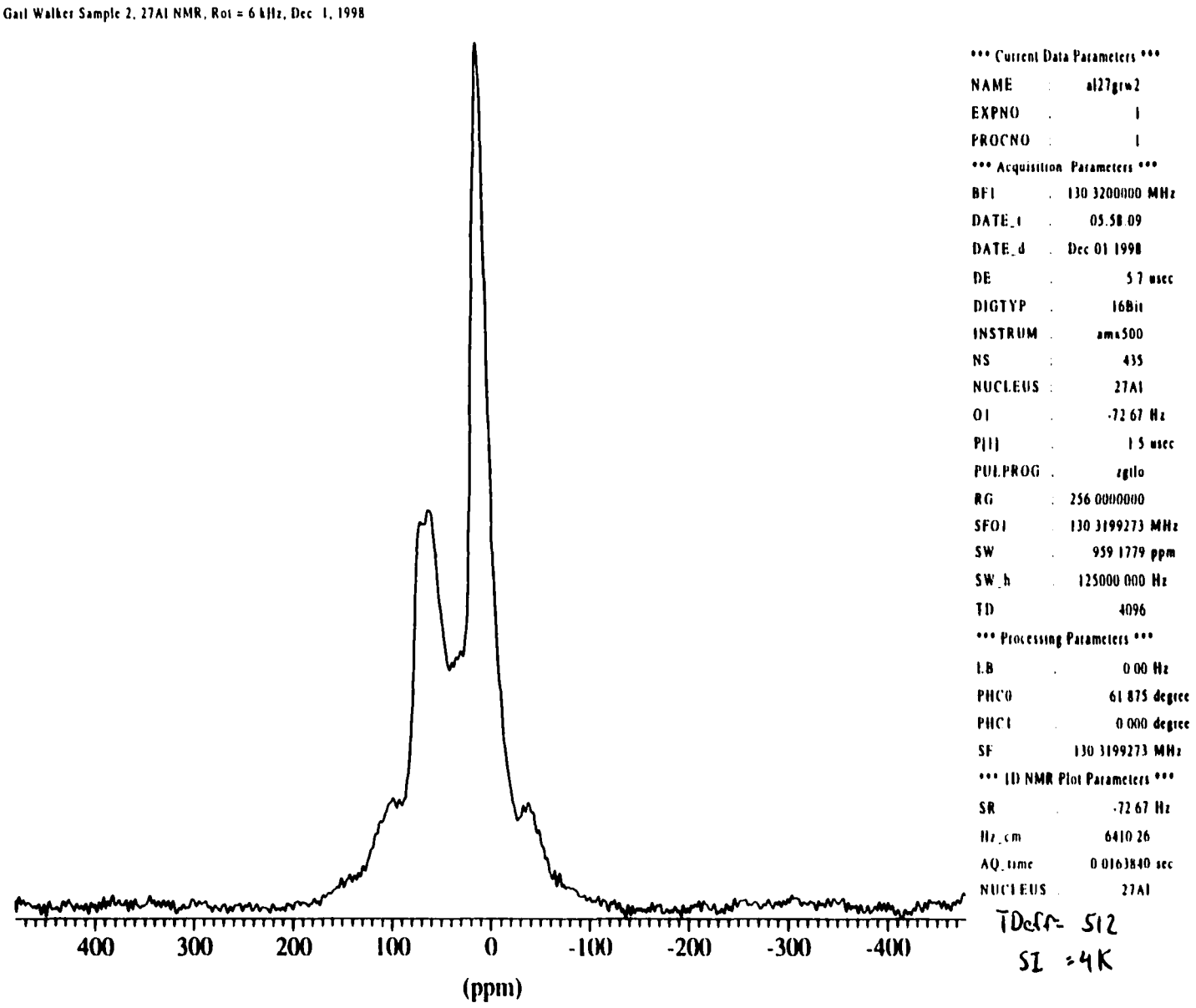



**Figure Al.7: $^{27}$Al MAS NMR for Y Zeolite**

## A1.6 TGA/DTA

### A1.6.1 Experimental

Measurements were performed on a TA Instruments SDT 2960 system using fresh, calcined catalyst as the reference material. A 10 mg quantity was measured for both the sample and the reference material. A reactive gas (10 % $O_2$ in Ar) was used to combust and remove material trapped in the catalyst pores of the spent catalysts.

In freshly prepared catalysts, TGA/DTA measurements evaluated the temperature required to completely combust and remove the 18-crown-6 ether template. This provides insight into the selection of an appropriate calcination temperature for EMT.

TGA/DTA analysis on spent catalysts measured the amount of adsorbed species retained in the catalyst pores after deactivation. In general, it can be said that the temperature required for desorption is directly related to the molecular weight of the species retained in the pore network. That is, a high desorption temperature is required to remove a high molecular weight compound and a lower desorption temperature facilitates removal of low molecular weight species. In this manner, the desorption temperature provided insight into the relative size of the species, and the loss in mass was indicative of the amount of species.

The desorption temperature region ($25°C \geq T_d \geq 425°C$) was divided into three ranges: $T_d < 200°C$, $200°C \geq T_d \geq 300°C$ and $T_d > 300°C$. The % of material desorbed within each of these ranges provided an indication of low, medium and high molecular weight species retained on the catalyst surface. The sum of all of these ranges giave the total amount of material retained on the spent catalyst.

### A1.6.2 Sample Calculation

The sample weight % was recorded for each temperature boundary range (see Table A1.4) for run F29Y (see Figure A1.8). The % material desorbed was given by the loss in mass % of the sample.

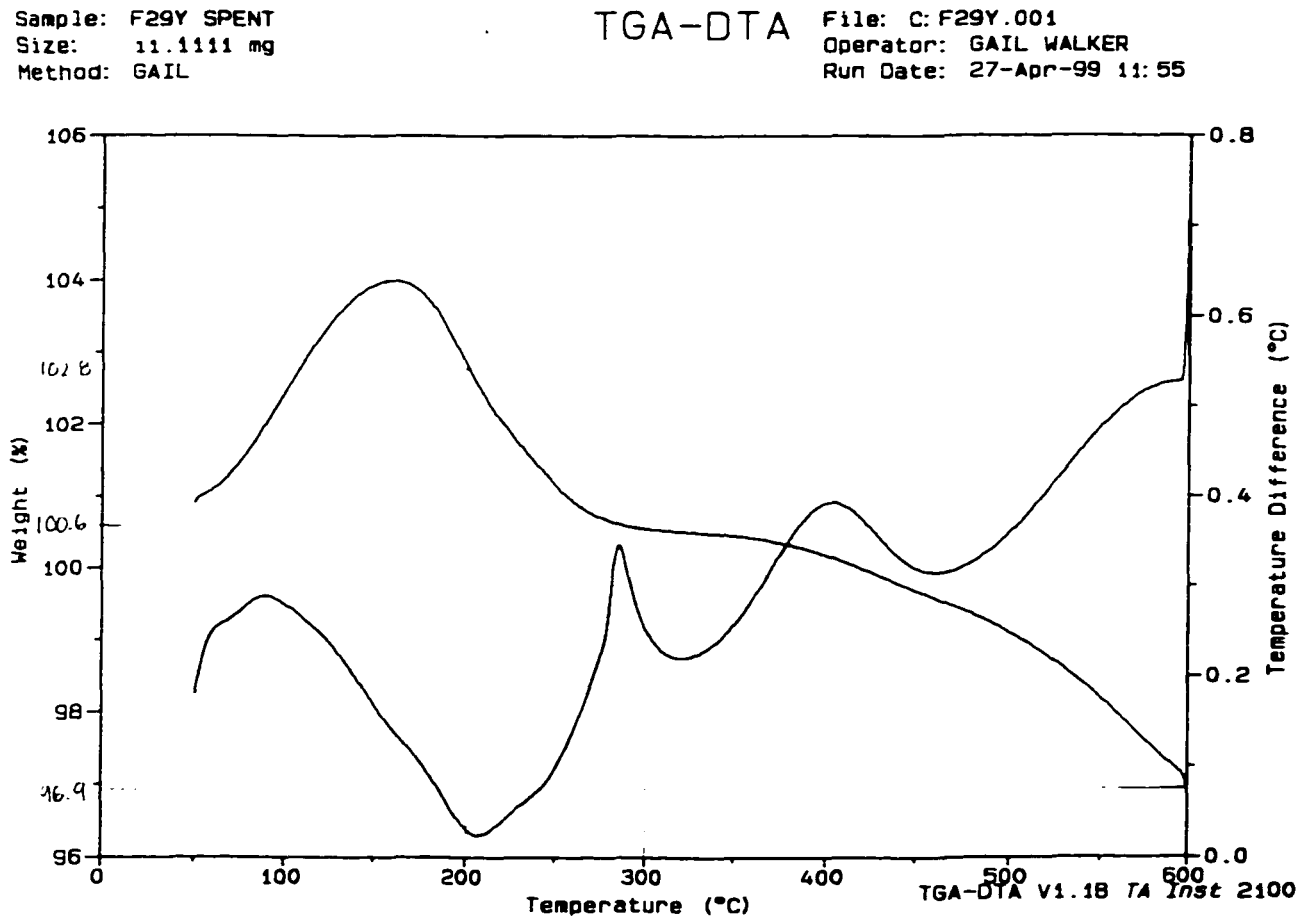



**Figure A1.8:** TGA/DTA Data for Run F29Y

**Table A1.4:** $T_d$ vs. Weight % from TGA/DTA Data for F29Y (Figure A1.8)

| $T_d$ [°C] | Weight % |
|---|---|
| Initial | 104.0 |
| 200 | 102.8 |
| 300 | 100.6 |
| 600 | 96.9 |

$$\% \text{ Loss in Mass } (T_d < 200°C) = \frac{104.0 - 102.8}{104.0} \times 100\ \%$$

$$= 1.2\ \%$$

## A1.7 BET SURFACE AREA ANALYSIS

### A1.7.1 Experimental

A Quantachrome Autosorb-1 system was employed for $N_2$ adsorption measurements to estimate catalyst surface area. The optimal sample size is one in which the total area measured is between 20 and 50 $m^2$. For fresh catalysts, a sample size of 0.1 g was employed. For spent catalyst measurements, the sample size was increased to 0.2 g.

The sample was outgassed at 100°C under vacuum for 3 h to remove physisorbed species. A known quantity of $N_2$ was admitted to the sample and the cell pressure was measured once equilibrium is established. This procedure was repeated until the maximum relative pressure ($P/P^\circ$ where P = cell pressure and $P^\circ$ = saturation pressure of $N_2$ at liquid nitrogen temperature) was reached. The linear region of this isotherm was used for data reduction to estimate the surface area. For microporous materials, this occurred at $P/P^\circ < 0.1$ range of the isotherm.

The multipoint BET (Brunauer-Emmett-Teller) method was employed to estimate the surface area:

$$\underbrace{\frac{1}{W\,[(P/P^\circ) - 1]}}_{y} = \underbrace{\frac{1}{W_m\,C}}_{\text{intercept}} + \underbrace{\frac{C - 1}{W_m\,C}}_{\text{slope}} \cdot \underbrace{\frac{P}{P^\circ}}_{x} \qquad \text{(A1-2)}$$

where

$W$ = mass of $N_2$ adsorbed at a relative pressure, $P/P^\circ$ [g $N_2$]

$P$ = pressure measured in sample cell [mm Hg]

$P^\circ$ = saturation pressure of the $N_2$ at the dewar (liquid $N_2$) bath temperature [mm Hg]

$W_m$ = mass of $N_2$ required for monolayer surface coverage [g $N_2$/g sample]

$C$ = constant related to the energy of adsorption of the first monolayer [dimensionless]

The best fit line through the linear portion (5 points) of the plot of $\{1/[W\,(P/P^\circ - 1)]\}$ versus $\{P/P^\circ\}$ was used to solve for $W_m$ and C. The surface area was calculated as:

$$S = \frac{W_m\,N\,A}{M} \qquad \text{(A1-3)}$$

where

$S$ = specific surface area [$m^2$/g sample]

$N$ = Avogadro's number

= $6.022 \times 10^{23}$ molecules/mole

$A$ = X-sectional area of $N_2$ molecule

= $16.2 \times 10^{-20}$ $m^2$/molecule $N_2$

m = mass of sample [g sample]

M = molar mass of nitrogen

= 28.0134 g $N_2$/mol $N_2$

### AI.7.2 Sample Calculation

From the Multipoint BET plot, the y-intercept was found to be -3.291 x $10^{-4}$ and the slope was estimated to be 9.312 (see Figure A1.9).

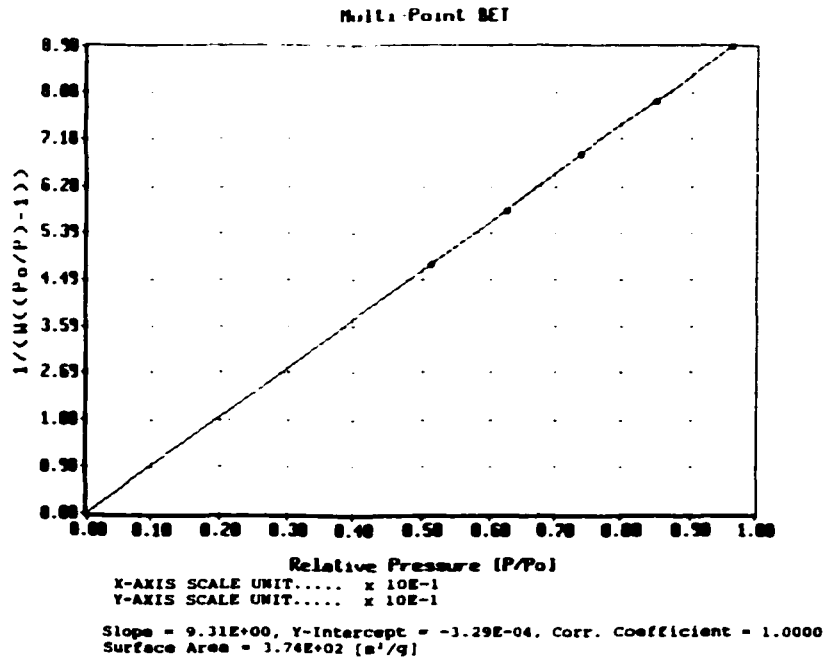



**Figure A1.9:** Multipoint BET plot for F29Y

Therefore,

$$\frac{1}{W_m C} = \frac{1}{-3.291 \times 10^{-4}} \qquad \text{(A1-4)}$$

and

$$\frac{C - 1}{W_m C} = 9.312 \qquad \text{(A1-5)}$$

There are two equations (equations (A1-4) and (1-5)) and two unknowns ($W_m$ and C). Solve for $W_m$.

$W_m$ = 0.10739 g $N_2$/g catalyst

Substitute the value for $W_m$ into equation (A1-3) and solve for specific surface area.

$$S = \frac{0.10739 \text{ g } N_2}{\text{g catalyst}} \left| \frac{6.022 \times 10^{23} \text{ molec. } N_2}{\text{mol } N_2} \right| \frac{16.2 \times 10^{-20} \text{ m}^2}{\text{molec. } N_2} \left| \frac{\text{mol } N_2}{28.013 \text{ g } N_2} \right.$$

$$= 374 \text{ m}^2/\text{g}$$

## A1.8 MEASUREMENT OF Pt DISPERSION

### A1.8.1 Experimental

A Quantachrome Autosorb-1 system was used to perform $H_2$ chemisorption measurements. The isotherm generated from this data was used to evaluate the number of active sites of Pt per gram of sample. This method was used to estimate the percent Pt dispersion in the sample.

Approximately 1 g of solid was measured in the sample cell and inserted in the Analysis station. Prior to analysis, the sample must be treated to clean and stabilize the catalyst surface. This was accomplished by increasing the cell temperature at a rate of 5°C/min to 325°C in flowing helium (40 mL/min). The sample was outgassed at this temperature for 3 h. Upon completion of the calcination cycle, the sample was reduced at 425°C in a stream of 10 % $H_2$ in Ar flowing at 40 mL/min for 1 h. The gas flow was terminated and the cell was evacuated at 425°C for 2 h to remove all traces of hydrogen. The sample cell was cooled (under vacuum) to room temperature for adsorption measurements.

A total of 10 combined (physisorbed and chemisorbed gas measured together) points were collected in the pressure range of 80 and 800 mm Hg. A tolerance of 1 was employed for targeting the pressure set points, an equilibrium time of 3 min and a thermal equilibrium time of 10 min were specified as criteria for data acquisition.

Preselected amounts of hydrogen were sequentially added to the sample cell. An isotherm was generated, by plotting the adsorbed volume (V) vs. equilibrium pressure (P). Both physisorption and chemisorption contributed to this combined isotherm. A straight line was extrapolated from three or more data points in the "plateau" or low-slope region of the combined isotherm, to zero gas pressure (P=0). The y-intercept of this best fit line represented the monolayer chemisorbed volume, $V_m$. The monolayer uptake, $N_m$, can be calculated using:

$$N_m = 44.61\, V_m \qquad \text{(A1-4)}$$

where

$N_m$ = monolayer uptake [μmol $H_2$/g sample]

$V_m$ = molayer chemisorbed volume [mL $H_2$/g sample]

Pt atoms located inside Pt particles do not participate in reactions and similarly, do not contribute to $H_2$ chemisorption measurements. The % Pt dispersion, D, measures the fraction of the active Pt metal exposed on the surface which participates in reactions. A high Pt dispersion is desirable as this is it represents the most efficient use of the noble metal. The % Pt dispersion can be calculated from the following equation once $N_m$ is known:

$$D = \frac{N_m S M}{100 L} \qquad \text{(A1-5)}$$

where

D = % Pt dispersion

S = adsorption stoichiometry

= 2 for $H_2$ chemisorption onto Pt

M = molar mass of Pt

L = % loading of Pt impregnated onto catalyst surface

### A1.8.2 Sample Calculation

The data for fresh 0.5%Pt/EMT is shown in Figure A1.10. The monolayer uptake was calculated to be 9.753 μmol/g. Using equation (A1-5), the % Pt Dispersion, D, was estimated to be:

$$D = \frac{9.753\ \mu mol\ H_2}{g\ sample} \left| \frac{2\ mol\ Pt}{mol\ H_2} \right| \frac{195.09\ g\ Pt}{mol\ Pt} \left| \frac{mol\ H_2}{10^6\ \mu mol\ H_2} \right| \frac{100\ g\ sample}{0.5\ g\ Pt} \times 100\%$$

$$= 76.1\ \%$$

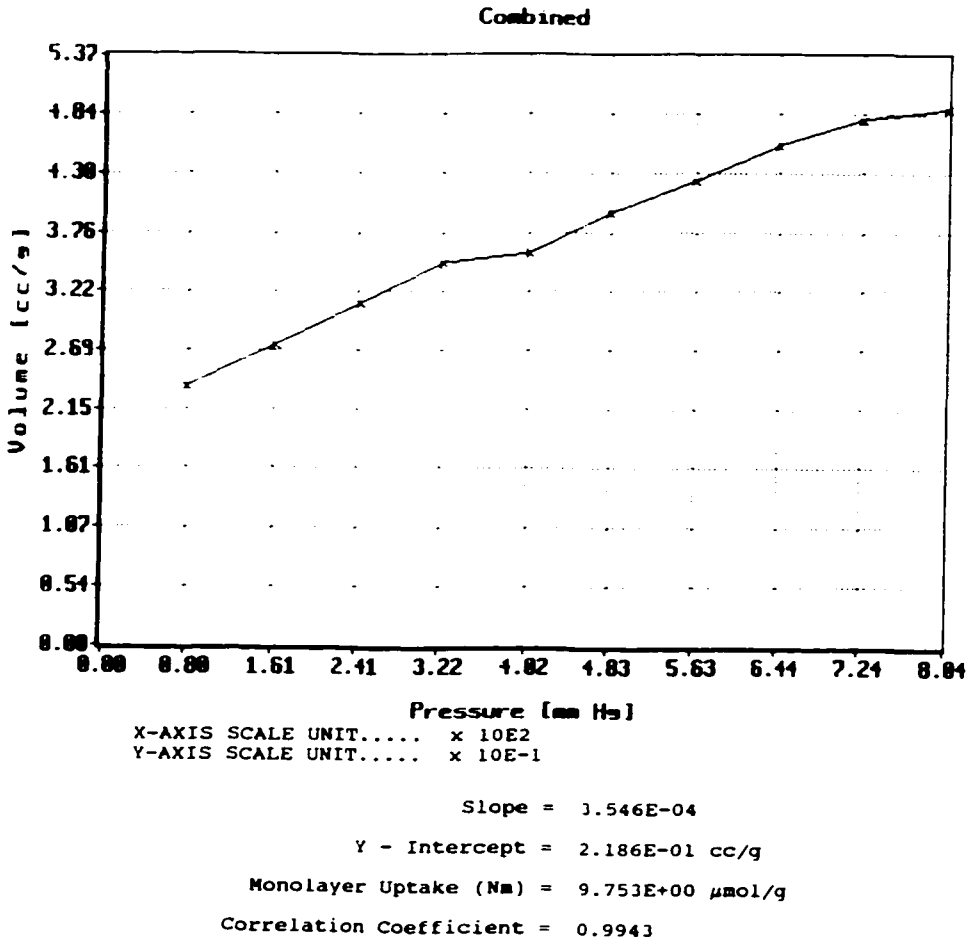



**Figure A1.10:** $H_2$ Chemisorption Data for 0.5%Pt/EMT

## A1.9 MEASUREMENT OF PORE VOLUME

### A1.9.1 Experimental

A Quantachrome Autosorb-1 system was utilized for nitrogen adsorption measurements to estimate pore volume. A 0.1 g sample was outgassed at 100°C under vacuum for 3 h to remove physisorbed species retained in the catalyst pores.

The adsorption isotherm using nitrogen as the adsorbate is determined. Particular attention is focussed in the region where the relative pressure, $P/P_o$ (where P=cell pressure and $P^o$=saturation pressure of $N_2$ at liquid nitrogen temperature), approaches unity. The volume of nitrogen vapour, $V_{ads}$, which is adsorbed as $P/P^o$ approaches unity is estimated. The volume of liquid nitrogen contained in the pores of the catalyst can be calculated using the following equation:

$$V_{liq} = \frac{P_a V_{ads} V_m}{R T} \qquad \text{(A1-6)}$$

Where

$V_{liq}$ = pore volume [$cm^3$/g cat]

$P_a$ = ambient pressure [atm]

$V_{ads}$ = volume of nitrogen vapour adsorbed [$cm^3$/g cat]

$V_m$ = molar volume of liquid nitrogen = 34.7 $cm^3$/mol

R = Universal Gas Constant

T = ambient temperature [K]

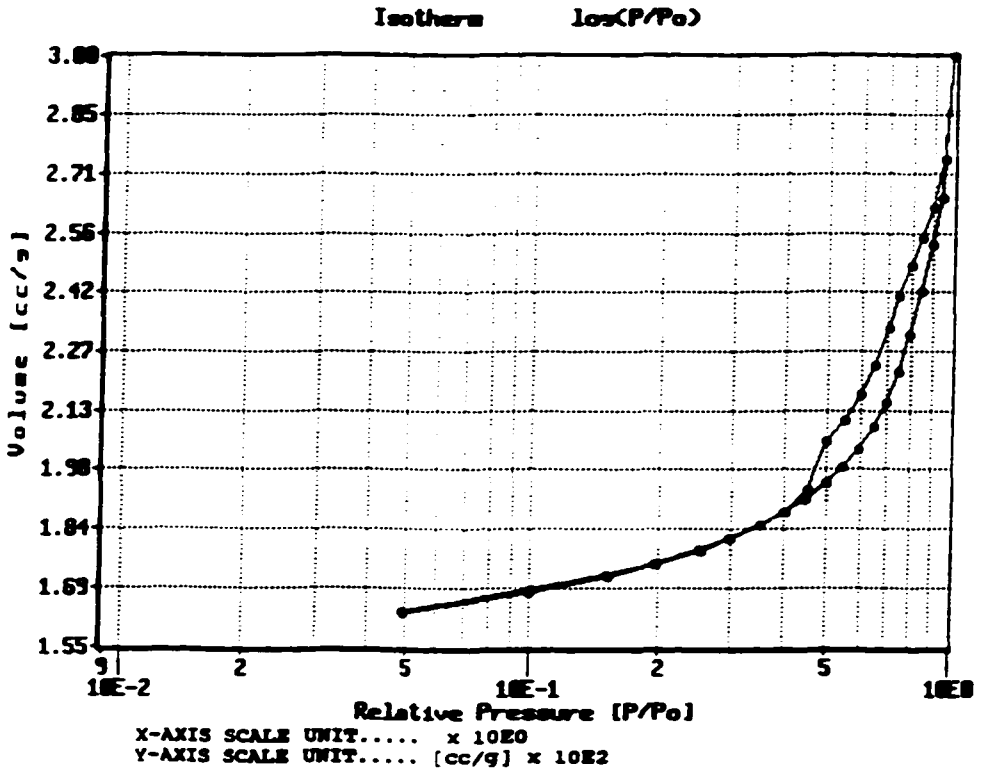
### A1.9.2 Sample Calculation

The data for Y zeolite is shown in Figure A1.11. The value for $V_{ads}$ is estimated to be 300 $cm^3$/g from the nitrogen isotherm. This value is substituted into equation (A1-6) to solve for $V_{liq}$.

$$V_{liq} = \frac{300\ cm^3}{g\ cat} \left| \frac{34.7\ cm^3}{mol\ N_2} \right| \frac{101.325\ kPa}{293\ K} \left| \frac{mol\ K}{8.314\ kPa\ L} \right| \frac{L}{1000\ cm^3}$$

$$= 0.43\ cm^3/g\ cat$$

The Autosorb-1 system software can provide an accurate estimate of the pore volume. The software estimates the pore volume to be 0.464 $cm^3/g$ for Y zeolite.




**PORE VOLUME DATA**

| | | |
|---|---|---|
| Total Pore Volume for pores with Radius less than 1357.1 Å at P/Po = 0.99289..... | 4.639E-01 | [cc/g |
| * t-Method Micro Pore Volume..... | 2.206E-01 | [cc/g |
| * MP-Method Micro Pore Volume..... | 9.956E-02 | [cc/g |

**PORE SIZE DATA**

| | | |
|---|---|---|
| Average Pore Radius..... | 1.431E+01 | [Å] |

* Note: MP and t-Method values based on data points with t-Tags.

**Figure A1.11:** $N_2$ Isotherm for Y Zeolite

# Appendix 2:

# BTRS System Diary

## 1995

**June '95**

- reviewed Altimira and Autoclave Engineer (AE) proposals for computer controlled flow reactor system
- finalized basic design of flow reactor system

**Oct. '95**

- AE awarded flow reactor contract

**Nov. '95**

- determined utility (electrical, compressed air, water) and space requirements for reactor system
- investigated pump and MFC flow ranges available from source contractors

**Dec. '95**

- reviewed BTRS system blueprints
- identified errors, omissions, and areas of ambiguity

## 1996

**Jan. '96**

- communicated list of errors, omissions and areas of ambiguity to AE
- faxed outline of software needs for sample collection and reactor control to AE

**Feb. '96**

- contacted Valco and investigated seat materials available for multiposition valves
- collaborated with PE to design on-line splitter for GC to be located in Heated Enclosure

**Mar. '96**

- finalized flow ranges for pumps and MFCs and seat material for multiposition valves

**Apr. '96**

- installed lab benches and desks for BTRS equipment, PC and GC in walk-in fume hood in E1-3523A
- arranged installation of cylinder bays for GC and reactor gas cylinders
- arranged installation of utility (electrical, compressed air and water) sources

**May '96**

- GC installed in walk-in fume hood
- attended 2-day training session in Erie, Pennsylvania at AE site

**June '96**

- communicated hardware and software concerns identified during training session at AE manufacturing facility
    - unit fails pressure test - leak in system
    - program ability to link 5 recipes (18 steps each) together in Sample Control Window
    - Sample Control Window won't progress past step 2 - bug in software
    - program ability to link 5 recipes (10 steps each) together in Automatic Control Window
    - Reactor Status Valve display is Offline when reactor actually On-line
    - reactor Furnace set point is retained rather than being set to "0" after failsafe shutdown activated

**June '96 (Continued)**

- add real-time plot pop-up screens for reactor pressure and temperature as well as MFC and liquid pump outputs
- MFCs and pumps activating alarm - reason unknown
- tune parameters for BTRS oven, HTL and Heated Enclosure as large temperature overshoots occur
- error in overview flow schematic for valving of Separator bypass
- incorrect flow range for MFC2

- mediated resolution to above issues with AE personnel

**July '96**

- BTRS equipment delivered to U of W but no Operating Manual provided
- equipment unpacked and arranged in walk-in fume hood
- tubing installed to bring gas supplies from external cylinders to equipment located in barricade
- pressure regulator installed on compressed air line
- equipment modules connected by AE personnel
- oven would not turn on
- two faulty S.S. relay fuse boxes replaced to rectify problem
- CSA certification completed on-site

**Aug. '96**

- SSI finalizes design of inlet check valve prototype capable of withstanding high upstream pressure for use in HPLC pumps
- modified GC and integrator wiring to facilitate communication with and PLC
- modified GC plumbing such that head pressure of carrier gas flowing through Heated Enclosure can be regulated by GC MFC
- installed split injector prototype in Heated Enclosure using needle valve with Vernier handle to regulate split flow rate
- BTRS manual arrives

**Aug. '96**

- pressure and temperature test reactor
- Reactor Status Valve in BTRS oven making squeaking noise
- identified major leak in Reactor Status Valve and smaller one in 16 loop Multiposition valve in Heated Enclosure
- numerous software bugs identified
    - DDE conversations not initiated upon start-up of software
    - furnace set point in active recipe and oven set point overridden and set to default values when Automatic Cycle program initiated
    - problem with Dwell Time and GC Enable in step 9 of Sample Control recipe
    - Sample Control won't progress past step 11 in recipe
    - duration of Sample Valve position coupled to Automatic Control recipe dwell times
    - Sample Valve only maintained in inject position for 1 min and then reverts to back to collect position. This injects contamination region after sample injection making analysis impossible
    - logic for sending Start signal to GC through Sample Control recipe needs redevelopment

**Sept. '96**

- replaced Valcon T seat in Reactor Status Valve
- aligned valve and leak tested
- split ratio of split injector prototype drifts significantly during sampling causing poor reproducibility in the analysis of standard mixture - consult with PE to identify potential causes
- tried to heat Heated Enclosure to high temperature to seal 16-loop valve - maximum temperature possible is ~ 250°C
- heater cartridge under designed for Heater Enclosure

**Oct. '96**

- new software bugs identified
    - Reactor Status valve switches to Offline position without instructions from Automatic Cycle recipe
- requested second inlet check valve matching prototype
- AE manual operating valves (6) leaking
- BPR leaking

**Nov. '96**

- installed higher wattage heater cartridge in heater block of Heated Enclosure
- tested operation of new cartridge
- AE personnel installed new AE manual operating valves with higher temperature seat rating
- AE personnel replaced Kalrez "O" ring, teflon back-up ring and seat in BPR
- AE personnel coded revision to software to correct identified bugs in system

**Dec. '96**

- re-designed split injector prototype in Heated Enclosure using piece of column to regulate flow rate of vented sample
- poor analysis of standard mixture still achieved using second split injector prototype

## 1997

**Jan. '97**

- independent thermocouple measurements indicate Heated Enclosure air temperature is 100°C less than block heater temperature

**Feb. '97**

- AE notified of Heated Enclosure temperature problem and authorization given to return unit

**Mar. '97**

- AE acknowledges inability of Heated Enclosure to reach blueprint temperature specifications
- AE attempts are unsuccessful to retrofit Heated Enclosure with a fan for the purpose of air circulation
- AE proposes new Heated Enclosure design similar to BTRS oven

**June '97**

- newly designed Heated Enclosure arrives at U of W

**July '97**

- Heated Enclosure tested
- new split injector prototype designed and installed in GC
- satisfactory reproducibility obtained

**Aug. '97**

- reactor skin temperature alarm sporadically activated triggering 100 % output from furnace - DANGEROUS!
- possible sources of problem identified as:
  - faulty thermocouple
  - software bug
  - faulty PLC module
- install new thermocouple for reactor skin temperature and alarm problem disappears

**Nov. '97**

- HTL temperature control problem sporadically activating alarm and initiating reactor shut-down
- broken ground solder on HTL pin connector isolated as source of problem
- HTL pin re-soldered and tested
- BPR found to be leaking again
- Teflon back-up ring and Kalrez "O" ring assembled in incorrect order!
- wrong BPR literature supplied in BTRS manual!!

**Nov. '97 (Continued)**

- outstanding software bugs identified
    - memory effect on Sample Control Window - GC Enable commands for first recipe retained for all subsequent recipes regardless of commands stored in recipe file
    - coupling between Automatic Cycle Recipe and Sample Control recipe preventing sample collection during transitional times
- Reactor Status valve squeaking and leaking again
- developed method to flush contamination region in Heated Enclosure to vent prior to sample injection
- alter plumbing of GC to permit venting of contamination region while still maintaining carrier flow to GC column
- tested system and verified operation

**Dec. '97**

- replaced Kalrez "O" ring, Teflon back-up ring and seat in BPR
- installed Valcon E seat in Reactor Status valve and align
- modified BTRS oven software to reflect reduced upper temperature limit for Valcon E seat
- second inlet check valve arrives
- new software bugs identified:
    - problem with Step 15 of Sample Control window - Step 16 initiated after 5 min. maximum if value greater than 5 min. entered for Dwell Time of step 15
- disk containing latest corrections to software bugs arrives
- installed software onto PC

# 1998

**Jan. '98**

- tested two pumps operating simultaneously for first time
- corrected software installed in Dec. '97 employed outdated version of software as a basis
    - GC indicated Ready by software even if it is not Ready
    - GC Start signal sent without command being issued
    - coupling of GC Delay and Dwell time in Sample Control window
    - Sample Valve won't switch from Collect to Inject despite instructions from Automatic Control recipe - no samples can be injected to GC
- some previously "cured" software bugs revisited!
- healthiest version of software sent to AE to have corrections re-coded
- revised software returned by AE

**Feb. '98**

- loaded corrected software onto PC and test
- first successful run with actual data achieved!

**Mar. - Apr. '98**

- seventeen successful runs performed on flow reactor

**May '98**

- colour problems on display of Overview screen
- 16-loop valve sticking making actuation impossible
- Valco recommends re-conditioning valve
- requested modification to software from AE to permit operation of Heated Enclosure at conditioning temperature conditions
- installed revised software onto PC
- flow restricted when reactor placed on-line
- in-line filters installed backwards!
- in-line filters replaced in upstream and downstream locations of reactor and filter holders oriented correctly

**June '98**

- reconditioned 16-loop valve
- actuation achieved but valve still squeaks
- inlet pump loses prime when flow rates greater than 40 % capacity attempted
- removed and cleaned pump head in ultrasonic bath
- re-installed pump head and confirmed operation
- reactor skin temperature problem resurfaces
- MFC malfunctioning and activating alarm
- replaced reactor skin temperature thermocouple
- alarm problems persist making operation of equipment impossible
- virus scanner installed onto PC and Word and Excel viruses detected
- re-loaded Wonderware software onto PC

**July '98**

- source of reactor skin temperature and MFC alarm problems identified as faulty PLC module
- replacement module sent by AE
- module installed and alarm problems corrected

**Sept. '98**

- needle, 3-way and check valves for manual control of liquid flow fail
- manual control system for liquid feed re-designed
- new valves and fresh in-line filters installed in all inlet gas and liquid feed lines

**Oct. '98**

- 16-loop valve sticks again
- re-condition valve successfully but valve squeaks during actuation

**Nov. '98**

- 16 loop valve sticks
- re-conditioning cannot correct problem
- 16-loop valve removed and shipped to Valco for servicing

**Nov. '98 (Continued)**

- Valcon E seat installed in 16-loop valve by Valco

**Dec. 98**

- repaired 16-loop valve arrives at U of W
- 16-loop valve installed and aligned
- Heated Enclosure software modified to reflect reduced upper temperature limit

## 1999

**Mar. '99**

- tube failure on inlet side of reactor due to metal fatigue (as a result of repeated reactor head assembly removal for the purpose of catalyst loading)
- reactor head tubing design improved to reduce likelihood of metal fatigue in the future
- new tubing installed and reactor pressure tested
- pump losing prime

**Apr. '99**

- unreliable pump operation

**May '99**

- pump operation continues to be unreliable
- last experiment completed

# Appendix 3:

# Flow Reactor Operation and Sample Calculations

## A3.1 OPERATION OF FLOW REACTOR

### A3.1.1 Overview of Wonderware Software

Computer control of the BTRS reactor and on-line sampling systems, are accessible through Wonderware software. Although reactor pressure regulation is manually controlled, pressure detection and data logging, are supported by the software. Programming of the GC is also manual. However, Wonderware software displays GC Ready signal, if both the integrator and GC are in the Ready status. In addition, the software provides means to communicate a Start signal the GC to activate GC analysis.

The System Overview window is a flow schematic of the entire reactor system, providing a real-time status of all measurable parameters. Manual control of all components of the BTRS system, excluding the Sample Valve position and Multiposition Trapping Valve position (see Sample Control window), are facilitated through the System Overview window. Set point temperatures for the BTRS oven, HTLs and Heated Enclosure are entered through this screen, as programmed changes of these elements, are not supported by the software. The Automatic Cycle,

Sample Control, Historical Data Display and PLC Alarm windows are linked to the System Overview screen.

The Automatic Control window allows for the creation, storage and activation of programmed events for elements in the BTRS reactor system. These include furnace control (ramp rate, set point, dwell time), Reactor Status Valve position (Online/Offline), MFC flow rates and pump flow rates. Specific settings for these inputs can be stored in a recipe. Five recipes, each containing 10 steps, can be linked together providing a total of 50 possible events for programmed control. Activation/termination of automatic control of the BTRS system is facilitated through the Automatic Cycle window. Entering a Start command initiates programmed control of the reactor according to the steps outlined in the active recipe. Automatic control can be interrupted or terminated at any time, through the Hold or Stop commands respectively.

The Sample Control window regulates sample collection and management in the Heated Enclosure. The loop position and direction of rotation of the Multiposition Trapping Valve, and the position of Sample Valve, are all controlled through this screen. In addition, a Start signal can be issued to the GC to activate GC analysis. A total of 18 steps are available in each recipe, with the ability to link 5 recipes together, for programmed control. Initiation of the recipe is automatically activated when a Start signal is toggled from the Automatic Cycle window.

The PLC Alarms window is a colour coded screen which displays the current status of all system alarms. If a dangerous operating condition is detected by the PLC, an alarm is immediately annunciated. The PLC Alarm icon flashes red on the System Overview screen and the specific alarm condition flashes red on the PLC Alarm window. A two-level protocol for alarms is employed: High alarm and High/High Alarm. The first level (High alarm) warns the operator, that a condition approaching dangerous levels is detected. This allows time for the operator to intervene and correct the problem. The second alarm level (High/High alarm) is activated when a dangerous operating condition is measured and automatically disables the system. Reactant flow to the system is immediately terminated and the

Reactor Status Valve is switched to the off-line position. All furnaces and heaters are shut off and computer control is disengaged. Once the alarm condition has cleared, the alarm can be Reset, the system Enabled and normal operation resumed.

A data log, recording the levels of all operating conditions, alarm activations and set-point changes of controllers, is automatically activated upon start-up of Wonderware software. A history of all measurable elements in the system, can be viewed through the Historical Data Display window.

### A3.1.2 Catalyst Addition

The reactor was removed from the system by disconnecting V-R12 and V-R13 (see the AE BTRS Oven Flow Schematic blueprint). The gland at the reactor bottom was detached and glass wool was inserted around the thermowell base assembled to the gland. This serves to trap solids or glass beads that may become entrained in the flowing mixture. The gland was re-attached to the reactor base. This procedure was routinely performed every 20 experiments.

The top gland of the reactor was removed to permit catalyst addition. Silica beads (1 mm diameter) were poured into the reactor to a depth of 16.25 cm (see Figure A3.1). Three grams of uncalcined catalyst ($250\mu m \leq d_p \leq 500\mu m$) were physically combined with 3 g silica beads. This mixture was poured on top of the glass beads, achieving a bed height of approximately 9.0 cm. Silica beads were added to the top of the catalyst bed, to fill the remaining void space in the reactor (approximately 16.25 cm depth). Glass wool was placed on top of the glass beads, to contain them during the gland assembly, as well as in the gland opening to trap particulate matter that may become entrained. The gland was re-connected to the reactor and the entire assembly was re-attached to the BTRS system. Three thermocouples were inserted at varying depths to monitor the temperatures in the pre-reaction zone, the catalyst bed and the post-reaction zone (see Figure A3.1).

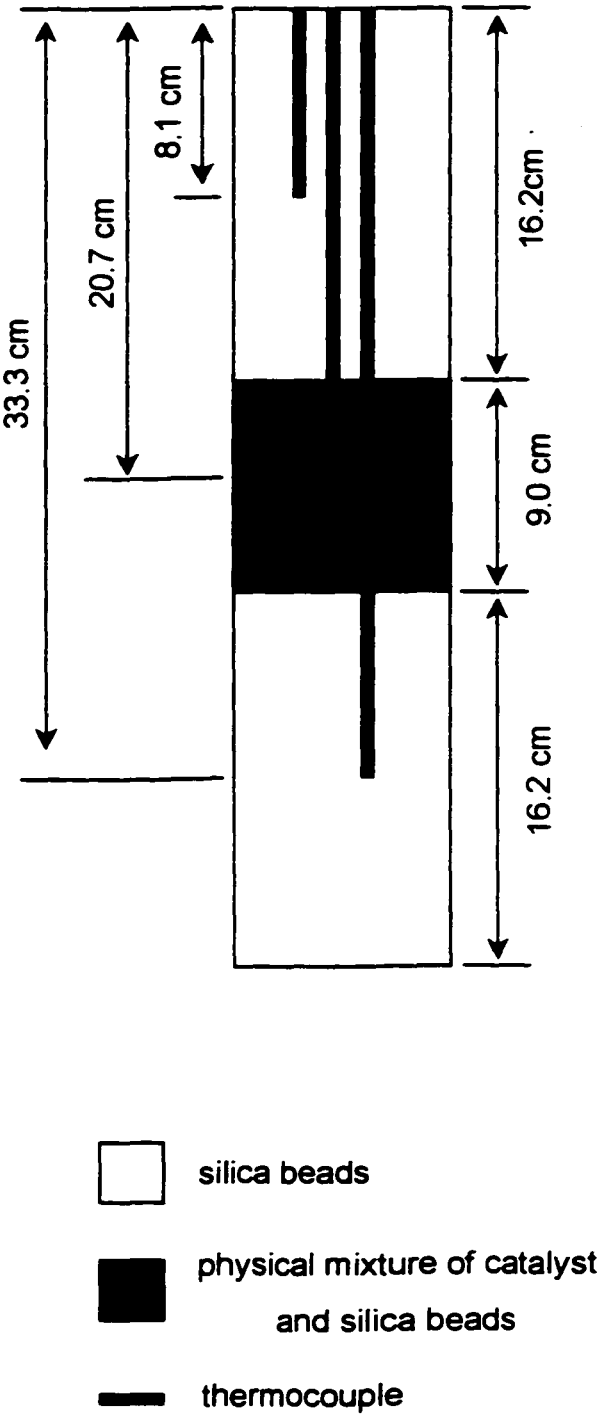



**Figure A3.1:** Catalyst Bed in Flow Reactor

### A3.1.3 Calcination/Reduction Procedure

The Wonderware software was loaded and the system was Enabled from the System Overview screen. Valves V-R14, V-R12, V-R16, V-R13 and V-R15 were opened, putting the feed stream on-line to the reactor. The Reactor Status Valve was activated to the off-line position and nitrogen was flushed through the Reactor Purge Feed line for a few minutes by opening V-S11, V-S12 and V-S13. Upon completion of the flush step, these three valves were closed and Reactor Status Valve was returned to the on-line position.

The catalyst was calcined *in situ* prior to the experiment. The gas supply for the calcination cycle was determined by the position of two three-way valves on the input sides of both MFCs (see Figure A3.2). The three-way valves connect nitrogen, bench air and a gas mixture of 10 % hydrogen in argon to the MFC inlets such that pure nitrogen, air or nitrogen/hydrogen/argon mix can selected as the on-line supply for the system.

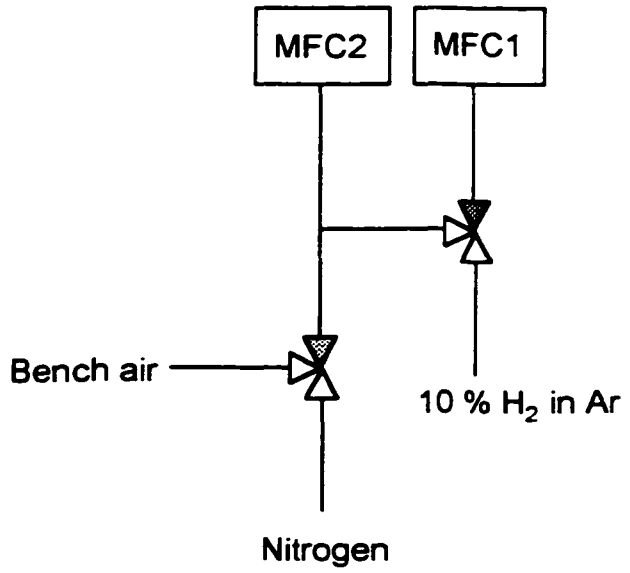



**Figure A3.2:** Gas supplies for MFC Inlets

The calcination program was entered through the Automatic Cycle window (see sample calcination program in Table A3.1). A $N_2$ flow rate of 50 sccm (sum of MF1 and MF2) was employed for the calcination cycle, with equal flow rates being supplied by each MFC (see Step 1 in Table A3.1). The reactor temperature was increased at a rate of 5°C/min to 425°C (Rxr Temp) and maintained at this temperature for 5 h or 300 minutes (Dwell). The Transition Time column of the recipe, was the period required for the reactor temperature to increase from the initial condition to the Rxr Temp level. Since the desired rate of temperature increase was 5°C/min, the time required to reach 425°C from room temperature (20°C), is 81 minutes. The Rxr Status was programmed to the on-line position to permit regulation of gas flow using the MFCs. The effluent from the reactor was vented through the drain tube of the Separator by closing valves V-P13 and V-P14 and opening V-P11 and V-P12. This is desirable to prevent deposition of contaminants, which may be removed by the calcination cycle, in the components of the Heated Enclosure.

**Table A3.1:** Automatic Cycle Recipe for Calcination Cycle

| Step | MFC1 [sccm] | MFC2 [sccm] | Pump-1 [mL/min] | Pump-2 [mL/min] | Rxr Status | Rxr Temp [°C] | Transition [min] | Dwell [min] |
|---|---|---|---|---|---|---|---|---|
| 1 | 25 | 25 | 0.00 | 0.00 | Online | 425 | 81 | 300 |
| 2 | 10 | 10 | 0.00 | 0.00 | Offline | 50 | 10 | 999 |

Once the calcination cycle (Step 1) was completed, the reactor was cooled to the reaction temperature level (in this example, the reaction temperature is 50°C) through Step 2 of the Calcination Program. If bench air was used during the calcination cycle, the gas flow was switched to nitrogen for the last 5 minutes of the calcination program.

No samples were collected during the calcination cycle. The Multiposition trapping valve was maintained in the same position throughout the calcination period. This was achieved by using the sample recipe provided in Table A3.2 for Sample Control.

**Table A3.2:** Sample Control Recipe for Calcination Cycle

| Step | Loop No. | Direction (CW/CCW) | Sample (Collect/Inject) | GC Delay [sec] | Dwell Time [min] | GC Enable Enable/Disable |
|---|---|---|---|---|---|---|
| 1 | 1 | CW | Collect | 0 | 999 | Disable |
| 2 | 1 | CW | Collect | 0 | 999 | Disable |

### A3.1.4 Feed Sampling

The set point for the BTRS oven was calculated as being the reaction temperature minus a few degrees. This value was manually entered on the System Overview Screen. Temperatures of 200°C were entered for the set points of both HTLs, which provide connections to and from the Heated Enclosure. The Heated Enclosure was set at 200°C and the Reactor Status Valve directed to the off-line position, through manual entry on the System Overview screen. The feed analysis program was loaded onto the GC.

The flow rates for MFC1 and MFC2 were increased to 50 % of the maximum range and the BPR position was adjusted such that a system pressure of 450 psi is measured. The MFC rates were reduced to the levels which were to be employed in the experiment and the position of the BPR was fine tuned such that the pressure was maintained constant at 382 psi.

The liquid pumps were primed by isolating the pump through closure of valves V-F32 and V-F42. Starting with pump 1, a flow rate was entered on the System Overview screen, choosing a rate of approximately 10 % of the total pump range (1 mL/min). Once a increase in the pump head pressure was observed, the flow rate is gradually increased to approximately 50 % of the pump range. This pump rate was maintained until a pressure of approximately 1000 psi is measured. At this point, valve V-F32 was opened to permit liquid flow to the reactor system and the pump flow was adjusted to experiment level. An analogous approach was employed to prime pump 2.

Verification of liquid delivery was accomplished by manual flow measurement of the effluent exiting the Reactant Vent line. A dramatic increase in the flow rate occurred when the liquid front reaches the vent line. Once this event was detected, the feed sampling program was activated. The pump flow rates employed in the reaction program were applied in the feed sampling program (see Table A3.3).

**Table A3.3:** Automatic Cycle Recipe for Feed Sampling Program ($T_{furn}$=48°C; $N_2$ flow=35 sccm; Liquid Feed=2.76mL/min)

| Step | MFC1 [sccm] | MFC2 [sccm] | Pump-1 [mL/min] | Pump-2 [mL/min] | Rxr Status | Rxr Temp [°C] | Transition [min] | Dwell [min] |
|---|---|---|---|---|---|---|---|---|
| 1 | 21 | 14 | 0.00 | 2.76 | Offline | 48 | 1 | 999 |

Liquid flow was sustained for 30 min prior to collection of the first sample. This is important to provide uniform feed composition throughout the system as well as ensuring consistent sample injection into the GC. A total of 5 feed samples were collected and stored for analysis. At the conclusion of the sampling period, the loops were sequentially flushed and sent to the on-line GC system for detection. Note that the contamination region (orange lines in Figure 4.2) must be flushed prior to injection of the first sample to the GC (facilitated by Step 7 in Table A3.4).

**Table A3.4:** Sample Control Recipe for Feed Analysis

| Step | Loop No | Direction (CW/CCW) | Sample (Collect/ Inject) | GC Delay [sec] | Dwell Time [min] | GC Enable (Enable/ Disable) | GC Valve[1] (Off/On) |
|---|---|---|---|---|---|---|---|
| 1 | 1 | CW | Collect | 0 | 30 | Disable | Off |
| 2 | 2 | CW | Collect | 0 | 1 | Disable | Off |
| 3 | 3 | CW | Collect | 0 | 1 | Disable | Off |
| 4 | 4 | CW | Collect | 0 | 1 | Disable | Off |
| 5 | 5 | CW | Collect | 0 | 1 | Disable | Off |
| 6 | 6 | CW | Collect | 0 | 1 | Disable | Off |
| 7 | 6 | CW | Inject | 0 | 10 | Disable | On |
| 8 | 5 | CCW | Inject | 0 | 5 | Enable | Off |
| 9 | 4 | CCW | Inject | 0 | 5 | Disable | Off |
| 10 | 3 | CCW | Inject | 0 | 5 | Disable | Off |
| 11 | 2 | CCW | Inject | 0 | 5 | Disable | Off |
| 12 | 1 | CCW | Inject | 0 | 15 | Disable | Off |

1 GC Valve position manually controlled through touch pad of GC

The GC analysis of the five samples were compared. If consistent feed composition was measured, the feed analysis program was terminated and the reaction program was initiated. Feed flow was maintained off line between the feed analysis and reaction period.

### A3.1.5 Reaction Sampling and Product Analysis

An acetone/ice water bath mixture was prepared in a 2 L beaker. The opening of a 250 mL Erlenmeyer flask was covered with parafilm and a small cut was made in the center of the parafilm cover. The alkylate analysis program was loaded onto the GC and the GC valve was set to the Off position.

The reaction recipes were loaded onto the Automatic Cycle (see Table A3.5). and Sample Control (see table A3.6) windows. Note that a delay of 5 min was provided for the reaction front to reach the Heated Enclosure (dwell time of 6 min in Step 1 includes delay of 5 min plus 1 min sample collection time period). The

program, with the exception of the active step of the recipe, can be edited during programmed operation, if the delay is observed to be longer than 5 min.

Programmed operation of the equipment was activated from the Automatic Cycle window. The flow rate of the effluent from the Reactant Vent was immediately measured with a bubble flow meter. When the reaction front was detected, the current sample loop of the Multiposition valve was noted. The sample contents of this loop are for 1 min TOS. The Reactant Vent line was immediately immersed in the acetone/ice water bath, with the end of the tubing placed through the parafilm hole and pointing into the Erlenmeyer flask. The Erlenmeyer flask was partially immersed in the acetone/ice water bath. This will serve to collect the liquid product over the course of the reaction.

**Table A3.5:** Automatic Cycle Recipe for Reaction
($T_{furn}$=48°C; $N_2$ flow=35 sccm; Liquid Feed=2.76mL/min; $t_{rxn}$=1h)

| Step | MFC1 [sccm] | MFC2 [sccm] | Pump-1 [mL/min] | Pump-2 [mL/min] | Rxr Status | Rxr Temp [°C] | Transition [min] | Dwell [min] |
|---|---|---|---|---|---|---|---|---|
| 1 | 21 | 14 | 0.00 | 2.76 | On-line | 48 | 1 | 70 |
| 2 | 21 | 14 | 0.00 | 0.00 | Off-line | 25 | 1 | 10 |
| 3 | 5 | 5 | 0.00 | 0.00 | Off-line | 25 | 1 | 999 |
| 4 | 5 | 5 | 0.00 | 0.00 | Off-line | 25 | 1 | 999 |

Samples were collected every 1 min for the first 10 min of the reaction period (see Table A3.6). Thereafter, the samples were collected at different time frequencies to monitor the progression of catalyst activity over a total reaction period of 1 h. At the conclusion of the 1 h reaction period, the Erlenmeyer flask and the mass of the bulk liquid sample were measured. The GC valve was positioned in the On position to permit venting of the contamination region during Step 17 of Table A3.6.

**Table A3.6:** Sample Control Recipe for Reaction - Sample Collection (15 samples collected, $t_{rxn}$=1h)

| Step | Loop No | Direction (CW/CCW) | Sample (Collect/ Inject) | GC Delay [sec] | Dwell Time [min] | GC Enable (Enable/ Disable) | GC Valve[1] (Off/On) |
|---|---|---|---|---|---|---|---|
| 1 | 1 | CW | Collect | 0 | 6 | Disable | Off |
| 2 | 2 | CW | Collect | 0 | 1 | Disable | Off |
| 3 | 3 | CW | Collect | 0 | 1 | Disable | Off |
| 4 | 4 | CW | Collect | 0 | 1 | Disable | Off |
| 5 | 5 | CW | Collect | 0 | 1 | Disable | Off |
| 6 | 6 | CW | Collect | 0 | 1 | Disable | Off |
| 7 | 7 | CW | Collect | 0 | 1 | Disable | Off |
| 8 | 8 | CW | Collect | 0 | 1 | Disable | Off |
| 9 | 9 | CW | Collect | 0 | 1 | Disable | Off |
| 10 | 10 | CW | Collect | 0 | 1 | Disable | Off |
| 11 | 11 | CW | Collect | 0 | 2 | Disable | Off |
| 12 | 12 | CW | Collect | 0 | 3 | Disable | Off |
| 13 | 13 | CW | Collect | 0 | 5 | Disable | Off |
| 14 | 14 | CW | Collect | 0 | 10 | Disable | Off |
| 15 | 15 | CW | Collect | 0 | 30 | Disable | Off |
| 16 | 16 | CW | Collect | 0 | 1 | Disable | Off |
| 17 | 16 | CW | Inject | 0 | 10 | Disable | On |

1 GC Valve position manually controlled through touch pad of GC

Once the contamination region was flushed out, the samples were sequentially sent to the GC for analysis (see Table A3.7). Analysis time for each sample (including cool down time) was 105 min during summer months, but can be reduced to 95 min during winter months.

At the conclusion of the product analysis, the reaction program was stopped from the Automatic Cycle screen. The reactor was removed by disconnecting valves V-R12 and V-R13. The top gland of the reactor was removed and the entire contents were poured into a large beaker. The catalyst was separated from the glass beads by sieving, and retained for spent catalyst characterization. The glass beads were re-cycled by washing with double de-ionized water until all particulate matter was removed, and then dried overnight at 80°C. The reactor was cleaned to remove catalyst residue from the internal surfaces ,and prepare it for the next experiment.

**Table A3.7:** Sample Control Recipe for Reaction - Product Analysis
(15 samples analysed)

| Step | Loop No | Direction (CW/CCW) | Sample (Collect/ Inject) | GC Delay [sec] | Dwell Time [min] | GC Enable (Enable/ Disable) | GC Valve[1] (Off/On) |
|---|---|---|---|---|---|---|---|
| 1 | 1 | CW | Inject | 0 | 105 | Enable | Off |
| 2 | 2 | CW | Inject | 0 | 105 | Enable | Off |
| 6 | 3 | CW | Inject | 0 | 105 | Enable | Off |
| 4 | 4 | CW | Inject | 0 | 105 | Enable | Off |
| 5 | 5 | CW | Inject | 0 | 105 | Enable | Off |
| 6 | 6 | CW | Inject | 0 | 105 | Enable | Off |
| 7 | 7 | CW | Inject | 0 | 105 | Enable | Off |
| 8 | 8 | CW | Inject | 0 | 105 | Enable | Off |
| 9 | 9 | CW | Inject | 0 | 105 | Enable | Off |
| 10 | 10 | CW | Inject | 0 | 105 | Enable | Off |
| 11 | 11 | CW | Inject | 0 | 105 | Enable | Off |
| 12 | 12 | CW | Inject | 0 | 105 | Enable | Off |
| 13 | 13 | CW | Inject | 0 | 105 | Enable | Off |
| 14 | 14 | CW | Inject | 0 | 105 | Enable | Off |
| 15 | 15 | CW | Inject | 0 | 105 | Enable | Off |
| 16 | 16 | CW | Collect | 0 | 999 | Disable | Off |
| 17 | 16 | CW | Collect | 0 | 999 | Disable | Off |

1 GC Valve position manually controlled through touch pad of GC

## A3.2 SAMPLE CALCULATIONS

### A3.2.1 Butene WHSV

(Run F66EMT)

The butene mass flow rate was calculated using GC feed analysis and pump flow rate (see Table A3.7).

From Table A3.7, 1-$C_4^=$ mass flow rate = 0.09197 g/min.

Butene WHSV

$$= \frac{0.09197 \text{ g } 1\text{-}C_4^{=}}{\text{min}} \left| \frac{60 \text{ min}}{\text{h}} \right| \frac{}{2.78 \text{ g calcined catalyst}}$$

$$= 2.0 \text{ h}^{-1}$$

**Table A3.7:** Calculation of Butene Mass Flow Rate for Run F66EMT (Total liquid feed flow = 2.78 mL/min)

| Component | GC Analysis [mass %] | Density[1] [g/mL] | Volume[2] [mL] | Volume[3] [%] | Volumetric Flow Rate[4] [mL/min] | Mass Flow Rate[5] [mL/min] |
|---|---|---|---|---|---|---|
| $C_3$ | 0.77 | 0.582 | 0.0132 | 0.74 | 0.02050 | 0.01193 |
| *i*-$C_4$ | 91.08 | 0.557 | 1.6353 | 91.54 | 2.54475 | 1.41743 |
| 1-$C_4^{=}$ | 5.91 | 0.595 | 0.0993 | 5.56 | 0.15457 | 0.09197 |
| *n*-$C_4$ | 2.24 | 0.579 | 0.0387 | 2.16 | 0.06017 | 0.03484 |
| Total | | | 1.78644 | | 2.78 | 1.55617 |

1 data from Reid et al, 1977
2 basis of 100 g feed mixture: volume of component i [mL] = mass of component i [g] x density of component i [g/mL]
3 volume % of component i = volume component i [mL] ÷ total feed volume [mL] (basis 100 g feed)
4 volumetric flow rate of component i [mL/min] = volume % component ÷ 100 x Total Feed Volumetric Flow Rate [mL/min]
5 Mass flow rate of component i [g/min] = volumetric flow rate of component i [mL/min] x density of component i [g/mL]

### A3.2.2 Butene Conversion

(Run F66EMT)

Mass Fraction of 1-$C_4^{=}$ Content in Feed = 0.0591 (see Table A3.7)

TOS = 1 min

1-$C_4^{=}$ Peak Area = 110200 (see Appendix A4.2)

Total Sample Peak Area = 61907245 (see Appendix A4.2)

Butene Conversion

$$= \frac{\left[ 0.0591 - \frac{110200}{61907245} \right]}{0.0591} \times 100\ \%$$

$$= 97\ \%$$

### A3.2.3 Mass Balance in Flow Reactor

(Run F66EMT)

IN

2.87 Mass of $C_4^=$ converted during 1 h reaction period [g]

1.80 Mass of *i*-$C_4$ converted during Useful Catalyst Lifetime[1] [g]

4.67 Total Mass In [g]

OUT

1.43 Mass Liquid Collected over 1 h reaction period [g]

0.24 Mass Solid retained on Catalyst Surface (TGA/DTA)[2] [g]

1.67 Total Mass Out [g]

1 mass of *i*-$C_4$ converted ~ $C_4^=$ mass flow rate x Useful Catalyst Lifetime period

2 mass solid retained = total mass % (TGA/DTA) x 2.78 g catalyst

Mass Balance

$$= \frac{1.67}{4.67} \times 100\ \%$$

$$= 36\ \%$$

### A3.2.4 Number of Successful Catalyst Cycles

(Run F21Y)

$C_4^=$ mass flow rate = 0.1167814 g/min

Useful Catalyst Lifetime period = 4.5 min

mass catalyst = 2.781 g (calcined)

Acid site density = 110 + 41 = 151 μmol Al/g catalyst (see Table 2.5)

Time Required to Saturate Catalyst Surface with Butene

$$= \frac{2.781\ \text{g calcined catalyst}}{} \left| \frac{(110+41)\ \mu\text{mol Al}}{\text{g cat}} \right| \frac{1\ \mu\text{mol } C_4^=}{1\ \mu\text{mol Al}} \left| \frac{\text{mol } C_4^=}{10^6\ \mu\text{mol } C_4^=} \right.$$

$$\times \frac{56.108\ \text{g } C_4^=}{\text{mol } C_4^=} \left| \frac{\text{min}}{0.1167814\ C_4^=} \right.$$

= 0.201757 min for saturation of all acid sites with $C_4^=$

# Successful Catalyst Cycles

$$= \frac{4.5\ \text{min}}{0.201757\ \text{min}}$$

= 22 cycles

### A3.2.5 Lennard Jones Diameter

The Lennard-Jones diameters were calculated for the TMP isomers using method outlined in Reid et al, 1977, pg 24

$$\sigma\left(\frac{P_c}{T_c}\right)^{1/3} = 2.3551 - 0.087\,\omega$$

Values for $P_c$, $T_c$ and $\omega$ are taken from Reid et al, 1977.

**Table A3.8:** Calculation of Lennard-Jones Diameter for TMP Isomers

| Component | $P_c$ [atm] | $T_c$ [K] | $\omega$ | Lennard-Jones Diameter [Å] |
|---|---|---|---|---|
| 2,2,4-TMP | 25.3 | 543.9 | 0.303 | 6.5 |
| 2,2,3-TMP | 26.9 | 563.4 | 0.297 | 6.4 |
| 2,3,4-TMP | 26.9 | 566.3 | 0.317 | 6.4 |
| 2,3,3-TMP | 27.8 | 573.5 | 0.290 | 6.4 |

# Appendix 4:

# Raw Data

## A4.1 EXPERIMENTAL SUMMARY FOR PROCESS AND CATALYST EFFECTS

**Table A4.1:** Experimental Summary for Effect of Calcination Temperature ($t_{calc}$=3h; P=382psig; I/O=11; $t_{rxn}$=1h)

| Catalyst | $T_{rxn}$ [°C] | $T_{calc}$=425°C | $T_{calc}$=540°C |
|---|---|---|---|
| EMT | 55 | F28EMT | F23EMT |
| | 77 | F31EMT | |
| | 88 | | F22EMT |
| | 100 | F34EMT | |
| Y | 70 | F29Y | |
| | 86 | | F21Y |
| | 100 | F33Y | |

**Table A4.2:** Experimental Summary for Effect of Reaction Temperature ($T_{calc}$=425°C; $t_{calc}$=3h; P=382psig; I/O=11; $t_{rxn}$=1h)

| Catalyst | $T_{rxn}$ [°C] | Run Number |
|---|---|---|
| EMT | 33 | F25EMT |
| | 55 | F28EMT |
| | 77 | F31EMT |
| | 100 | F34EMT |
| Y | 29 | F27Y |
| | 53 | F24Y, F36Y |
| | 70 | F29Y |
| | 100 | F33Y |

**Table A4.3:** Experimental Summary for Effect of Butene WHSV
(Y; $T_{calc}$=540°C; $t_{calc}$=3h ;$T_{rxn}$=80°C; P=382psig)

| Butene WHSV [$h^{-1}$] | Duration [min] | I/O | Run Number |
|---|---|---|---|
| 0.51 | 19 | 58 | F11Y |
| | 55 | 58 | F13Y |
| 2.57 | 19 | 12 | F21Y |

**Table A4.4:** Experimental Summary for Effect of Pt Supported on Acidic Carrier
($T_{calc}$=325°C; $t_{calc}$=3h; $T_{red}$=425°C; $t_{red}$=3h; $T_{rxn}$=50°C; P=382psig; I/O=15)

| Catalyst | Pt Loading [mass %] | Nomenclature | Fresh | Regenerated |
|---|---|---|---|---|
| EMT | 0 | EMT | F66EMT<br>F68AEMT | F67EMTr |
| | 0.1 | 0.1%Pt/EMT | F62Pt1EMT | F45Pt1EMTr<br>F63Pt1EMTr |
| | 0.5 | 0.5%Pt/EMT | F49Pt5EMT | F48Pt5EMTr<br>F50Pt5EMTr<br>F60Pt5EMTr |
| Y | 0 | Y | F54Y | F55Yr |
| | 0.5 | 0.5%Pt/Y | F44Pt5Y<br>F56Pt5Y | F58Pt5Yr |

**Table A4.5: Complete Experimental Summary**

| Run | Catalyst System | $T_{calc}$ [°C] | $T_{red}$ [°C] | $T_{rxn}$ [°C] | Duration [min] | I/O (molar) | $C_4^=$ WHSV [$h^{-1}$] | S.A. Spent [$m^2/g$] | S.A. Fresh [$m^2/g$] | Yield [$gC_5^+/gcat/gC_4^=fed$] |
|---|---|---|---|---|---|---|---|---|---|---|
| F11Y | Y | 540 | n.a. | 80 | 19 | 57.8 | 0.51 | 407 | 620 | n.a. |
| F13Y | Y | 540 | n.a. | 80 | 55 | 58.4 | 0.51 | 284 | 620 | n.a. |
| F15Y Pulse | Y, Pulse feed | 540 | n.a. | 80 | 40 | 59 | 0.49 | 396 | 620 | n.a. |
| | | | | | 30 | 3000 | 0.01 | | | |
| | | | | | 30 | 59 | 0.49 | | | |
| | | | | | 20 | 3000 | 0.01 | | | |
| F21Y | Y | 540 | n.a. | 86 | 19 | 12.0 | 2.57 | 205 | 620 | n.a. |
| F22EMT | EMT | 540 | n.a. | 88 | 15 | 11.6 | 2.62 | 121 | 755 | n.a. |
| F23EMT | EMT | 540 | n.a. | 56 | 13 | 11.7 | 2.55 | 148 | 755 | n.a. |
| F24Y | Y | 425 | n.a. | 56 | 60 | 11.1 | 2.70 | 372 | 620 | n.a. |
| F25EMT | EMT | 425 | n.a. | 33 | 60 | 11.1 | 2.71 | 470 | 755 | n.a. |
| F27Y | Y | 425 | n.a. | 29 | 60 | 11.2 | 2.72 | 386 | 620 | n.a. |
| F28EMT | EMT | 425 | n.a. | 55 | 60 | 11.3 | 2.68 | 377 | 755 | 0.101 |
| F29Y | Y | 425 | n.a. | 70 | 60 | 11.2 | 2.67 | 374 | 620 | 0.084 |
| F31EMT | EMT | 425 | n.a. | 77 | 60 | 11.4 | 2.65 | 348 | 755 | 0.104 |
| F33Y | Y | 425 | n.a. | 100 | 60 | 11.5 | 2.62 | 329 | 620 | 0.088 |
| F34EMT | EMT | 425 | n.a. | 100 | 60 | 11.5 | 2.61 | 309 | 755 | 0.113 |
| F36Y | Y | 425 | n.a. | 49 | 60 | 11.5 | 2.61 | 350 | 620 | 0.064 |
| F44Pt5Y | 0.5%Pt/Y | 325 | 425 | 52 | 60 | 15.3 | 2.00 | 280 | 581 | 0.076 |
| F45Pt1EMTr | recalc. 0.1%Pt/EMT | 325 | 425 | 52 | 60 | 15.2 | 2.02 | 254 | 616 | 0.092 |
| F48Pt5EMTr | recalc. 0.5%Pt/EMT | 325 | 425 | 52 | 60 | 15.2 | 2.03 | 294 | 589 | 0.109 |
| F49Pt5EMT | 0.5%Pt/EMT | 325 | 425 | 51 | 60 | 15.2 | 2.02 | recalc | 589 | 0.095 |
| F50Pt5EMTr | recalc. 0.5%Pt/EMT | 325 | 425 | 50 | 60 | 15.0 | 2.05 | recalc | 589 | 0.081 |
| F54Y | Y | 425 | n.a. | 50 | 60 | 15.2 | 2.03 | 372 | 620 | 0.068 |
| F55Yr | recalc. Y | 425 | n.a. | 50 | 60 | 14.4 | 2.13 | 281 | 620 | 0.049 |
| F56Pt5Y | 0.5%Pt/Y | 325 | 425 | 53 | 60 | 14.5 | 2.12 | recalc | 581 | 0.050 |
| F58Pt5Yr | recalc. 0.5%Pt/Y | 325 | 425 | 52 | 60 | 14.5 | 2.11 | 260 | 581 | 0.050 |
| F60Pt5EMTr | recalc. 0.5%Pt/EMT | 325 | 425 | 52 | 60 | 14.5 | 2.11 | 198 | 589 | 0.073 |
| F62Pt1EMT | 0.1%Pt/EMT | 325 | 425 | 50 | 60 | 14.6 | 2.10 | recalc | 616 | 0.078 |
| F63Pt1EMTr | recalc. 0.1%Pt/EMT | 325 | 425 | 50 | 60 | 14.8 | 2.07 | 231 | 616 | 0.064 |
| F66EMT | EMT | 425 | n.a. | 53 | 60 | 14.9 | 2.07 | 377 | 755 | 0.079 |
| F67EMTr | recalc. EMT | 425 | n.a. | 52 | 60 | 15.0 | 2.06 | 287 | 755 | 0.062 |
| F68EMT | EMT | 425 | n.a. | 53 | 60 | 14.9 | 2.06 | 124 | 385.5 | 0.085 |

F11Y

(Y; Tcalc=540degC; Trxn=80degC; P=382psig; I/O=57.8; butene WHSV=0.51h-1; t=19min; mcat=2.78g)

| Samp t [min] | 6 | 20 | 25 | 30 | **** | 60 | | |
|---|---|---|---|---|---|---|---|---|
| **T.O.S. [min.]** | **1** | **15** | **20** | **25** | **51** | **55** | | |
| 1-C4= Disapp. [%] | 100 | 100 | 100 | 100 | | 100 | **** | data from pulse experiment (F15Y pulse) |
| t-2-C4= Prod. [%] | 0 | 0 | 0 | 0 | | 24 | | |
| c-2-C4= Prod. [%] | 0 | 0 | 0 | 0 | | 0 | | |
| **Butene Disapp. [%]** | **100** | **100** | **100** | **100** | **80** | **76** | | |
| n-Butane Change [%] | 3 | 1 | 1 | 5 | | 3 | | |
| | | | | | | | | |
| ***C5+ Product Analysis [mass %]*** | | | | | | | | |
| C5-C7 | 21 | 32 | 32 | 32 | | 15 | | |
| **C8** | **78** | **63** | **65** | **66** | | **83** | | |
| C9+ | 1 | 5 | 3 | 2 | | 2 | | |
| | | | | | | | | |
| ***C8 Distribution [mass %]*** | | | | | | | | |
| **TMP** | **83** | **76** | **75** | **76** | | **61** | | |
| DMH | 13 | 20 | 20 | 20 | | 27 | | |
| C8= | 3 | 4 | 5 | 5 | | 12 | | |
| | | | | | | | | |
| ***TMP Isomer Distribution [%]*** | | | | | | | | |
| **2,2,4-TMP** | 39 | 50 | 46 | 46 | | 30 | | |
| **2,2,3-TMP** | 7 | 9 | 8 | 8 | | 5 | | |
| **2,3,4-TMP** | 25 | 15 | 18 | 19 | | 33 | | |
| **2,3,3-TMP** | 30 | 26 | 28 | 28 | | 32 | | |
| | | | | | | | | |
| ***Indicators [mass fraction]*** | | | | | | | | |
| **TMP** | **6.18** | **3.89** | **3.75** | **3.89** | | **2.28** | | |
| **DMH** | | | | | | | | |
| TMP+DMH | 20.0 | 7.8 | 9.6 | 12.3 | | 6.3 | | |
| C8= + C9+ | | | | | | | | |
| (2,2,3-+2,2,4-TMP) | 0.83 | 1.45 | 1.18 | 1.15 | | 0.54 | | |
| (2,3,4-+2,3,3-TMP) | | | | | | | | |
| | | | | | | | | |
| ***DMH Isomer Distribution [%]*** | | | | | | | | |
| 2,5-DMH | 19 | 19 | 16 | 16 | | 0 | | |
| 2,4-DMH | 40 | 40 | 36 | 35 | | 21 | | |
| 2,3-DMH | 41 | 35 | 37 | 37 | | 36 | | |
| 3,4-DMH | 0 | 6 | 11 | 12 | | 42 | | |

F11Y

(Y, Tcalc=540degC, Trxn=80degC, P=382psig, I/O=57 8, butene WHSV=0 51h-1, t=19min, mcat=2 78g)

| TOS [min] | 1 | 15 | 20 | 25 | 51 | 55 | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Propane | 343700 | 375740 | 361180 | 452700 | | 442320 | | | | | |
| Isobutane | 39386540 | 37916100 | 39916360 | 50170900 | | 50037100 | | | | | |
| 1-butene | | | | | | | | | | | |
| n-butane | 1071920 | 1022900 | 1070260 | 1412900 | | 1352460 | | | | | |
| t-2-butene | | | | | | 218100 | | | | | |
| c-2-butene | | | | | | | | | | | |
| | | | | | | | | | | | |
| **C5-C7** | 113390 | 280196 | 284538 | 372467 | | 42337 | | | | | |
| C5 | | 108020 | 110020 | 141400 | | | | | | | |
| 2,3-DMB | 39571 | 53547 | 55887 | 73472 | | 14620 | | | | | |
| 2,2-DMP | 9505 | 17744 | 17095 | 21643 | | | | | | | |
| 3-MP | 9268 | 14752 | 14736 | 19566 | | 5500 | | | | | |
| 2,4-DMP | 36961 | 46244 | 47139 | 62896 | | 12608 | | | | | |
| 2,2,3-TMB | | | | | | | | | | | |
| 2-MHx | | 6032 | 5262 | 7350 | | | | | | | |
| 2,3-DMP | 18085 | 27511 | 28264 | 38161 | | 9609 | | | | | |
| 3-MHx | | 6346 | 6135 | 7979 | | | | | | | |
| | | | | | | | | | | | |
| **C8** | 413742 | 550303 | 584973 | 780762 | | 226433 | | | | | |
| **2,2,4-TMP** | 132852 | 209038 | 202122 | 271955 | | 41756 | | | | | |
| 2,5-DMHx | 10307 | 20161 | 19051 | 24668 | | | | | | | |
| 2,2,3-TMP | 22770 | 39700 | 35431 | 45379 | | 6931 | | | | | |
| 2,4-DMHx | 22389 | 43617 | 41889 | 53598 | | 13063 | | | | | |
| 2,3,4-TMP | 85449 | 63911 | 79493 | 110318 | | 45652 | | | | | |
| 2,3,3-TMP | 103011 | 107701 | 122434 | 165427 | | 44621 | | | | | |
| 2,3-DMHx | 23001 | 38110 | 43260 | 56436 | | 21948 | | | | | |
| 1 DMHx= | | | | | | | | | | | |
| 3,4-DMHx | | 6073 | 12974 | 17614 | | 25846 | | | | | |
| 2 DMHx= | | | | | | 14384 | | | | | |
| 3 DMHx= | | | | | | 7193 | | | | | |
| 4 DMHx= | | | | | | | | | | | |
| 5 DMHx= | 13963 | 21992 | 22997 | 28429 | | 5039 | | | | | |
| 6 DMHx= | | | 5322 | 6938 | | | | | | | |
| 7 DMHx= | | | | | | | | | | | |
| 8 DMHx= | | | | | | | | | | | |
| | | | | | | | | | | | |
| **C9+** | 6032 | 46099 | 29478 | 25190 | | 5322 | | | | | |
| | | | | | | | | | | | |
| **C5+** | 533164 | 876598 | 898989 | 1178419 | | 274092 | | | | | |
| | | | | | | | | | | | |
| Tot Peak Area | 41335324 | 40191338 | 42246789 | 53214919 | | 52324072 | | | | | |
| | | | | | | | | | | | |
| ***Feed Analysis*** | Inj 1 | Inj 2 | Inj 3 | Inj 4 | | Inj 5 | Inj 6 | Inj 7 | Inj 8 | Avg | Mass % |
| C3 | 21811 | 22132 | 23017 | 23695 | | 20052 | 23270 | 20836 | 24148 | 22370 | 0 86 |
| i-C4 | 2413079 | 2252501 | 2532986 | 2627719 | | 2191759 | 2514630 | 2173455 | 2657030 | 2420395 | 94 85 |
| 1-C4= | 36806 | 35099 | 47252 | 36807 | | 47987 | 35109 | 45815 | 35111 | 39998 | 1 77 |
| n-C4 | 62822 | 59993 | 67270 | 71747 | | 56347 | 66435 | 57014 | 70493 | 64015 | 2 52 |
| **I/O Mass Ratio** | 65 56 | 64 18 | 53 61 | 71 39 | | 45 67 | 71 62 | 47 44 | 75 68 | **60.51** | |

F13Y

(Y; Tcalc=540degC; Trxn=80degC; P=382psig; I/O=58.42; butene WHSV=0.51h-1; t=55min; mcat=2.78g)

| Samp t [min] | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 17 | 20 | 25 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **T.O.S. [min.]** | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** | **9** | **10** | **12** | **15** | **20** |
| 1-C4= Disapp. [%] | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| t-2-C4= Prod. [%] | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| c-2-C4= Prod. [%] | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| **Butene Disapp. [%]** | **100** | **100** | **100** | **100** | **100** | **100** | **100** | **100** | **100** | **100** | **100** | **100** | **100** |
| n-Butane Change [%] | 6 | 7 | 5 | 5 | 6 | -1 | 6 | 7 | 7 | 7 | 4 | 6 | 6 |
| ***C5+ Product Analysis [mass %]*** | | | | | | | | | | | | | |
| C5-C7 | 18 | 16 | 36 | 35 | 35 | 27 | 34 | 22 | 22 | 23 | 23 | 32 | 30 |
| **C8** | **67** | **56** | **57** | **64** | **61** | **73** | **58** | **69** | **78** | **76** | **75** | **65** | **63** |
| C9+ | 16 | 28 | 7 | 1 | 3 | 0 | 7 | 8 | 0 | 1 | 2 | 3 | 6 |
| ***C8 Distribution [mass %]*** | | | | | | | | | | | | | |
| **TMP** | **81** | **80** | **78** | **77** | **77** | **78** | **76** | **77** | **78** | **77** | **78** | **76** | **75** |
| DMH | 15 | 16 | 18 | 19 | 19 | 19 | 20 | 19 | 18 | 19 | 19 | 20 | 20 |
| C8= | 4 | 4 | 4 | 4 | 4 | 3 | 4 | 4 | 4 | 4 | 3 | 5 | 5 |
| ***TMP Isomer Distribution [%]*** | | | | | | | | | | | | | |
| **2,2,4-TMP** | **48** | **49** | **52** | **51** | **53** | **54** | **53** | **51** | **49** | **50** | **51** | **48** | **47** |
| 2,2,3-TMP | 9 | 10 | 11 | 11 | 11 | 12 | 11 | 10 | 9 | 10 | 9 | 9 | 8 |
| 2,3,4-TMP | 17 | 15 | 14 | 14 | 13 | 12 | 13 | 14 | 16 | 15 | 14 | 16 | 18 |
| 2,3,3-TMP | 26 | 26 | 24 | 24 | 23 | 22 | 23 | 25 | 26 | 26 | 25 | 27 | 28 |
| ***Indicators [mass fraction]*** | | | | | | | | | | | | | |
| **TMP** | **6.39** | **3.50** | **3.48** | **4.02** | **3.98** | **4.06** | **3.78** | **4.12** | **4.35** | **4.17** | **4.08** | **3.85** | **3.79** |
| **DMH** | | | | | | | | | | | | | |
| TMP+DMH | 3.5 | 1.8 | 5.8 | 15.5 | 10.1 | 29.4 | 5.6 | 6.1 | 26.1 | 18.0 | 15.0 | 10.4 | 6.2 |
| C8= + C9+ | | | | | | | | | | | | | |
| (2,2,3-+2,2,4-TMP) | 1.33 | 1.44 | 1.68 | 1.67 | 1.80 | 1.95 | 1.72 | 1.58 | 1.41 | 1.46 | 1.56 | 1.32 | 1.22 |
| (2,3,4-+2,3,3-TMP) | | | | | | | | | | | | | |
| ***DMH Isomer Distribution [%]*** | | | | | | | | | | | | | |
| 2,5-DMH | 22 | 22 | 23 | 21 | 22 | 23 | 22 | 21 | 20 | 20 | 20 | 18 | 17 |
| 2,4-DMH | 44 | 45 | 45 | 42 | 44 | 47 | 45 | 45 | 43 | 43 | 46 | 40 | 39 |
| 2,3-DMH | 35 | 33 | 33 | 32 | 30 | 29 | 34 | 34 | 38 | 37 | 34 | 37 | 37 |
| 3,4-DMH | 0 | 0 | 0 | 5 | 5 | 0 | 0 | 0 | 0 | 0 | 0 | 6 | 7 |

F13Y

(Y, Tcalc=540degC, Trxn=80degC, P=382psig, I/O=58 42, butene WHSV=0 51h-1, t=55min, mcat=2 78g)

| TOS [min] | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 12 | 15 | 20 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Propane | 295980 | 103900 | 284600 | 333920 | 313200 | 271860 | 247800 | 280480 | 302100 | 273620 | | 322820 | 321740 |
| Isobutane | 36150300 | 14091200 | 30434160 | 37866480 | 35353320 | 23818240 | 29806340 | 31409320 | 32863680 | 29198560 | 12106300 | 36079460 | 36385780 |
| 1-butene | | | | | | | | | | | | | |
| n-butane | 943700 | 371140 | 787400 | 986060 | 931080 | 575980 | 784640 | 825580 | 861280 | 771040 | 308020 | 949900 | 952600 |
| t-2-butene | | | | | | | | | | | | | |
| c-2-butene | | | | | | | | | | | | | |
| **C6-C7** | 108674 | 68785 | 266162 | 354706 | 328330 | 81491 | 299562 | 139576 | 110014 | 124476 | 60761 | 266573 | 268358 |
| C5 | | | 111380 | 135260 | 130840 | | 118060 | | | | | 102140 | 101060 |
| 2,3-DMB | 34187 | 22517 | 49730 | 67384 | 61199 | 27720 | 56149 | 42380 | 37259 | 41812 | 20055 | 51232 | 52290 |
| 2,2-DMP | 10277 | 6700 | 16672 | 24063 | 21305 | 10307 | 20330 | 15061 | 11754 | 13690 | 6803 | 16404 | 16538 |
| 3-MP | 9390 | 5989 | 13136 | 18718 | 16462 | 7896 | 15806 | 11953 | 9734 | 11222 | 5526 | 13836 | 14085 |
| 2,4-DMP | 35617 | 21936 | 41805 | 57527 | 53237 | 22479 | 47001 | 36131 | 32360 | 36219 | 18000 | 44598 | 45077 |
| 2,2,3-TMB | | | | | | | | | | | | | |
| 2-MHx | | | 5631 | 8450 | 7728 | | 7225 | 5382 | | | | 5492 | 5696 |
| 2,3-DMP | 19203 | 11643 | 22625 | 34807 | 30298 | 13089 | 27919 | 22857 | 18907 | 21533 | 10377 | 26762 | 27552 |
| 3-MHx | | | 5183 | 8497 | 7261 | | 7072 | 5812 | | | | 6109 | 6060 |
| **C8** | 409673 | 234892 | 414051 | 650486 | 567028 | 220680 | 505648 | 434145 | 387425 | 417734 | 200328 | 549012 | 554710 |
| **2,2,4-TMP** | **158516** | **92196** | **167640** | **257046** | **230593** | **93167** | **201061** | **171089** | **148720** | **161297** | **80021** | **199882** | **194356** |
| 2,5-DMHx | 13395 | 8191 | 16474 | 25775 | 23590 | 9842 | 21924 | 17378 | 13791 | 15782 | 7790 | 19607 | 18939 |
| 2,2,3-TMP | 31402 | 18303 | 34964 | 55245 | 49142 | 20003 | 40340 | 34379 | 28565 | 31002 | 14703 | 36531 | 34346 |
| 2,4-DMHx | 27102 | 17043 | 32669 | 52566 | 47495 | 19974 | 45089 | 36565 | 29651 | 33431 | 17401 | 42602 | 42479 |
| 2,3,4-TMP | 55705 | 28951 | 44278 | 68650 | 55942 | 21032 | 51260 | 47786 | 47145 | 48456 | 22314 | 67472 | 73180 |
| 2,3,3-TMP | 86626 | 47968 | 76670 | 118588 | 99330 | 37058 | 89269 | 82189 | 78978 | 82809 | 38385 | 111008 | 115031 |
| 2,3-DMHx | 21560 | 12690 | 23909 | 39884 | 32886 | 12344 | 34157 | 27458 | 26285 | 28382 | 12865 | 39301 | 41178 |
| 1 DMHx= | | | | | | | | | | | | 5024 | 5667 |
| 3,4-DMHx | | | | 6135 | 5212 | | | | | | | 6119 | 7366 |
| 2 DMHx= | | | | | | | | | | | | | |
| 3 DMHx= | | | | | | | | | | | | | |
| 4 DMHx= | | | | | | | | | | | | | |
| 5 DMHx= | 15367 | 9550 | 17447 | 26597 | 22838 | 7260 | 22548 | 17301 | 14290 | 16575 | 6849 | 21466 | 22169 |
| 6 DMHx= | | | | | | | | | | | | | |
| **C9+** | 96962 | 118918 | 50434 | 13738 | 31119 | 0 | 64181 | 51030 | 0 | 5761 | 6032 | 23587 | 56827 |
| **C6+** | 615309 | 422595 | 730647 | 1018930 | 926477 | 302171 | 869391 | 624751 | 497439 | 547971 | 267121 | 839172 | 879895 |
| Tot Peak Area | 38005289 | 14884935 | 32236807 | 40205390 | 37524077 | 24968251 | 31708171 | 33140131 | 34524499 | 30791191 | 12681441 | 38191352 | 38540015 |
| ***Feed Analysis*** | Inj 1 | Inj 2 | Inj 3 | Inj 4 | Inj 5 | Inj 6 | Inj 7 | Inj 8 | Avg | Mass % | | | |
| C3 | 14971 | 11396 | 13370 | 13643 | 15565 | 14025 | 13852 | 14427 | 13906 | 0 92 | | | |
| i-C4 | 1774607 | 1046230 | 1382735 | 1544128 | 1855039 | 1632041 | 1530496 | 1635923 | 1550150 | 95 14 | | | |
| 1-C4= | 29137 | 18425 | 23354 | 24713 | 33291 | 25524 | 24331 | 28423 | 25900 | 1 61 | | | |
| n-C4 | 44016 | 24789 | 33947 | 38993 | 45873 | 40636 | 37740 | 40317 | 38289 | 2 34 | | | |
| I/O Mass Ratio | 60 91 | 56 78 | 59 21 | 62 48 | 55 72 | 63 94 | 62 90 | 57 56 | 59 85 | | | | |

F15Y Pulse

(Y pulse feed; Tcalc=540degC; Trxn=80degC; P=382psig; I/O=59(40min),I/O=3000(30min),I/O=59(30min),I/O=3000(20min); t=2h; mcat=2.78g)

| Samp t [min] | 6 | 20 | 35 | 40 | 45 | 55 | 60 | 70 | 85 | 90 | 100 | 105 | 125 | 125 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **T.O.S. [min.]** | **1** | **15** | **30** | **35** | **40** | **50** | **55** | **65** | **80** | **85** | **95** | **100** | **120** | **120** |
| 1-C4= Disapp. [%] | 100 | 100 | 100 | 100 | 100 | 76 | 77 | 74 | 100 | 100 | 100 | 100 | 100 | 100 |
| t-2-C4= Prod. [%] | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 5 | 0 |
| c-2-C4= Prod. [%] | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| **Butene Disapp. [%]** | **100** | **100** | **100** | **100** | **100** | **76** | **77** | **74** | **100** | **100** | **100** | **100** | **95** | **100** |
| n-Butane Change [%] | -12 | 2 | 0 | 4 | -2 | 3 | 4 | 6 | 3 | 1 | 3 | 2 | 45 | -100 |
| | | | | | | | | | | | | | | |
| ***C5+ Product Analysis [mass %]*** | | | | | | | | | | | | | | |
| C5-C7 | 0 | 32 | 18 | 15 | 6 | 6 | 11 | 0 | 18 | 17 | 14 | 9 | 7 | 100 |
| **C8** | **6** | **62** | **70** | **69** | **48** | **54** | **77** | **49** | **69** | **67** | **75** | **61** | **45** | **0** |
| C9+ | 94 | 6 | 12 | 16 | 46 | 39 | 12 | 51 | 13 | 17 | 11 | 30 | 48 | 0 |
| | | | | | | | | | | | | | | |
| ***C8 Distribution [mass %]*** | | | | | | | | | | | | | | |
| **TMP** | **100** | **76** | **74** | **82** | **90** | **90** | **91** | **100** | **76** | **76** | **84** | **92** | **85** | **0** |
| DMH | 0 | 20 | 21 | 16 | 10 | 10 | 9 | 0 | 20 | 20 | 16 | 8 | 11 | 0 |
| C8= | 0 | 4 | 4 | 2 | 0 | 0 | 0 | 0 | 4 | 4 | 0 | 0 | 4 | 0 |
| | | | | | | | | | | | | | | |
| ***TMP Isomer Distribution [%]*** | | | | | | | | | | | | | | |
| **2,2,4-TMP** | **100** | **52** | **44** | **42** | **41** | **38** | **37** | **49** | **40** | **37** | **32** | **33** | **32** | **0** |
| 2,2,3-TMP | 0 | 10 | 8 | 7 | 5 | 5 | 5 | 0 | 6 | 5 | 4 | 0 | 4 | 0 |
| 2,3,4-TMP | 0 | 14 | 19 | 21 | 23 | 26 | 27 | 25 | 24 | 27 | 32 | 34 | 34 | 0 |
| 2,3,3-TMP | 0 | 24 | 30 | 30 | 31 | 31 | 32 | 26 | 30 | 31 | 32 | 33 | 31 | 0 |
| | | | | | | | | | | | | | | |
| ***Indicators [mass fraction]*** | | | | | | | | | | | | | | |
| **TMP** | **inf** | **3.77** | **3.47** | **5.30** | **8.82** | **8.53** | **10.39** | **#DIV/0!** | **3.83** | **3.80** | **5.10** | **11.93** | **7.63** | **0.00** |
| **DMH** | | | | | | | | | | | | | | |
| TMP+DMH | 0.07 | 7.25 | 4.57 | 3.94 | 1.04 | 1.38 | 6.46 | 0.95 | 4.36 | 3.32 | 6.56 | 2.02 | 0.86 | 0.00 |
| C8= + C9+ | | | | | | | | | | | | | | |
| **(2,2,3-+2,2,4-TMP)** | **infinite** | **1.64** | **1.06** | **0.95** | **0.85** | **0.76** | **0.71** | **0.95** | **0.84** | **0.73** | **0.57** | **0.49** | **0.55** | **0.00** |
| **(2,3,4-+2,3,3-TMP)** | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | |
| ***DMH Isomer Distribution [%]*** | | | | | | | | | | | | | | |
| **2,5-DMH** | **0** | **19** | **16** | **17** | **0** | **0** | **0** | **0** | **14** | **13** | **0** | **0** | **0** | **0** |
| **2,4-DMH** | **0** | **44** | **40** | **40** | **45** | **40** | **43** | **0** | **32** | **31** | **25** | **0** | **33** | **0** |
| **2,3-DMH** | **0** | **32** | **38** | **43** | **55** | **60** | **57** | **0** | **40** | **42** | **51** | **100** | **67** | **0** |
| **3,4-DMH** | **0** | **5** | **6** | **0** | **0** | **0** | **0** | **0** | **14** | **15** | **25** | **0** | **0** | **0** |

F15Y Pulse

(Y pulse feed, Tcalc=540degC, Trxn=80degC, P=382psig, I/O=59(40min),I/O=3000(30min),I/O=59(30min),I/O=3000(20min), t=2h, mcat=2 78g)

| TOS (min) | 1 | 15 | 30 | 35 | 40 | 50 | 55 | 65 | 80 | 85 | 95 | 100 | 120 | 120 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Propane | 110600 | 306780 | 280040 | 336320 | 207520 | 297040 | 329760 | 287900 | 346300 | 388240 | 414520 | 346140 | 2873500 | |
| Isobutane | 10521360 | 33938820 | 27255120 | 37532120 | 20957260 | 31772420 | 37252840 | 33927080 | 39156760 | 39957180 | 45583580 | 36199720 | 206100760 | |
| 1-butene | | | | | | 101600 | 112560 | 117300 | | | | | | |
| n-butane | 241800 | 914020 | 717720 | 1011900 | 532640 | 848140 | 1003040 | 925500 | 1057260 | 1056440 | 1209700 | 950820 | 7781720 | |
| t-2-butene | | | | | | | | | | | | | 147840 | |
| c-2-butene | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | |
| **C5-C7** | 0 | 295058 | 120260 | 76049 | 15065 | 16377 | 23155 | 0 | 152509 | 133482 | 41894 | 12165 | 35561 | 22323 |
| **Unknowns** | | | | | | | | | | | | | 7096 | |
| C5 | | 111620 | | | | | | | | | | | | |
| 2,3-DMB | | 56904 | 32956 | 25262 | 7454 | 8025 | 8561 | | 50163 | 44711 | 16634 | 6133 | 13996 | |
| 2,2-DMP | | 19460 | 10351 | 6556 | | | | | 13580 | 12197 | | | | |
| 3-MP | | 15480 | 9023 | 6446 | | | | | 13156 | 12107 | | | | |
| 2,4-DMP | | 49457 | 29790 | 23544 | 7611 | 8352 | 9371 | | 43253 | 39489 | 15557 | 6032 | 13200 | |
| 2,2,3-TMB | | | 19070 | | | | | | | | | | | |
| 2-MHx | | 6511 | | | | | | | | | | | | |
| 2,3-DMP | | 28879 | 19070 | 14241 | | | 5223 | | 26897 | 24978 | 9703 | | 8365 | |
| 3-MHx | | 6747 | | | | | | | 5460 | | | | | |
| | | | | | | | | | | | | | | |
| **C8** | 12667 | 568092 | 471016 | 354301 | 112191 | 139206 | 160008 | 26495 | 588083 | 538299 | 221501 | 80470 | 240690 | |
| **Unknowns** | | | | | | | | | | | | | | |
| **2,2,4-TMP** | **12667** | **226020** | **152182** | **122949** | **40822** | **47437** | **53426** | **12898** | **178692** | **151428** | **59921** | **24420** | **64407** | |
| 2,5-DMHx | | 21732 | 15993 | 9104 | | | | | 16111 | 13728 | | | | |
| 2,2,3-TMP | | 42562 | 27523 | 19660 | 5367 | 6346 | 7144 | | 26716 | 21235 | 7270 | | 7797 | |
| 2,4-DMHx | | 50261 | 40403 | 22237 | 5090 | 5865 | 6037 | | 37409 | 33055 | 8936 | | 8774 | |
| 2,3,4-TMP | | 59575 | 65778 | 62265 | 23052 | 31842 | 38773 | 6754 | 107618 | 111218 | 59569 | 25238 | 68596 | |
| 2,3,3-TMP | | 104388 | 104230 | 87194 | 31528 | 38977 | 46617 | 6845 | 136107 | 126720 | 58411 | 24590 | 63227 | |
| 1 DMHx= | | | | | | | | | | | | | | |
| 2,3-DMHx | | 37203 | 38211 | 23782 | 6332 | 8739 | 8011 | | 46897 | 45128 | 18407 | 6222 | 17969 | |
| 2 DMHx= | | | | | | | | | | | | | | |
| 3,4-DMHx | | 5464 | 6206 | | | | | | 16786 | 16094 | 8987 | | | |
| 3 DMHx= | | | | | | | | | | | | | | |
| 4 DMHx= | | | | | | | | | | | | | | |
| 5 DMHx= | | 20887 | 20490 | 7110 | | | | | 21747 | 19693 | | | 9920 | |
| 6 DMHx= | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | |
| **C9+** | 193368 | 54618 | 78118 | 81097 | 107566 | 100625 | 24780 | 27767 | 108288 | 136684 | 33786 | 39922 | 258745 | |
| | | | | | | | | | | | | | | |
| **C5+** | 206035 | 917768 | 669394 | 511447 | 234822 | 256208 | 207943 | 54262 | 848880 | 808465 | 297181 | 132557 | 534996 | 1295073 |
| | | | | | | | | | | | | | | |
| Tot Peak Area | 11079795 | 36077388 | 28922274 | 39391787 | 21932242 | 33275408 | 38906143 | 35312042 | 41409200 | 42210325 | 47504981 | 37629237 | 217438816 | 22323 |
| | | | | | | | | | | | | | | |
| **FEED ANAL.** | Inj 1 | Inj 2 | Inj 3 | Inj 4 | Inj 5 | Inj 6 | Inj 7 | Inj 8 | Avg | Mass % | | | | |
| **C3** | 20292 | 21483 | 22487 | 19923 | 18960 | 22270 | 19309 | 19577 | 20538 | 0 92 | | | | |
| **i-C4** | 2211568 | 2402444 | 2332710 | 2014358 | 2059596 | 2497250 | 1879306 | 2100364 | 2187200 | 95 34 | | | | |
| **1-C4=** | 34848 | 41680 | 31082 | 37258 | 27617 | 45973 | 24739 | 43129 | 35791 | 1 27 | | | | |
| **n-C4** | 56359 | 63921 | 60478 | 51606 | 51376 | 64387 | 46759 | 53769 | 56082 | 2 47 | | | | |

Run F21Y

(Y; Tcalc=540degC; Trxn=86degC; P=382psig; I/O=12 0; butene WHSV=2.57h-1; t=19min, mcat=2 78g)

| Samp t [min] | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 18 | 20 | 24 | 26 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **T.O.S. [min.]** | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** | **9** | **11** | **13** | **17** | **19** |
| 1-C4= Disapp. [%] | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 97 | 100 | 100 | 85 | 27 |
| t-2-C4= Prod. [%] | 0 | 0 | 0 | 0 | 7 | 21 | 28 | 33 | 36 | 40 | 38 | 33 | 10 |
| c-2-C4= Prod. [%] | 0 | 0 | 0 | 0 | 3 | 10 | 14 | 17 | 19 | 23 | 23 | 21 | 7 |
| **Butene Disapp. [%]** | **100** | **100** | **100** | **100** | **90** | **70** | **58** | **49** | **42** | **37** | **39** | **30** | **10** |
| n-Butane Change [%] | -2 | 12 | 11 | 8 | 6 | 4 | 3 | 2 | 3 | 10 | 6 | 2 | -1 |
| | | | | | | | | | | | | | |
| ***C5+ Product Analysis [mass %]*** | | | | | | | | | | | | | |
| C5-C7 | 18 | 42 | 32 | 32 | 26 | 12 | 0 | 0 | 0 | 0 | 0 | 0.0 | 0.0 |
| **C8** | **45** | **45** | **34** | **43** | **42** | **41** | **13** | **21** | **35** | **27** | **44** | **43** | **65** |
| C9+ | 37 | 14 | 34 | 25 | 32 | 47 | 87 | 79 | 65 | 73 | 56 | 57 | 35 |
| | | | | | | | | | | | | | |
| ***C8 Distribution [mass %]*** | | | | | | | | | | | | | |
| **TMP** | **63** | **68** | **76** | **64** | **58** | **48** | **23** | **0** | **0** | **2** | **0** | **0** | **0** |
| DMH | 26 | 24 | 17 | 23 | 22 | 31 | 38 | 33 | 36 | 29 | 33 | 30 | 17 |
| C8= | 11 | 8 | 7 | 12 | 20 | 22 | 39 | 67 | 64 | 68 | 67 | 70 | 83 |
| | | | | | | | | | | | | | |
| ***TMP Isomer Distribution [%]*** | | | | | | | | | | | | | |
| **2,2,4-TMP** | **41** | **52** | **48** | **45** | **39** | **33** | **50** | **0** | **0** | **0** | **0** | **0** | **0** |
| 2,2,3-TMP | 6 | 6 | 3 | 4 | 3 | 10 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 2,3,4-TMP | 22 | 18 | 21 | 23 | 27 | 29 | 50 | 0 | 0 | 100 | 0 | 0 | 0 |
| 2,3,3-TMP | 31 | 25 | 28 | 28 | 30 | 28 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| | | | | | | | | | | | | | |
| ***Indicators [mass fraction]*** | | | | | | | | | | | | | |
| **TMP** | **2.46** | **2.89** | **4.44** | **2.74** | **2.63** | **1.55** | **0.60** | **0.00** | **0.00** | **0.08** | **0.00** | **0.00** | **0.00** |
| **DMH** | | | | | | | | | | | | | |
| TMP+DMH | 0.95 | 2.37 | 0.88 | 1.26 | 0.84 | 0.57 | 0.09 | 0.08 | 0.14 | 0.09 | 0.17 | 0.15 | 0.13 |
| C8= + C9+ | | | | | | | | | | | | | |
| (2,2,3-+2,2,4-TMP) | 0.89 | 1.36 | 1.07 | 0.96 | 0.75 | 0.75 | 1.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| (2,3,4-+2,3,3-TMP) | | | | | | | | | | | | | |
| | | | | | | | | | | | | | |
| ***DMH Isomer Distribution [%]*** | | | | | | | | | | | | | |
| 2,5-DMH | 17 | 20 | 19 | 17 | 15 | 5 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 2,4-DMH | 42 | 47 | 31 | 43 | 36 | 4 | 0 | 13 | 10 | 11 | 11 | 11 | 0 |
| 2,3-DMH | 39 | 33 | 50 | 40 | 49 | 35 | 0 | 11 | 8 | 10 | 10 | 10 | 0 |
| 3,4-DMH | 2 | 0 | 0 | 0 | 0 | 56 | 100 | 76 | 82 | 80 | 79 | 79 | 100 |

Run F21Y

(Y, Tcalc=540degC, Trxn=86degC, P=382psig, I/O=12 0, butene WHSV=2 57h-1, t=19min, mcat=2 78g)

| TOS [min] | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 11 | 13 | 17 | 19 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Propane | 197360 | 266660 | 114040 | 300200 | 309100 | 314440 | | 200840 | 294500 | 250000 | 221200 | 287860 | 321660 |
| Isobutane | 19094400 | 30900000 | 13999080 | 36630580 | 38480580 | 39680740 | 11480800 | 24952760 | 37637480 | 31340200 | 27405980 | 36570860 | 39773660 |
| 1-butene | | | | | | | | | 102960 | | | 459660 | 2388560 |
| n-butane | 490740 | 839500 | 383740 | 965040 | 979480 | 985400 | 282600 | 603640 | 922100 | 834380 | 685660 | 887640 | 955320 |
| t-2-butene | | | | | 228300 | 664540 | 262780 | 676440 | 1085800 | 1028200 | 842120 | 989600 | 324740 |
| c-2-butene | | | | | 100600 | 311460 | 129900 | 346300 | 591860 | 604640 | 497580 | 617300 | 218340 |
| | | | | | | | | | | | | | |
| **C5-C7** | 567828 | 949572 | 402667 | 855476 | 557041 | 127628 | 0 | 0 | 0 | 5568 | 0 | 0 | 0 |
| C5 | 200920 | 373020 | 159160 | 330140 | 211720 | | | | | | | | |
| 2,3-DMB | 96971 | 173942 | 73835 | 155887 | 100527 | 36235 | | | | | | | |
| 2,2-DMP | 39514 | 72310 | 30126 | 61807 | 39212 | 13956 | | | | | | | |
| 3-MP | 32959 | 58367 | 25579 | 56286 | 41085 | 19512 | | | | | | | |
| 2,4-DMP | 90190 | 130924 | 55035 | 114872 | 73046 | 24801 | | | | 5568 | | | |
| 2,2,3-TMB | | 7340 | | 7569 | | | | | | | | | |
| 2-MHx | 19232 | 24455 | 10236 | 20983 | 13691 | | | | | | | | |
| 2,3-DMP | 68111 | 84774 | 37764 | 84209 | 60927 | 25261 | | | | | | | |
| 3-MHx | 19931 | 24440 | 10932 | 23723 | 16833 | 7863 | | | | | | | |
| | | | | | | | | | | | | | |
| **C8** | 1386395 | 1020392 | 432771 | 1153335 | 912362 | 431328 | 44439 | 145081 | 251237 | 327216 | 196454 | 228332 | 35002 |
| **2,2,4-TMP** | **360879** | **363343** | **158709** | **333022** | **208795** | **69060** | **5048** | | | | | | |
| 2,5-DMHx | 61949 | 48950 | 13882 | 46858 | 29537 | 7171 | | | | | | | |
| 2,2,3-TMP | 53681 | 38661 | 10640 | 30713 | 17697 | 19889 | | | | | | | |
| 2,4-DMHx | 149394 | 113366 | 22847 | 116075 | 72736 | 5573 | | 6082 | 8634 | 10238 | 7306 | 7866 | |
| 2,3,4-TMP | 190655 | 123066 | 67331 | 170298 | 142203 | 60105 | 5066 | | | 7653 | | | |
| 2,3,3-TMP | 272877 | 173156 | 91246 | 207763 | 161648 | 57402 | | | | | | | |
| 2,3-DMHx | 139421 | 79267 | 37082 | 107583 | 99445 | 45816 | | 5571 | 7301 | 9351 | 6430 | 6953 | |
| 3,4-DMHx | 5990 | | | | | 74103 | 16886 | 36927 | 73454 | 75976 | 51191 | 54705 | 6114 |
| 1-DMHx= | 39207 | 23666 | 15830 | 71524 | 119519 | 70505 | 17439 | 81687 | 131373 | 169030 | 108824 | 122678 | 23641 |
| 2-DMHx= | 8502 | 5645 | | 9380 | 19484 | | | | | | | | |
| 3-DMHx= | | | | | | | | | | | | | |
| 4-DMHx= | | | | | | | | | | | | | |
| 5-DMHx= | 103840 | 51272 | 15204 | 60119 | 41298 | 7756 | | | | | | | |
| 6-DMHx= | | | | | | 14928 | | 14814 | 30475 | 54968 | 22703 | 36130 | 5247 |
| | | | | | | | | | | | | | |
| **C9+** | 1144247 | 316172 | 426107 | 659877 | 690649 | 503640 | 299566 | 530183 | 458645 | 894334 | 250626 | 307794 | 19235 |
| | | | | | | | | | | | | | |
| **C6+** | 3098470 | 2286136 | 1261545 | 2668688 | 2160052 | 1062596 | 344005 | 675264 | 709882 | 1227118 | 447080 | 536126 | 54237 |
| | | | | | | | | | | | | | |
| Tot Peak Area | 22880970 | 34292296 | 15758405 | 40564508 | 42258112 | 43019176 | 12500085 | 27108944 | 40752722 | 34679898 | 29602040 | 39731746 | 43818177 |
| | | | | | | | | | | | | | |
| ***Feed Analysis*** | Inj 1 | Inj 2 | Inj 3 | Inj 4 | Inj 5 | Avg | Mass % | | | | | | |
| C3 | 14196 | 14797 | 13279 | 17012 | 11677 | 14192 | 0 80 | | Avg Mass I/O Ratio | | 11 98 | | |
| i-C4 | 1745833 | 1815391 | 1349449 | 2119341 | 897858 | 1585574 | 89 54 | | Avg Molar I/O Ratio | | **11.562** | | |
| 1-C4= | 145978 | 152839 | 115276 | 173169 | 74169 | 132286 | 7 47 | | | | | | |
| n-C4 | 43097 | 45605 | 33722 | 51401 | 20355 | 38836 | 2 19 | | | | | | |
| **I/O Mass Ratio** | 11 960 | 11 878 | 11 706 | 12 239 | 12 106 | **11.978** | | | | | | | |

F22EMT

(EMT; Tcalc=540degC; Trxn=88degC; P=382psig; I/O=11.6; butene WHSV=2.62h-1; t=15min; mcat=2 78g)

| Samp t [min] | 9 | 10 | 11 | 13 | 14 | 15 | 16 | 18 | 19 |
|---|---|---|---|---|---|---|---|---|---|
| **T.O.S. [min.]** | **1** | **2** | **3** | **5** | **6** | **7** | **8** | **10** | **11** |
| 1-C4= Disapp. [%] | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| t-2-C4= Prod. [%] | 0 | 0 | 0 | 0 | 0 | 6 | 16 | 27 | 30 |
| c-2-C4= Prod. [%] | 0 | 0 | 0 | 0 | 0 | 0 | 7 | 11 | 13 |
| **Butene Disapp. [%]** | **100** | **100** | **100** | **100** | **100** | **94** | **78** | **61** | **57** |
| n-Butane Change [%] | 7 | 7 | 11 | 9 | 7 | 6 | 4 | 2 | 4 |
| | | | | | | | | | |
| ***C5+ Product Analysis [mass %]*** | | | | | | | | | |
| C5-C7 | 31 | 30 | 37 | 31 | 26 | 22 | 10 | 2 | 1 |
| **C8** | **48** | **39** | **45** | **48** | **50** | **39** | **35** | **37** | **41** |
| C9+ | 21 | 31 | 18 | 21 | 24 | 40 | 55 | 61 | 58 |
| | | | | | | | | | |
| ***C8 Distribution [mass %]*** | | | | | | | | | |
| **TMP** | **65** | **63** | **64** | **63** | **59** | **60** | **47** | **11** | **10** |
| DMH | 27 | 28 | 29 | 28 | 28 | 25 | 26 | 17 | 20 |
| C8= | 9 | 9 | 8 | 9 | 14 | 15 | 27 | 71 | 70 |
| | | | | | | | | | |
| ***TMP Isomer Distribution [%]*** | | | | | | | | | |
| **2,2,4-TMP** | **54** | **56** | **58** | **53** | **45** | **40** | **36** | **34** | **38** |
| 2,2,3-TMP | 14 | 14 | 13 | 10 | 8 | 5 | 4 | 0 | 0 |
| 2,3,4-TMP | 12 | 10 | 10 | 14 | 20 | 26 | 29 | 37 | 35 |
| 2,3,3-TMP | 20 | 20 | 18 | 24 | 28 | 29 | 31 | 30 | 26 |
| | | | | | | | | | |
| ***Indicators [mass fraction]*** | | | | | | | | | |
| **TMP** | **2.39** | **2.23** | **2.24** | **2.30** | **2.13** | **2.40** | **1.78** | **0.64** | **0.48** |
| **DMH** | | | | | | | | | |
| TMP+DMH | 1.72 | 1.03 | 1.92 | 1.76 | 1.41 | 0.73 | 0.40 | 0.12 | 0.14 |
| C8= + C9+ | | | | | | | | | |
| (2,2,3-+2,2,4-TMP) | 2.12 | 2.31 | 2.50 | 1.69 | 1.11 | 0.82 | 0.66 | 0.51 | 0.62 |
| (2,3,4-+2,3,3-TMP) | | | | | | | | | |
| | | | | | | | | | |
| ***DMH Isomer Distribution [%]*** | | | | | | | | | |
| 2,5-DMH | 21 | 21 | 21 | 19 | 15 | 13 | 7 | 19 | 21 |
| 2,4-DMH | 48 | 50 | 51 | 45 | 38 | 32 | 24 | 17 | 17 |
| 2,3-DMH | 28 | 27 | 25 | 37 | 45 | 55 | 62 | 30 | 35 |
| 3,4-DMH | 2 | 2 | 2 | 0 | 2 | 0 | 7 | 34 | 28 |

F22EMT

(EMT, Tcalc=540degC, Trxn=88degC, P=382psig, I/O=11 6, butene WHSV=2 62h-1, t=15min, mcat=2 78g)

| TOS [min] | 1 | 2 | 3 | 6 | 6 | 7 | 8 | 10 | 11 |
|---|---|---|---|---|---|---|---|---|---|
| Propane | 244140 | 242540 | 240580 | 210680 | 308600 | 329320 | 245080 | 256580 | 244700 |
| Isobutane | 28503780 | 26976340 | 27992260 | 25605920 | 37726640 | 40848800 | 28958980 | 31264360 | 30759840 |
| 1-butene | | | | | | | | | |
| n-butane | 758880 | 712380 | 763820 | 684980 | 983880 | 1037780 | 719340 | 755140 | 754620 |
| t-2-butene | | | | | | 216380 | 372280 | 680920 | 746440 |
| c-2-butene | | | | | | | 153260 | 288240 | 315520 |
| | | | | | | | | | |
| **C5-C7** | 887698 | 752833 | 864223 | 670806 | 710072 | 503037 | 119231 | 13307 | 7047 |
| C5 | 300820 | 286400 | 325320 | 232060 | 254080 | 174940 | | | |
| 2,3-DMB | 142695 | 123098 | 143663 | 112155 | 116240 | 83783 | 27864 | | |
| 2,2-DMP | 68698 | 60129 | 70984 | 52219 | 51262 | 35748 | 12696 | | |
| 3-MP | 52073 | 43874 | 51413 | 43549 | 47749 | 39135 | 17021 | 7751 | 7047 |
| 2,4-DMP | 147915 | 110715 | 126339 | 98033 | 96599 | 65852 | 22229 | | |
| 2,2,3-TMB | 11251 | 8183 | 8833 | 8307 | 9346 | 7353 | | | |
| 2-MHx | 36097 | 26788 | 30753 | 24475 | 24264 | 15452 | 5923 | | |
| 2,3-DMP | 97323 | 70396 | 80435 | 76611 | 84908 | 62019 | 24718 | 5556 | |
| 3-MHx | 30826 | 23250 | 26483 | 23397 | 25624 | 18755 | 8780 | | |
| | | | | | | | | | |
| **C8** | 1366956 | 968889 | 1034054 | 1038669 | 1403040 | 900023 | 427672 | 221820 | 217739 |
| **2,2,4-TMP** | **474061** | **341480** | **383391** | **349779** | **372096** | **217151** | **72639** | **8291** | **8042** |
| 2,5-DMHx | 78016 | 57480 | 62410 | 53038 | 58614 | 30432 | 7331 | 7448 | 9277 |
| 2,2,3-TMP | 125456 | 85062 | 88558 | 63343 | 62069 | 27810 | 7329 | | |
| 2,4-DMHx | 177444 | 137439 | 151921 | 128521 | 148067 | 72098 | 27415 | 6619 | 7214 |
| 2,3,4-TMP | 101815 | 62841 | 69343 | 89462 | 161238 | 141146 | 58156 | 9077 | 7394 |
| 2,3,3-TMP | 180668 | 122031 | 119615 | 154983 | 229936 | 156896 | 62105 | 7339 | 5475 |
| 2,3-DMHx | 104683 | 73592 | 74228 | 104811 | 173692 | 123823 | 69593 | 11505 | 15084 |
| 3,4-DMHx | 8147 | 5975 | 6635 | | 6649 | | 7856 | 13026 | 12046 |
| 1 DMHx= | 20443 | 15666 | 17233 | 30211 | 90922 | 64802 | 52973 | 43154 | 36686 |
| 2 DMHx= | 8002 | 6444 | 6225 | 6710 | 9680 | 20354 | 42658 | 83511 | 82670 |
| 3 DMHx= | | | | | | | | | |
| 4 DMHx= | | | | | | | | | |
| 5 DMHx= | 88201 | 60879 | 54495 | 57811 | 90078 | 45511 | 14337 | 6193 | 5851 |
| 6 DMHx= | | | | | | | 5380 | 25657 | 28000 |
| | | | | | | | | | |
| **C9+** | 609781 | 778551 | 421309 | 441102 | 667325 | 925111 | 670326 | 366414 | 311629 |
| | | | | | | | | | |
| **C5+** | 2864435 | 2500273 | 2319586 | 2150577 | 2780437 | 2328171 | 1217229 | 601541 | 536415 |
| | | | | | | | | | |
| Tot Peak Area | 32371235 | 30431533 | 31316246 | 28652157 | 41799557 | 44760451 | 31512909 | 33558541 | 33042015 |
| | | | | | | | | | |
| ***Feed Analysis*** | | Inj 1 | Inj 2 | Inj 3 | Inj 4 | Inj 5 | Avg | Mass % | |
| C3 | | 12713 | 15149 | 15494 | 10412 | 16026 | 13959 | 0 76 | |
| i-C4 | | 1231112 | 1834205 | 1915520 | 1025992 | 1976396 | 1596645 | 89 54 | |
| 1-C4= | | 102431 | 153700 | 160960 | 85525 | 164380 | 133399 | 7 48 | |
| n-C4 | | 29681 | 45273 | 47670 | 24340 | 48972 | 39187 | 2 20 | |
| **I/O Mass Ratio** | | 12 019 | 11 934 | 11 901 | 11 996 | 12 023 | **11.975** | | |

F23EMT

(EMT; Tcalc=540degC; Trxn=56degC; P=382psig; I/O=11.7; butene WHSV=2.55h-1; t=13min; mcat=2.78g)

| Samp t [min] | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 20 | 21 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **T.O.S. [min.]** | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** | **9** | **10** | **11** | **13** | **14** |
| 1-C4= Disapp. [%] | 91 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| t-2-C4= Prod. [%] | 0 | 0 | 0 | 0 | 4 | 8 | 13 | 18 | 21 | 23 | 25 | 29 | 31 |
| c-2-C4= Prod. [%] | 0 | 0 | 0 | 0 | 0 | 3 | 0 | 8 | 10 | 11 | 12 | 15 | 17 |
| **Butene Disapp. [%]** | **91** | **100** | **100** | **100** | **96** | **89** | **87** | **74** | **69** | **66** | **63** | **56** | **52** |
| n-Butane Change [%] | 5 | 16 | 18 | 14 | 9 | 12 | 12 | 9 | 7 | 10 | 11 | 9 | 9 |
| | | | | | | | | | | | | | |
| ***C5+ Product Analysis [mass %]*** | | | | | | | | | | | | | |
| C5-C7 | 20 | 24 | 29 | 25 | 19 | 18 | 10 | 7 | 9 | 8 | 7 | 5 | 4 |
| **C8** | **49** | **53** | **54** | **56** | **51** | **50** | **41** | **34** | **46** | **48** | **39** | **43** | **38** |
| C9+ | 32 | 23 | 17 | 19 | 30 | 32 | 49 | 59 | 45 | 44 | 54 | 52 | 58 |
| | | | | | | | | | | | | | |
| ***C8 Distribution [mass %]*** | | | | | | | | | | | | | |
| **TMP** | **79** | **78** | **81** | **75** | **68** | **63** | **69** | **60** | **51** | **46** | **42** | **23** | **19** |
| DMH | 11 | 12 | 11 | 13 | 17 | 19 | 12 | 15 | 15 | 14 | 18 | 12 | 20 |
| C8= | 10 | 10 | 8 | 12 | 15 | 18 | 19 | 24 | 34 | 40 | 40 | 65 | 61 |
| | | | | | | | | | | | | | |
| ***TMP Isomer Distribution [%]*** | | | | | | | | | | | | | |
| **2,2,4-TMP** | **32** | **32** | **37** | **34** | **34** | **33** | **37** | **34** | **32** | **32** | **34** | **38** | **41** |
| **2,2,3-TMP** | **13** | **12** | **8** | **14** | **9** | **9** | **8** | **6** | **9** | **9** | **6** | **8** | **9** |
| **2,3,4-TMP** | **23** | **23** | **23** | **22** | **26** | **26** | **24** | **27** | **27** | **26** | **27** | **17** | **26** |
| **2,3,3-TMP** | **32** | **33** | **33** | **29** | **32** | **32** | **31** | **32** | **31** | **32** | **33** | **38** | **24** |
| | | | | | | | | | | | | | |
| ***Indicators [mass fraction]*** | | | | | | | | | | | | | |
| **TMP** | **7.14** | **6.29** | **7.31** | **5.76** | **4.01** | **3.41** | **5.63** | **3.89** | **3.49** | **3.30** | **2.32** | **1.97** | **0.92** |
| **DMH** | | | | | | | | | | | | | |
| TMP+DMH | 1.20 | 1.70 | 2.27 | 1.94 | 1.15 | 1.00 | 0.60 | 0.38 | 0.51 | 0.46 | 0.34 | 0.19 | 0.18 |
| C8= + C9+ | | | | | | | | | | | | | |
| (2,2,3-+2,2,4-TMP) | 0.80 | 0.78 | 0.79 | 0.96 | 0.74 | 0.72 | 0.82 | 0.69 | 0.71 | 0.70 | 0.66 | 0.83 | 1.00 |
| (2,3,4-+2,3,3-TMP) | | | | | | | | | | | | | |
| | | | | | | | | | | | | | |
| ***DMH Isomer Distribution [%]*** | | | | | | | | | | | | | |
| 2,5-DMH | 18 | 17 | 20 | 18 | 13 | 11 | 19 | 10 | 8 | 7 | 11 | 0 | 0 |
| 2,4-DMH | 14 | 13 | 26 | 13 | 31 | 32 | 30 | 17 | 6 | 8 | 9 | 19 | 13 |
| 2,3-DMH | 68 | 70 | 54 | 70 | 56 | 54 | 51 | 62 | 58 | 48 | 58 | 46 | 29 |
| 3,4-DMH | 0 | 0 | 0 | 0 | 0 | 2 | 0 | 10 | 27 | 37 | 22 | 35 | 58 |

F23EMT

(EMT, Tcalc=540degC Tran=56degC, P=382psig I/O=11 7 butene WHSV=2 55h-1 t=13min, mcat=2 78g)

| TOS [min] | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 13 | 14 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Propane | 323520 | 349500 | 166800 | 415640 | 426980 | 406180 | 125460 | 279380 | 417460 | 430080 | 312580 | 348920 | 348400 |
| Isobutene | 35718640 | 40436920 | 20518000 | 46591340 | 46918000 | 46384100 | 15738840 | 32577260 | 46058500 | 50505200 | 36845700 | 41566360 | 41689040 |
| 1-butene | 265000 | | | | | | | | | | | | |
| n-butane | 933800 | 1127120 | 571600 | 1256260 | 1229520 | 1236480 | 419000 | 847060 | 1170600 | 1303960 | 969640 | 1068260 | 1073200 |
| t-2-butene | | | | | 135760 | 297040 | 161420 | 477700 | 772480 | 938840 | 738200 | 964740 | 1034620 |
| c-2-butene | | | | | | 115580 | | 214820 | 360820 | 435700 | 351520 | 502960 | 554180 |
| C5-C7 | 702038 | 585641 | 284011 | 599256 | 548811 | 434097 | 70825 | 110845 | 145478 | 106870 | 72203 | 38617 | 32256 |
| C5 | 196340 | 220620 | 113920 | 223120 | 189340 | 151520 | | | | | | | |
| 2,3-DMB | 121943 | 91576 | 47084 | 92599 | 84389 | 65610 | 18022 | 25927 | 31871 | 25488 | 16761 | 9782 | 8250 |
| 2,2-DMP | 41018 | 31213 | 16812 | 34315 | 32301 | 26224 | 7326 | 10589 | 13193 | 10831 | 6991 | | |
| 3-MP | 58050 | 42302 | 21980 | 45500 | 44719 | 38155 | 11092 | 17486 | 22487 | 19047 | 12970 | 10023 | 8978 |
| 2,4-DMP | 133483 | 90403 | 44191 | 88747 | 81501 | 61092 | 17521 | 24470 | 30507 | 22345 | 13765 | 7976 | 6330 |
| 2,2,3-TMB | 14069 | 9434 | | 9472 | 9186 | 6918 | | | | | | | |
| 2-MHx | 17989 | 13441 | 6911 | 14780 | 14764 | 11166 | | | 6238 | | | | |
| 2,3-DMP | 98229 | 70342 | 34654 | 72839 | 73686 | 57155 | 16664 | 24264 | 30964 | 24086 | 15961 | 10836 | 8698 |
| 3-MHx | 21717 | 16310 | 8459 | 17884 | 18925 | 16257 | | 7909 | 10198 | 8273 | 5795 | | |
| C8 | 1711600 | 1308858 | 554984 | 1344447 | 1458850 | 1205116 | 283101 | 508309 | 700877 | 616885 | 394763 | 385085 | 329031 |
| 2,2,4-TMP | 429031 | 324164 | 163910 | 349231 | 339028 | 253487 | 73357 | 105097 | 126226 | 91200 | 56560 | 31935 | 24928 |
| 2,5-DMHx | 34999 | 27418 | 12383 | 30830 | 32005 | 25266 | 6510 | 8163 | 9482 | 6462 | 8216 | | |
| 2,2,3-TMP | 174115 | 122408 | 34377 | 146317 | 84002 | 66192 | 14753 | 19635 | 36572 | 26840 | 9185 | 6674 | 5714 |
| 2,4-DMHx | 26238 | 20958 | 15810 | 22682 | 76748 | 72491 | 10529 | 13294 | 7052 | 7040 | 6474 | 8283 | 8524 |
| 2,3,4-TMP | 313102 | 238713 | 101226 | 222099 | 253655 | 198775 | 47583 | 82601 | 106268 | 74888 | 44998 | 14491 | 16091 |
| 2,3,3-TMP | 438651 | 333741 | 148345 | 295609 | 314445 | 245965 | 60174 | 99232 | 122315 | 92848 | 55005 | 32057 | 14549 |
| 2,3-DMHx | 128333 | 113658 | 33052 | 122490 | 137546 | 121231 | 17723 | 49099 | 65446 | 41348 | 41400 | 19871 | 19163 |
| 3,4-DMHx | | | | | | 5212 | | 8201 | 30096 | 31859 | 15376 | 15133 | 38902 |
| 1 DMHx= | 94192 | 61067 | 30855 | 94048 | 141853 | 148781 | 37573 | 60728 | 132703 | 110149 | 54980 | 62772 | 49501 |
| 2 DMHx= | 6079 | 5095 | | 5875 | 10228 | 17051 | 7230 | 44972 | 93297 | 100324 | 77662 | 133191 | 118042 |
| 3 DMHx= | | | | | | | | | | | | | |
| 4 DMHx= | | | | | | | | | | 5167 | | | |
| 5 DMHx= | 63771 | 54271 | 15636 | 55266 | 64874 | 50665 | 7669 | 13165 | 13486 | 10037 | 7428 | 5032 | |
| 6 DMHx= | 5189 | 5163 | | | 5466 | | | 5121 | 18014 | 18634 | 17475 | 35626 | 33519 |
| C9+ | 1112314 | 569593 | 177720 | 459166 | 851254 | 768439 | 334881 | 899195 | 738428 | 567043 | 547532 | 442407 | 494665 |
| C5+ | 3526752 | 2461890 | 1026725 | 2402869 | 2856915 | 2407652 | 688607 | 1519148 | 1644883 | 1293778 | 1014558 | 846089 | 855852 |
| Tot Peak Area | 40767712 | 44375430 | 22283125 | 50666109 | 51567175 | 50847032 | 17133327 | 35700548 | 50063923 | 54471858 | 39880678 | 44794369 | 45001112 |

| FEED ANAL. | Inj 1 | Inj 2 | Inj 3 | Inj 4 | Inj 5 | Avg | Mass % |
|---|---|---|---|---|---|---|---|
| C3 | 17710 | 13541 | 13120 | 8895 | 16547 | 13963 | 0 78 |
| i-C4 | 2165189 | 1642138 | 1539647 | 663485 | 2049673 | 1612026 | 89 64 |
| 1-C4= | 176032 | 137267 | 129680 | 54009 | 168435 | 133085 | 7 40 |
| n-C4 | 52276 | 40534 | 38449 | 14623 | 50214 | 39219 | 2 18 |
| I/O Mass Ratio | 12 300 | 11 963 | 11 873 | 12 285 | 12 169 | 12 118 | g Mass I/O Ratio |

Avg. Mass I/O Ratio 12.12

Avg. Molar I/O Ratio 11 800

Run F24Y

(Y; Tcalc=425degC; Trxn=56degC; P=382psig, I/O=11.1; butene WHSV=2.70h-1; t=1h; mcat=2.78g)

| Samp t [min] | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 20 | 23 | 28 | 38 | 68 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **T.O.S. [min.]** | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** | **9** | **10** | **12** | **15** | **20** | **30** | **60** |
| 1-C4= Disapp. [%] | 95 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 97 | 97 | 100 | 96 | 96 | 93 |
| t-2-C4= Prod. [%] | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 8 | 22 | 32 | 34 | 43 | 39 | 41 | 43 |
| c-2-C4= Prod. [%] | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 3 | 9 | 15 | 17 | 25 | 24 | 28 | 32 |
| **Butene Disapp. [%]** | **95** | **100** | **100** | **100** | **100** | **100** | **100** | **89** | **68** | **50** | **46** | **32** | **34** | **27** | **19** |
| n-Butane Change [%] | 8 | -2 | 9 | 7 | 9 | 8 | 6 | 7 | -6 | 3 | 2 | 12 | 1 | 2 | 3 |
| | | | | | | | | | | | | | | | |
| ***C5+ Product Analysis [mass %]*** | | | | | | | | | | | | | | | |
| C5-C7 | 31 | 13 | 30 | 31 | 30 | 27 | 23 | 18 | 1 | 1 | 0 | 0 | 0 | 0 | 0 |
| **C8** | **48** | **29** | **49** | **49** | **48** | **47** | **51** | **46** | **9** | **31** | **40** | **54** | **53** | **54** | **50** |
| C9+ | 21 | 59 | 21 | 20 | 21 | 27 | 26 | 36 | 90 | 67 | 60 | 46 | 47 | 46 | 50 |
| | | | | | | | | | | | | | | | |
| ***C8 Distribution [mass %]*** | | | | | | | | | | | | | | | |
| **TMP** | **73** | **68** | **70** | **68** | **68** | **69** | **64** | **59** | **37** | **11** | **7** | **3** | **3** | **1** | **0** |
| DMH | 22 | 26 | 24 | 27 | 27 | 26 | 31 | 37 | 44 | 43 | 33 | 25 | 26 | 23 | 20 |
| C8= | 5 | 6 | 6 | 5 | 5 | 5 | 5 | 4 | 19 | 46 | 60 | 72 | 71 | 75 | 80 |
| | | | | | | | | | | | | | | | |
| ***TMP Distribution [%]*** | | | | | | | | | | | | | | | |
| **2,2,4-TMP** | **39** | **38** | **41** | **45** | **41** | **39** | **35** | **29** | **24** | **26** | **20** | **0** | **0** | **0** | **0** |
| 2,2,3-TMP | 5 | 6 | 6 | 6 | 5 | 5 | 4 | 3 | 5 | 14 | 0 | 0 | 0 | 0 | 0 |
| 2,3,4-TMP | 24 | 23 | 22 | 19 | 22 | 25 | 29 | 33 | 36 | 38 | 62 | 100 | 100 | 100 | 0 |
| 2,3,3-TMP | 31 | 33 | 31 | 30 | 31 | 32 | 32 | 35 | 35 | 22 | 19 | 0 | 0 | 0 | 0 |
| | | | | | | | | | | | | | | | |
| ***Indicators [mass fraction]*** | | | | | | | | | | | | | | | |
| **TMP** | **3.27** | **2.66** | **2.95** | **2.53** | **2.49** | **2.67** | **2.02** | **1.62** | **0.85** | **0.25** | **0.21** | **0.11** | **0.11** | **0.06** | **0.00** |
| **DMH** | | | | | | | | | | | | | | | |
| TMP+DMH | 1.94 | 0.45 | 1.89 | 1.99 | 1.92 | 1.53 | 1.70 | 1.18 | 0.07 | 0.21 | 0.19 | 0.18 | 0.18 | 0.15 | 0.11 |
| C8= + C9+ | | | | | | | | | | | | | | | |
| (2,2,3-+2,2,4-TMP) | 0.80 | 0.78 | 0.87 | 1.02 | 0.87 | 0.76 | 0.64 | 0.47 | 0.41 | 0.65 | 0.24 | 0.00 | 0.00 | 0.00 | 0.00 |
| (2,3,4-+2,3,3-TMP) | | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | | |
| ***DMH Distribution [%]*** | | | | | | | | | | | | | | | |
| 2,5-DMH | 13 | 12 | 13 | 12 | 11 | 11 | 8 | 4 | 4 | 0 | 0 | 0 | 0 | 0 | 0 |
| 2,4-DMH | 33 | 28 | 30 | 31 | 29 | 26 | 23 | 15 | 2 | 5 | 7 | 9 | 9 | 10 | 11 |
| 2,3-DMH | 31 | 35 | 39 | 37 | 38 | 41 | 31 | 28 | 20 | 8 | 6 | 7 | 6 | 7 | 17 |
| 3,4-DMH | 23 | 24 | 17 | 19 | 22 | 22 | 38 | 54 | 74 | 86 | 88 | 84 | 85 | 84 | 72 |

Run F24Y
(Y, Tcalc=425degC, Trxn=56degC, P=382psig, I/O=11 1, butene WHSV=2 70h-1, t=1h, mcal=2 78g)

| TOS (min) | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 12 | 15 | 20 | 30 | 60 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Propane | 478240 | 433580 | 375740 | 432380 | 458180 | 363160 | 394820 | 398200 | 468620 | 425300 | 341800 | 289520 | 425420 | 440060 | 423880 |
| Isobutane | 57981300 | 46762180 | 42169220 | 49763740 | 52446320 | 42046560 | 44714500 | 46053640 | 56357700 | 50122400 | 40235980 | 36437700 | 50164820 | 53706600 | 48621840 |
| 1-butene | 227980 | | | | | | | | | 133220 | 118580 | | 155020 | 159600 | 266620 |
| n-butane | 1560000 | 1223920 | 1153740 | 1344840 | 1427620 | 1145720 | 1188140 | 1224600 | 1451680 | 1286980 | 1025700 | 1024040 | 1257440 | 1366080 | 1239280 |
| t-2-butene | | | | | | | | 322780 | 1177640 | 1341340 | 1150140 | 1311820 | 1641140 | 1866220 | 1741080 |
| c-2-butene | | | | | | | | 120300 | 495620 | 640400 | 584120 | 780960 | 991640 | 1249080 | 1323620 |
| **C5-C7** | **964087** | **806069** | **788008** | **1020967** | **968433** | **719647** | **595215** | **368418** | **90945** | **19585** | **0** | **0** | **0** | **0** | **0** |
| C5 | 390280 | 291900 | 314260 | 388400 | 375360 | 272120 | 210460 | 135140 | | | | | | | |
| 2,3-DMB | 172916 | 133817 | 136795 | 179766 | 172450 | 124856 | 102491 | 61784 | 20387 | 5960 | | | | | |
| 2,2-DMP | 57235 | 48312 | 50570 | 68592 | 62447 | 44150 | 34920 | 20705 | 7465 | | | | | | |
| 3-MP | 69322 | 57870 | 57778 | 77112 | 74433 | 55150 | 49905 | 34453 | 17628 | 7915 | | | | | |
| 2,4-DMP | 136544 | 117477 | 100548 | 135007 | 123788 | 94453 | 79247 | 44382 | 15323 | | | | | | |
| 2,2,3-TMB | 10305 | 8410 | 6742 | 9273 | 8779 | 7112 | 5356 | | | | | | | | |
| 2-MHx | 21430 | 21150 | 17709 | 24167 | 20943 | 15959 | 13382 | 7411 | | | | | | | |
| 2,3-DMP | 101003 | 100385 | 81451 | 108666 | 102865 | 84039 | 79034 | 50977 | 22775 | 5710 | | | | | |
| 3-MHx | 25052 | 26748 | 22155 | 29984 | 27368 | 21808 | 20420 | 13566 | 7367 | | | | | | |
| **C8** | **1526309** | **1809119** | **1281970** | **1602610** | **1546279** | **1263305** | **1324238** | **966664** | **707819** | **444019** | **459696** | **435049** | **438337** | **428476** | **284967** |
| **2,2,4-TMP** | **437481** | **469659** | **367655** | **496374** | **431925** | **339038** | **293537** | **163948** | **61834** | **12232** | **6171** | | | | |
| 2,5-DMHx | 43150 | 54286 | 41142 | 52574 | 47393 | 36758 | 33238 | 12457 | 13734 | | | | | | |
| 2,2,3-TMP | 56478 | 70401 | 50488 | 61244 | 54455 | 40173 | 34756 | 18333 | 14099 | 6513 | | | | | |
| 2,4-DMHx | 112508 | 131436 | 92407 | 132907 | 122472 | 85969 | 96317 | 51861 | 6890 | 10214 | 10091 | 10492 | 10212 | 9918 | 6011 |
| 2,3,4-TMP | 269094 | 289286 | 199143 | 211235 | 232218 | 218081 | 240082 | 188145 | 94061 | 18126 | 19549 | 12601 | 12545 | 6027 | |
| 2,3,3-TMP | 346320 | 404046 | 282395 | 328057 | 325600 | 278267 | 272666 | 201897 | 92838 | 10641 | 5903 | | | | |
| 2,3-DMHx | 105271 | 164090 | 120473 | 160365 | 158902 | 133125 | 130584 | 97693 | 61262 | 16204 | 8617 | 7255 | 7067 | 6510 | 9850 |
| 3,4-DMHx | 78325 | 113275 | 51084 | 83019 | 90104 | 71260 | 156176 | 190494 | 228690 | 165405 | 133475 | 93006 | 96211 | 83268 | 40859 |
| 1 DMHx= | | | | | | | | | | | | | | | |
| 2 DMHx= | 6586 | 7788 | 6281 | 6312 | 6707 | 5835 | 7036 | 10473 | 97195 | 165180 | 204970 | 227401 | 231487 | 236088 | 167595 |
| 3 DMHx= | | | | | | | | | | | | | | | |
| 4 DMHx= | | | | | | | | | 5313 | | | | | | |
| 5 DMHx= | 71096 | 99745 | 70902 | 80523 | 76503 | 55799 | 59866 | 30365 | 11605 | 5137 | | | | | |
| 6 DMHx= | | 5107 | | | | | | | 20298 | 34367 | 70820 | 84294 | 80815 | 86665 | 60672 |
| **C9+** | 670751 | 3691397 | 561401 | 675847 | 676912 | 724632 | 670948 | 745413 | 7524410 | 949420 | 701910 | 369044 | 392520 | 359462 | 286845 |
| **C5+** | 3181147 | 6306585 | 2631379 | 3299424 | 3191624 | 2707584 | 2590401 | 2079495 | 8323174 | 1413024 | 1161506 | 804093 | 830857 | 787938 | 571832 |
| Tot Peak Area | 63428667 | 54726265 | 46330079 | 54840384 | 57523744 | 46263024 | 48887861 | 50199015 | 67778814 | 54722264 | 44033706 | 39867173 | 54474697 | 58326498 | 52864532 |
| **FEED ANAL.** | | Inj 1 | Inj 2 | Inj 3 | Inj 4 | Inj 5 | Avg | Mass % | | | | | | | |
| **C3** | | 24431 | 22311 | 22336 | 21579 | 22700 | 22671 | 0 75 | | | | | | | |
| **i-C4** | | 2877294 | 2661261 | 2611696 | 2533882 | 2725376 | 2681902 | 89 23 | | | | | | | |
| **1-C4=** | | 250745 | 233177 | 228710 | 215995 | 233654 | 232456 | 7 73 | | | | | | | |
| **n-C4** | | 73578 | 68343 | 66882 | 65706 | 69206 | 68743 | 2 29 | | | | | | | |
| **I/O Mass Ratio** | | 11 475 | 11 413 | 11 419 | 11 731 | 11 664 | **11.541** | | | | | | | | |

Run F25EMT

(EMT; Tcalc=425degC; Trxn=33degC; P=382psig; I/O=11.1; butene WHSV=2.71h-1; t=1h; mcat=2.78g)

| **Samp t [min]** | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 21 | 24 | 29 | 69 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **T.O.S. [min.]** | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** | **9** | **10** | **12** | **15** | **20** | **60** |
| 1-C4= Disapp. [%] | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 96 |
| t-2-C4= Prod. [%] | 0 | 0 | 0 | 0 | 6 | 10 | 13 | 20 | 21 | 24 | 30 | 32 | 35 | 40 |
| c-2-C4= Prod. [%] | 0 | 0 | 0 | 0 | 0 | 0 | 4 | 6 | 6 | 8 | 11 | 13 | 17 | 29 |
| **Butene Disapp. [%]** | **100** | **100** | **100** | **100** | **94** | **90** | **83** | **74** | **73** | **67** | **58** | **55** | **49** | **27** |
| n-Butane Change [%] | 7 | 8 | 9 | 5 | 3 | 2 | 4 | 24 | 5 | 0 | 7 | 2 | 1 | 0 |
| | | | | | | | | | | | | | | |
| ***C5+ Product Analysis [mass %]*** | | | | | | | | | | | | | | |
| C5-C7 | 27 | 26 | 19 | 7 | 5 | 4 | 4 | 4 | 3 | 1 | 1 | 1 | 0 | 0 |
| **C8** | **37** | **51** | **47** | **43** | **29** | **23** | **46** | **32** | **37** | **27** | **32** | **40** | **36** | **54** |
| C9+ | 36 | 23 | 34 | 49 | 67 | 74 | 50 | 64 | 60 | 72 | 68 | 59 | 64 | 46 |
| | | | | | | | | | | | | | | |
| ***C8 Distribution [mass %]*** | | | | | | | | | | | | | | |
| **TMP** | **82** | **75** | **70** | **60** | **56** | **50** | **34** | **20** | **11** | **6** | **0** | **0** | **0** | **0** |
| DMH | 17 | 23 | 28 | 35 | 39 | 46 | 56 | 74 | 67 | 61 | 45 | 34 | 30 | 23 |
| C8= | 1 | 2 | 2 | 5 | 5 | 4 | 10 | 6 | 22 | 34 | 55 | 66 | 70 | 77 |
| | | | | | | | | | | | | | | |
| ***TMP Isomer Distribution [%]*** | | | | | | | | | | | | | | |
| **2,2,4-TMP** | **33** | **33** | **30** | **26** | **22** | **19** | **12** | **13** | **0** | **0** | **0** | **0** | **0** | **0** |
| 2,2,3-TMP | 10 | 5 | 4 | 4 | 4 | 3 | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 2,3,4-TMP | 24 | 27 | 30 | 32 | 37 | 39 | 43 | 33 | 32 | 51 | 0 | 0 | 0 | 0 |
| 2,3,3-TMP | 33 | 36 | 36 | 38 | 38 | 39 | 42 | 54 | 68 | 49 | 0 | 0 | 0 | 0 |
| | | | | | | | | | | | | | | |
| ***Indicators [mass fraction]*** | | | | | | | | | | | | | | |
| **TMP** | **4.91** | **3.27** | **2.53** | **1.70** | **1.42** | **1.11** | **0.60** | **0.27** | **0.16** | **0.09** | **0.00** | **0.00** | **0.00** | **0.00** |
| **DMH** | | | | | | | | | | | | | | |
| TMP+DMH | 0.98 | 2.11 | 1.30 | 0.79 | 0.40 | 0.29 | 0.75 | 0.46 | 0.41 | 0.22 | 0.17 | 0.16 | 0.12 | 0.15 |
| C8= + C9+ | | | | | | | | | | | | | | |
| (2,2,3-+2,2,4-TMP) | 0.73 | 0.61 | 0.52 | 0.43 | 0.34 | 0.28 | 0.18 | 0.15 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| (2,3,4-+2,3,3-TMP) | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | |
| ***DMH Isomer Distribution [%]*** | | | | | | | | | | | | | | |
| 2,5-DMH | 12 | 7 | 5 | 3 | 3 | 0 | 1 | 0 | 3 | 2 | 0 | 0 | 0 | 0 |
| 2,4-DMH | 9 | 9 | 7 | 7 | 7 | 4 | 4 | 3 | 2 | 3 | 6 | 9 | 9 | 10 |
| 2,3-DMH | 26 | 24 | 22 | 25 | 19 | 16 | 14 | 9 | 6 | 4 | 4 | 0 | 4 | 11 |
| 3,4-DMH | 53 | 60 | 65 | 65 | 71 | 80 | 81 | 88 | 89 | 91 | 89 | 91 | 87 | 79 |

Run F25EM1

(EMT, Tcalc=425degC, Trxn=33degC, P=382psig, I/O=11 1, butene WHSV=2 71h-1, t=1h, mcat=2 78g)

| TOS [min] | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 12 | 15 | 20 | 60 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Propane | 618940 | 443020 | 422900 | 432000 | 466320 | 384800 | 444140 | 205100 | 420620 | 454000 | 346260 | 430200 | 357000 | 460840 |
| Isobutane | 68025220 | 48715880 | 48326620 | 50439080 | 53097260 | 42625020 | 49274480 | 35556660 | 50571960 | 49198720 | 38110860 | 49813240 | 44845600 | 52891420 |
| 1-butene | | | | | | | | | | | | | | 190760 |
| n-butane | 1762400 | 1274440 | 1282920 | 1310060 | 1367820 | 1095600 | 1272820 | 1091120 | 1294800 | 1224760 | 1013940 | 1255760 | 1123520 | 1315220 |
| t-2-butene | | | | | 273720 | 368840 | 546440 | 589920 | 870540 | 999080 | 959340 | 1313760 | 1309420 | 1770980 |
| c-2-butene | | | | | | | 149320 | 172720 | 268860 | 348400 | 367160 | 537320 | 623680 | 1264420 |
| **C6-C7** | **442880** | **345674** | **306316** | **169191** | **123596** | **81970** | **74828** | **31316** | **27379** | **17704** | **7463** | **6129** | **0** | **0** |
| C5 | 171080 | 122460 | 109580 | | | | | | | | | | | |
| 2,3-DMB | 67877 | 49249 | 41217 | 34439 | 24264 | 13627 | 9314 | | | | | | | |
| 2,2-DMP | 23022 | 17420 | 14910 | 13113 | 9719 | 6045 | 5359 | | | | | | | |
| 3-MP | 44738 | 34687 | 30854 | 28795 | 25163 | 19178 | 19839 | 14703 | 12840 | 11097 | 7463 | 6129 | | |
| 2,4-DMP | 56531 | 46800 | 38533 | 31244 | 20943 | 11459 | 7281 | | | | | | | |
| 2,2,3-TMB | 7917 | 6865 | 5560 | | | | | | | | | | | |
| 2-MHx | 8175 | 7768 | 7314 | 6387 | | | | | | | | | | |
| 2,3-DMP | 50978 | 48119 | 45336 | 42781 | 33177 | 23082 | 22706 | 10617 | 8594 | 6607 | | | | |
| 3-MHx | 12562 | 12306 | 12011 | 12432 | 10330 | 8579 | 10329 | 5996 | 5945 | | | | | |
| **C8** | **605274** | **578043** | **753667** | **971670** | **746299** | **510688** | **867959** | **259788** | **360657** | **432112** | **292728** | **297816** | **408349** | **396567** |
| **2,2,4-TMP** | **161449** | **165476** | **158756** | **150029** | **90163** | **48263** | **34625** | **6899** | | | | | | |
| 2,5-DMHx | 11703 | 10512 | 10921 | 11910 | 8736 | | 5617 | | 7535 | 5941 | | | | |
| 2,2,3-TMP | 47217 | 27044 | 23055 | 23806 | 15149 | 7791 | 9526 | | | | | | | |
| 2,4-DMHx | 9555 | 14590 | 15036 | 24459 | 21026 | 10229 | 19198 | 5524 | 5345 | 7914 | 8484 | 9099 | 10662 | 9343 |
| 2,3,4-TMP | 121143 | 135128 | 156385 | 186688 | 152768 | 100026 | 124587 | 17029 | 11891 | 12152 | | | | |
| 2,3,3-TMP | 166019 | 180825 | 190993 | 220769 | 159273 | 101575 | 123795 | 28308 | 25316 | 11748 | | | | |
| 2,3-DMHx | 25736 | 36712 | 46591 | 84431 | 54775 | 36696 | 68788 | 17581 | 12977 | 10961 | 5734 | | 5352 | 10251 |
| 3,4-DMHx | 53903 | 93913 | 136309 | 220518 | 208442 | 185911 | 394498 | 169603 | 208955 | 237928 | 116417 | 92661 | 108267 | 73390 |
| 1 DMHx= | | | | | | | | | | | | | | |
| 2 DMHx= | | | | | 7978 | 8978 | 56825 | 14844 | 62304 | 121944 | 128414 | 155536 | 224873 | 221484 |
| 3 DMHx= | | | | | | | | | | | | | | |
| 4 DMHx= | | | | | | | 5076 | | | | | | | |
| 5 DMHx= | 8549 | 13843 | 15621 | 43745 | 27989 | 11229 | 11936 | | | | | | | |
| 6 DMHx= | | | | 5215 | | | 13488 | | 16334 | 23524 | 33679 | 40520 | 59195 | 82099 |
| **C9+** | 601373 | 301564 | 552767 | 1117285 | 1741862 | 1674213 | 952231 | 517635 | 577359 | 1135386 | 624073 | 438267 | 735968 | 337468 |
| **C5+** | 1649527 | 1325281 | 1611749 | 2258046 | 2611757 | 2266871 | 1895018 | 808739 | 955395 | 1585202 | 924264 | 742212 | 1144317 | 734035 |
| Tot Peak Area | 72056087 | 51758621 | 51644189 | 54439186 | 57816877 | 46741131 | 53582218 | 38424259 | 54113315 | 53461762 | 41354664 | 53555172 | 48779857 | 57363255 |
| ***Feed Analysis*** | | Inj 1 | Inj 2 | Inj 3 | Inj 4 | Inj 5 | Avg | Mass % | | | | | | |
| C3 | | 22467 | 19825 | 21286 | 22183 | | 21440 | 0 76 | Avg Mass I/O Ratio | | | 11 54 | | |
| i-C4 | | 2614861 | 2323278 | 2491499 | 2648377 | | 2519504 | 89 22 | Avg Molar I/O Ratio | | | **11.142** | | |
| 1-C4= | | 227202 | 203480 | 215985 | 226225 | | 218223 | 7 73 | | | | | | |
| n-C4 | | 66698 | 60362 | 64289 | 67139 | | 64622 | 2 29 | | | | | | |
| **I/O Mass Ratio** | | 11 509 | 11 418 | 11 536 | 11 707 | | **11.642** | | | | | | | |

Run F27Y
(Y; Tcalc=425degC; Trxn=29degC, P=382psig; I/O=11.2; butene WHSV=2.72h-1; t=1h; mcat=2.78g)

| Samp t [min] | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 20 | 23 | 28 | 38 | 68 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| T.O.S. [min.] | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 12 | 15 | 20 | 30 | 60 |
| 1-C4= Disapp. [%] | 91 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 96 | 96 | 96 | 94 | 86 |
| t-2-C4= Prod. [%] | 0 | 0 | 0 | 0 | 0 | 4 | 13 | 20 | 30 | 29 | 37 | 31 | 32 | 31 | 28 |
| c-2-C4= Prod. [%] | 0 | 0 | 0 | 0 | 0 | 0 | 5 | 8 | 18 | 21 | 35 | 29 | 32 | 38 | 41 |
| Butene Disapp. [%] | 91 | 100 | 100 | 100 | 100 | 96 | 82 | 72 | 51 | 50 | 24 | 37 | 33 | 25 | 17 |
| n-Butane Change [%] | 5 | 8 | 25 | 9 | -6 | 4 | 4 | 3 | 22 | 7 | 25 | 3 | 3 | 2 | -2 |
| | | | | | | | | | | | | | | | |
| *C5+ Product Analysis [mass %]* | | | | | | | | | | | | | | | |
| C5-C7 | 34 | 31 | 32 | 26 | 5 | 13 | 8 | 3 | 1 | 1 | 0 | 0 | 0 | 0 | 0 |
| C8 | 16 | 37 | 59 | 51 | 20 | 35 | 50 | 37 | 43 | 46 | 34 | 34 | 45 | 49 | 37 |
| C9+ | 50 | 33 | 8 | 23 | 75 | 53 | 42 | 60 | 56 | 53 | 66 | 66 | 55 | 51 | 63 |
| | | | | | | | | | | | | | | | |
| *C8 Distribution [mass %]* | | | | | | | | | | | | | | | |
| TMP | 87 | 83 | 74 | 71 | 62 | 64 | 57 | 42 | 21 | 8 | 3 | 2 | 2 | 2 | 0 |
| DMH | 13 | 15 | 25 | 27 | 33 | 34 | 40 | 50 | 56 | 50 | 28 | 24 | 25 | 20 | 14 |
| C8= | 0 | 1 | 1 | 2 | 5 | 3 | 3 | 8 | 23 | 41 | 69 | 74 | 73 | 78 | 86 |
| | | | | | | | | | | | | | | | |
| *TMP Distribution [%]* | | | | | | | | | | | | | | | |
| 2,2,4-TMP | 0 | 31 | 30 | 29 | 22 | 23 | 18 | 12 | 7 | 0 | 0 | 0 | 0 | 0 | 0 |
| 2,2,3-TMP | 6 | 4 | 4 | 4 | 5 | 3 | 4 | 4 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 2,3,4-TMP | 45 | 29 | 29 | 29 | 32 | 33 | 39 | 42 | 50 | 70 | 100 | 100 | 100 | 100 | 0 |
| 2,3,3-TMP | 50 | 37 | 37 | 38 | 40 | 40 | 40 | 42 | 44 | 30 | 0 | 0 | 0 | 0 | 0 |
| | | | | | | | | | | | | | | | |
| *Indicators [mass fraction]* | | | | | | | | | | | | | | | |
| TMP | 6.58 | 5.46 | 2.99 | 2.64 | 1.86 | 1.89 | 1.44 | 0.84 | 0.38 | 0.16 | 0.11 | 0.10 | 0.06 | 0.09 | 0.00 |
| DMH | | | | | | | | | | | | | | | |
| TMP+DMH | 0.33 | 1.10 | 6.51 | 2.16 | 0.25 | 0.63 | 1.12 | 0.54 | 0.49 | 0.37 | 0.12 | 0.10 | 0.14 | 0.12 | 0.05 |
| C8= + C9+ | | | | | | | | | | | | | | | |
| (2,2,3-+2,2,4-TMP) | 0.06 | 0.53 | 0.51 | 0.51 | 0.37 | 0.37 | 0.27 | 0.19 | 0.07 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | #DIV/0! |
| (2,3,4-+2,3,3-TMP) | | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | | |
| *DMH Distribution [%]* | | | | | | | | | | | | | | | |
| 2,5-DMH | 0 | 10 | 6 | 6 | 6 | 4 | 3 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 0 |
| 2,4-DMH | 37 | 20 | 19 | 18 | 14 | 6 | 6 | 4 | 2 | 3 | 6 | 11 | 8 | 10 | 0 |
| 2,3-DMH | 32 | 18 | 24 | 25 | 27 | 26 | 17 | 11 | 4 | 3 | 8 | 0 | 10 | 0 | 0 |
| 3,4-DMH | 31 | 52 | 51 | 50 | 53 | 65 | 74 | 86 | 92 | 94 | 85 | 89 | 81 | 90 | 100 |

Run F27Y

(Y, Tcalc=425degC, Trxn=29degC, P=382psig, I/O=11 2, butene WHSV=2 72h-1, t=1h, mcat=2 78g)

| TOS (min) | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Propane | 581100 | 409000 | 238960 | 395820 | 422880 | 456400 | 341500 | 409420 | 206480 | 408480 | 169000 | 323400 | 401840 | 399000 | 447780 |
| Isobutane | 69689120 | 46447120 | 34153980 | 45519900 | 48629960 | 49642180 | 40587180 | 48424980 | 30909240 | 47903280 | 31183080 | 39040280 | 48073200 | 48122680 | 49940220 |
| 1-butene | 512800 | | | | | | | | | | 121260 | 116000 | 143820 | 232380 | 567440 |
| n-butane | 1757620 | 1220040 | 1051820 | 1205620 | 1247360 | 1280000 | 1037440 | 1226240 | 941180 | 1258380 | 997360 | 991220 | 1214640 | 1198700 | 1197340 |
| t-2-butene | | | | | | 178240 | 430500 | 795060 | 798540 | 1163920 | 993840 | 996580 | 1265100 | 1255860 | 1180060 |
| c-2-butene | | | | | | | 172860 | 333580 | 473780 | 820860 | 946320 | 946720 | 1290760 | 1501340 | 1687960 |
| **C5-C7** | **372971** | **505151** | **483867** | **413373** | **424383** | **319104** | **96804** | **46157** | **16111** | **5130** | **0** | **0** | **0** | **0** | **0** |
| C5 | 189100 | 170260 | 172280 | 154080 | 135980 | 101960 | | | | | | | | | |
| 2,3-DMB | 68011 | 98800 | 83049 | 68233 | 70898 | 56090 | 18145 | 6303 | | | | | | | |
| 2,2-DMP | 15477 | 27902 | 25916 | 22394 | 22665 | 15578 | 5687 | | | | | | | | |
| 3-MP | 29162 | 51807 | 46007 | 39054 | 42333 | 36241 | 17887 | 12242 | 7754 | 5130 | | | | | |
| 2,4-DMP | 36682 | 63857 | 59064 | 46644 | 50413 | 35855 | 14675 | 5014 | | | | | | | |
| 2,2,3-TMB | | 6451 | | | | | | | | | | | | | |
| 2-MHx | | 9265 | 10319 | 9111 | 10871 | 6649 | | | | | | | | | |
| 2,3-DMP | 29323 | 62713 | 69879 | 58733 | 71938 | 53471 | 31498 | 16192 | 8357 | | | | | | |
| 3-MHx | 5216 | 14096 | 17353 | 15124 | 19265 | 13260 | 7912 | 5406 | | | | | | | |
| **C8** | **190607** | **608910** | **690735** | **799159** | **1619036** | **875743** | **626484** | **609173** | **493887** | **421862** | **537680** | **257007** | **400269** | **303306** | **202276** |
| **2,2,4-TMP** | | **155427** | **195449** | **187585** | **222054** | **130874** | **63652** | **26334** | **6971** | | | | | | |
| 2,5-DMHx | | 9534 | 13403 | 12744 | 30815 | 10659 | 7201 | | 5917 | | | | | | |
| 2,2,3-TMP | 8827 | 21434 | 27928 | 23926 | 49010 | 18855 | 12835 | 8080 | | | | | | | |
| 2,4-DMHx | 8753 | 18821 | 42472 | 39842 | 74312 | 16954 | 14177 | 9121 | 6325 | 7158 | 9727 | 6435 | 8185 | 5883 | |
| 2,3,4-TMP | 69931 | 145346 | 193058 | 164360 | 323347 | 186312 | 140091 | 90245 | 51883 | 24418 | 16445 | 6111 | 6429 | 5203 | |
| 2,3,3-TMP | 78024 | 185615 | 242825 | 214687 | 404567 | 222548 | 142916 | 89342 | 45413 | 10550 | | | | | |
| 2,3-DMHx | 7716 | 16340 | 52722 | 54782 | 145544 | 76210 | 42510 | 26873 | 10797 | 6014 | 12907 | | 10456 | | |
| 3,4-DMHx | 7356 | 48268 | 111768 | 108956 | 286100 | 191326 | 185414 | 218536 | 251236 | 199300 | 129359 | 54441 | 81284 | 54157 | 28101 |
| 1 DMHx= | | | | | | | | | | | | | | | |
| 2 DMHx= | | | | | 7760 | 6045 | 7842 | 26348 | 95905 | 132880 | 268578 | 153204 | 229669 | 185767 | 139689 |
| 3 DMHx= | | | | | | | | | | | 5878 | | | | |
| 4 DMHx= | | | | | | | | | | | | | | | |
| 5 DMHx= | | 8125 | 11110 | 12277 | 70259 | 15960 | 9846 | 7614 | | | | | | | |
| 6 DMHx= | | | | | 5268 | | | 6680 | 19440 | 41542 | 94786 | 36816 | 64246 | 52295 | 34486 |
| **C9+** | 543719 | 539035 | 124000 | 352521 | 6125732 | 1336533 | 527152 | 823511 | 651282 | 485481 | 1046872 | 501726 | 479688 | 319772 | 341190 |
| **C5+** | 1097297 | 1653096 | 1498602 | 1565053 | 8169131 | 2531380 | 1249440 | 1377841 | 1161280 | 912473 | 1584552 | 758733 | 879957 | 623077 | 543466 |
| Tot Peak Area | 73637937 | 49729256 | 36943362 | 48686393 | 58469331 | 54088200 | 43818920 | 52567121 | 34016720 | 51646533 | 35049092 | 42226213 | 51978557 | 51831697 | 53876306 |
| **FEED ANAL.** | | Inj 1 | Inj 2 | Inj 3 | Inj 4 | Inj 5 | Avg | Mass % | | | | | | | |
| **C3** | | 22710 | | | | | 22710 | 0 76 | | | | | | | |
| **i-C4** | | 2672465 | | | | | 2672465 | 89 27 | | | | | | | |
| **1-C4=** | | 230606 | | | | | 230606 | 7 70 | | | | | | | |
| **n-C4** | | 67935 | | | | | 67935 | 2 27 | | | | | | | |
| **I/O Mass Ratio** | | 11 589 | | | | | **11.589** | | | | | | | | |

F28EMT

(EMT; Tcalc=425degC; Trxn=55degC, P=382psig; I/O=11.25; butene WHSV=2.7h-1; mcat=2.78g)

| Samp t [min] | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 20 | 23 | 28 | 38 | 68 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **T.O.S. [min.]** | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** | **9** | **10** | **12** | **15** | **20** | **30** | **60** |
| 1-C4= Disapp. [%] | 91 | 96 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 97 |
| t-2-C4= Prod. [%] | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 4 | 7 | 16 | 29 | 38 | 43 | 46 |
| c-2-C4= Prod. [%] | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 4 | 6 | 11 | 15 | 19 | 24 |
| **Butene Disapp. [%]** | **91** | **96** | **100** | **100** | **100** | **100** | **100** | **100** | **96** | **89** | **78** | **60** | **47** | **38** | **27** |
| n-Butane Change [% | 7 | 9 | 11 | 17 | 8 | 6 | 6 | 4 | 12 | 21 | 6 | 3 | 2 | 1 | -1 |
| | | | | | | | | | | | | | | | |
| ***C5+ Product Distribution [%]*** | | | | | | | | | | | | | | | |
| C5-C7 | 42 | 28 | 37 | 35 | 24 | 29 | 26 | 18 | 13 | 13 | 12 | 4 | 1 | 0 | 0 |
| C8 | 51 | 50 | 56 | 50 | 45 | 53 | 58 | 47 | 52 | 51 | 48 | 56 | 47 | 58 | 45 |
| C9+ | 7 | 21 | 7 | 15 | 30 | 19 | 16 | 35 | 35 | 36 | 40 | 40 | 53 | 42 | 55 |
| | | | | | | | | | | | | | | | |
| ***C8 Distribution [%]*** | | | | | | | | | | | | | | | |
| **TMP** | **82** | **78** | **77** | **77** | **70** | **72** | **69** | **61** | **61** | **59** | **55** | **16** | **0** | **0** | **0** |
| DMH | 15 | 17 | 18 | 23 | 24 | 23 | 26 | 32 | 33 | 34 | 40 | 47 | 33 | 26 | 23 |
| C8= | 3 | 5 | 5 | 0 | 6 | 5 | 6 | 8 | 6 | 7 | 5 | 37 | 67 | 74 | 77 |
| | | | | | | | | | | | | | | | |
| ***TMP Isomer Distribution [%]*** | | | | | | | | | | | | | | | |
| **2,2,4-TMP** | **47** | **43** | **45** | **43** | **44** | **45** | **42** | **38** | **41** | **38** | **33** | **31** | **0** | **0** | **0** |
| 2,2,3-TMP | 16 | 18 | 16 | 16 | 10 | 7 | 6 | 8 | 7 | 5 | 4 | 0 | 0 | 0 | 0 |
| 2,3,4-TMP | 12 | 14 | 14 | 15 | 18 | 19 | 22 | 23 | 23 | 26 | 30 | 35 | 0 | 0 | 0 |
| 2,3,3-TMP | 24 | 26 | 26 | 25 | 28 | 29 | 30 | 31 | 30 | 32 | 34 | 34 | 0 | 0 | 0 |
| | | | | | | | | | | | | | | | |
| ***Indicators [mass fraction]*** | | | | | | | | | | | | | | | |
| TMP | 5.42 | 4.58 | 4.38 | 3.27 | 2.98 | 3.19 | 2.67 | 1.91 | 1.88 | 1.73 | 1.37 | 0.33 | 0.00 | 0.00 | 0.00 |
| DMH | | | | | | | | | | | | | | | |
| TMP+DMH | 5.72 | 1.99 | 5.57 | 3.26 | 1.29 | 2.32 | 2.87 | 1.12 | 1.27 | 1.21 | 1.06 | 0.58 | 0.19 | 0.18 | 0.11 |
| C8= + C9+ | | | | | | | | | | | | | | | |
| (2,2,3-+2,2,4-TMP) | 1.75 | 1.54 | 1.55 | 1.46 | 1.18 | 1.08 | 0.94 | 0.83 | 0.90 | 0.70 | 0.58 | 0.44 | #DIV/0! | #DIV/0! | #DIV/0! |
| (2,3,4-+2,3,3-TMP) | | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | | |
| ***DMH Isomer Distribution [%]*** | | | | | | | | | | | | | | | |
| 2,5-DMH | 19 | 18 | 17 | 13 | 13 | 10 | 8 | 9 | 8 | 5 | 4 | 6 | 0 | 0 | 0 |
| 2,4-DMH | 13 | 10 | 11 | 8 | 27 | 24 | 23 | 22 | 17 | 17 | 11 | 5 | 9 | 11 | 13 |
| 2,3-DMH | 48 | 53 | 52 | 41 | 40 | 44 | 45 | 38 | 37 | 33 | 28 | 15 | 6 | 6 | 0 |
| 3,4-DMH | 21 | 19 | 20 | 38 | 20 | 23 | 24 | 31 | 39 | 46 | 58 | 74 | 86 | 84 | 87 |

F28EMT

(EMT, Tcalc=425degC, Trxn=55degC, P=382psig, I/O=11 25, butene WHSV=2 7h-1, mcat=2 78g)

| TOS [min] | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Propane | 398000 | 324900 | 381680 | 317800 | 418300 | 413360 | 384920 | 422620 | 266060 | 228720 | 380520 | 330900 | 411420 | 396080 | 410000 |
| isobutane | 51347680 | 40299320 | 44538880 | 41833780 | 49110120 | 45517780 | 35770180 | 46642060 | 28604260 | 33827600 | 46008580 | 39054340 | 48540860 | 46325000 | 46495780 |
| 1-butene | 363040 | 137940 | | | | | | | | | | | | | 117740 |
| n-butane | 1323440 | 1078400 | 1194980 | 1194980 | 1301380 | 1176260 | 934540 | 1203140 | 802460 | 1005420 | 1182560 | 967700 | 1211500 | 1149780 | 1125120 |
| t-2-butene | | | | | | | | | 108000 | 203960 | 597260 | 921020 | 1506640 | 1643240 | 1768260 |
| c-2-butene | | | | | | | | | | 118700 | 220460 | 355140 | 617020 | 747740 | 926300 |
| **C5-C7** | **646935** | **591666** | **596478** | **588381** | **641600** | **524368** | **463457** | **489285** | **262211** | **203624** | **126816** | **17636** | **5374** | **0** | **0** |
| C5 | 250900 | 221720 | 243920 | 251120 | 236900 | 184680 | 162460 | 169740 | | | | | | | |
| 2,3-DMB | 106766 | 92194 | 94252 | 93740 | 101328 | 80173 | 69878 | 74529 | 51597 | 49232 | 24957 | | | | |
| 2,2-DMP | 38509 | 34611 | 36188 | 35896 | 39697 | 31195 | 27486 | 30368 | 21731 | 19823 | 10870 | | | | |
| 3-MP | 49297 | 43506 | 44581 | 44061 | 51470 | 42424 | 37549 | 43644 | 34206 | 31059 | 22131 | 9373 | 5374 | | |
| 2,4-DMP | 96264 | 90120 | 81759 | 73730 | 91074 | 76741 | 65423 | 64261 | 54930 | 38295 | 22234 | | | | |
| 2,2,3-TMB | 9693 | 8924 | 8792 | 7416 | 9826 | 8312 | 7480 | 8147 | 7283 | | | | | | |
| 2-MHx | 14179 | 15220 | 13198 | 12498 | 16399 | 14432 | 13035 | 13749 | 12646 | 8496 | 5428 | | | | |
| 2,3-DMP | 65474 | 68329 | 60110 | 55612 | 74903 | 68503 | 63239 | 66301 | 61426 | 43611 | 30252 | 8263 | | | |
| 3-MHx | 15853 | 17042 | 15678 | 14308 | 20003 | 17908 | 16907 | 18546 | 18392 | 13008 | 10644 | | | | |
| **C8** | **781791** | **1055936** | **695008** | **647489** | **1191565** | **968100** | **1036655** | **1302991** | **1066648** | **810845** | **618672** | **260923** | **350187** | **392452** | **274575** |
| **2,2,4-TMP** | **302614** | **352473** | **309939** | **278135** | **368506** | **310887** | **299302** | **298309** | **264729** | **173212** | **93839** | **12532** | | | |
| 2,5-DMHx | 21861 | 31672 | 26794 | 25370 | 35325 | 20781 | 21816 | 35728 | 28384 | 13037 | 7840 | 7941 | | | |
| 2,2,3-TMP | 103052 | 146589 | 109546 | 106784 | 84142 | 47573 | 46314 | 61145 | 43977 | 23037 | 9914 | | | | |
| 2,4-DMHx | 15135 | 18221 | 17808 | 16630 | 76003 | 51032 | 60925 | 90413 | 57337 | 46581 | 22156 | 6164 | 10016 | 10948 | 8072 |
| 2,3,4-TMP | 79043 | 112601 | 93694 | 100374 | 147639 | 133228 | 155261 | 185677 | 148292 | 125167 | 83864 | 14371 | | | |
| 2,3,3-TMP | 153253 | 211105 | 177358 | 163720 | 237336 | 199351 | 211725 | 245639 | 194828 | 153861 | 95557 | 13804 | | | |
| 2,3-DMHx | 56022 | 95863 | 82271 | 80705 | 113009 | 95846 | 120453 | 157031 | 126818 | 89734 | 57468 | 18132 | 6587 | 5676 | |
| 3,4-DMHx | 24633 | 33953 | 30850 | 75771 | 56321 | 49225 | 63582 | 130215 | 134295 | 125623 | 119714 | 90812 | 99611 | 85389 | 53854 |
| 1 DMHx= | | | | | | | | | | | | | | | |
| 2 DMHx= | | | | | | | 5006 | 6603 | 6601 | 12202 | 14628 | 78660 | 173673 | 218837 | 176202 |
| 3 DMHx= | | | | | | | | | | | | | | | |
| 4 DMHx= | | | | | | | | | | | | | | | |
| 5 DMHx= | 26178 | 53459 | 46748 | | 68129 | 50177 | 52171 | 87225 | 60387 | 48391 | 13692 | | 5715 | | |
| 6 DMHx= | | | | | 5155 | | | 5006 | | | | 18507 | 54585 | 71602 | 36447 |
| **C9+** | 105832 | 451118 | 105542 | 259690 | 795724 | 340493 | 284359 | 971543 | 716532 | 560354 | 432381 | 187002 | 393763 | 289825 | 335114 |
| **C5+** | 1534558 | 2098720 | 1599028 | 1695560 | 2628889 | 1822961 | 1784371 | 2763819 | 2044391 | 1574723 | 1077569 | 465561 | 749324 | 682277 | 609689 |
| Tot Peak Area | 54966718 | 43939280 | 47714568 | 45042120 | 53458689 | 48930361 | 38874011 | 51031639 | 31825171 | 36840423 | 49246489 | 41739521 | 52419744 | 50196377 | 50526589 |
| ***Feed Analysis*** | | Inj 1 | Inj 2 | Inj 3 | Inj 4 | Inj 5 | Avg | Mass % | | | | | | | |
| C3 | | 22508 | 20201 | 19686 | 21330 | 20582 | 20861 | 0 75 | | Avg Mass I/O Ratio | | 11 65 | | | |
| i-C4 | | 2693271 | 2404112 | 2337586 | 2529444 | 2506328 | 2494148 | 89 33 | | Avg Molar I/O Ratio | | **11.250** | | | |
| 1-C4= | | 230820 | 207558 | 201995 | 217192 | 212358 | 213985 | 7 66 | | | | | | | |
| n-C4 | | 67669 | 60868 | 59583 | 64504 | 62763 | 63077 | 2 26 | | | | | | | |
| **I/O Mass Ratio** | | 11 668 | 11 583 | 11 572 | 11 646 | 11 802 | 11 654 | | | | | | | | |

Run F29Y

(Y; Tcalc=425degC; Trxn=70degC; P=382psig, I/O=11.2; butene WHSV=2.67h-1; t=1h; mcat=2.78g)

| Samp t [min] | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 23 | 26 | 31 | 41 | 71 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **T.O.S. [min.]** | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** | **10** | **15** | **20** | **30** | **60** |
| 1-C4= Disapp. [%] | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 96 | 96 | 97 |
| t-2-C4= Prod. [%] | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 25 | 43 | 49 | 47 | 47 |
| c-2-C4= Prod. [%] | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 11 | 22 | 26 | 26 | 22 |
| **Butene Disapp. [%]** | **100** | **100** | **100** | **100** | **100** | **100** | **100** | **100** | **64** | **36** | **20** | **24** | **28** |
| n-Butane Change [%] | 7 | 10 | 13 | 8 | -3 | 2 | 13 | 4 | 9 | 1 | 10 | 3 | 2 |
| | | | | | | | | | | | | | |
| ***C5+ Product Analysis [mass %]*** | | | | | | | | | | | | | |
| C5-C7 | 44 | 35 | 52 | 36 | 30 | 30 | 30 | 30 | 11 | 1 | 0 | 0 | 0 |
| **C8** | **45** | **50** | **43** | **54** | **53** | **48** | **54** | **50** | **56** | **58** | **73** | **67** | **67** |
| C9+ | 11 | 14 | 4 | 10 | 17 | 21 | 16 | 20 | 33 | 41 | 27 | 33 | 33 |
| | | | | | | | | | | | | | |
| ***C8 Distribution [mass %]*** | | | | | | | | | | | | | |
| **TMP** | **68** | **63** | **71** | **63** | **65** | **62** | **63** | **60** | **43** | **8** | **3** | **3** | **0** |
| DMH | 26 | 29 | 25 | 30 | 28 | 30 | 31 | 32 | 39 | 25 | 23 | 21 | 24 |
| C8= | 6 | 8 | 4 | 7 | 7 | 8 | 7 | 8 | 17 | 67 | 74 | 76 | 76 |
| | | | | | | | | | | | | | |
| ***TMP Isomer Distribution [%]*** | | | | | | | | | | | | | |
| **2,2,4-TMP** | **59** | **55** | **66** | **56** | **56** | **50** | **51** | **44** | **31** | **35** | **0** | **0** | **0** |
| 2,2,3-TMP | 9 | 9 | 9 | 9 | 7 | 7 | 6 | 5 | 3 | 0 | 0 | 0 | 0 |
| 2,3,4-TMP | 12 | 13 | 9 | 13 | 14 | 16 | 17 | 21 | 33 | 48 | 100 | 100 | 0 |
| 2,3,3-TMP | 21 | 23 | 17 | 22 | 23 | 27 | 25 | 29 | 33 | 17 | 0 | 0 | 0 |
| | | | | | | | | | | | | | |
| ***Indicators [mass fraction]*** | | | | | | | | | | | | | |
| **TMP** | **2.64** | **2.20** | **2.80** | **2.12** | **2.35** | **2.06** | **2.04** | **1.86** | **1.10** | **0.32** | **0.13** | **0.15** | **0.00** |
| **DMH** | | | | | | | | | | | | | |
| TMP+DMH | 2.98 | 2.49 | 6.89 | 3.46 | 2.35 | 1.77 | 2.52 | 1.94 | 1.10 | 0.24 | 0.23 | 0.19 | 0.19 |
| C8= + C9+ | | | | | | | | | | | | | |
| (2,2,3-+2,2,4-TMP) | 2.06 | 1.76 | 2.89 | 1.85 | 1.71 | 1.37 | 1.36 | 0.99 | 0.51 | 0.53 | 0.00 | 0.00 | 0.00 |
| (2,3,4-+2,3,3-TMP) | | | | | | | | | | | | | |
| | | | | | | | | | | | | | |
| ***DMH Isomer Distribution [%]*** | | | | | | | | | | | | | |
| 2,5-DMH | 23 | 21 | 24 | 21 | 19 | 18 | 17 | 14 | 5 | 5 | 0 | 0 | 0 |
| 2,4-DMH | 48 | 46 | 53 | 47 | 45 | 44 | 40 | 35 | 14 | 8 | 11 | 19 | 11 |
| 2,3-DMH | 23 | 25 | 19 | 26 | 28 | 30 | 33 | 34 | 26 | 10 | 9 | 0 | 7 |
| 3,4-DMH | 6 | 8 | 4 | 7 | 8 | 7 | 10 | 17 | 55 | 77 | 80 | 81 | 82 |

Run F29Y
(Y, Tcalc=425degC, Trxn=70degC, P=382psig, I/O=11 2, butene WHSV=2 67h-1, t=1h, mcat=2 78g)

| TOS [min] | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 10 | 15 | 20 | 30 | 60 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Propane | 325800 | 298800 | 230260 | 216400 | 248700 | 432780 | 234900 | 341040 | 258100 | 264420 | 275100 | 342560 | 359780 |
| Isobutane | 39820100 | 35965620 | 23818600 | 21026560 | 21452320 | 47146220 | 27668980 | 39469740 | 29675540 | 28133860 | 34335920 | 42767160 | 42994960 |
| 1-butene | | | | | | | | | | | 128500 | 128360 | 124220 |
| n-butane | 1087180 | 1015520 | 706160 | 644360 | 570520 | 1209820 | 814600 | 1030200 | 819040 | 710500 | 934160 | 1085980 | 1078560 |
| t-2-butene | | | | | | | | | 639320 | 1010340 | 1424400 | 1667320 | 1671360 |
| c-2-butene | | | | | | | | | 272460 | 512560 | 758540 | 926600 | 795240 |
| **C5-C7** | **1561423** | **1302602** | **1503007** | **1630892** | **1079464** | **1091064** | **979096** | **845081** | **196266** | **10919** | **0** | **0** | **0** |
| C5 | 588880 | 533080 | 512860 | 517240 | 272080 | 463100 | 323220 | 334420 | | | | | |
| 2,3-DMB | 280879 | 212075 | 287886 | 303479 | 185593 | 168112 | 161306 | 146519 | 52294 | | | | |
| 2,2-DMP | 131483 | 99980 | 143746 | 148931 | 89166 | 76922 | 73722 | 62901 | 20897 | 5399 | | | |
| 3-MP | 94695 | 71066 | 99915 | 107827 | 73743 | 59695 | 64546 | 54566 | 26314 | | | | |
| 2,4-DMP | 234222 | 184212 | 234735 | 260301 | 208207 | 141930 | 154022 | 110455 | 39767 | 5520 | | | |
| 2,2,3-TMB | 12263 | 8973 | 11665 | 13519 | 11668 | 8149 | 8989 | 5604 | | | | | |
| 2-MHx | 48009 | 42893 | 47496 | 59625 | 46595 | 33801 | 35444 | 22444 | 7433 | | | | |
| 2,3-DMP | 129356 | 112199 | 123535 | 164214 | 146160 | 105083 | 120037 | 83246 | 37984 | | | | |
| 3-MHx | 41636 | 38124 | 41169 | 55756 | 46242 | 34272 | 37809 | 24926 | 11566 | | | | |
| **C8** | **1611780** | **1851957** | **1243034** | **2439613** | **1911648** | **1756471** | **1749610** | **1384840** | **1002172** | **518872** | **459102** | **358225** | **366294** |
| **2,2,4-TMP** | **643772** | **837918** | **576763** | **863977** | **700438** | **660378** | **663639** | **368148** | **133167** | **14411** | | | |
| 2,5-DMHx | 93975 | 112438 | 76707 | 148732 | 103142 | 96192 | 90886 | 60979 | 19886 | 6061 | | | |
| 2,2,3-TMP | 93348 | 106696 | 74568 | 132925 | 88168 | 79647 | 67346 | 44650 | 13262 | | | | |
| 2,4-DMHx | 201037 | 246002 | 166000 | 337880 | 240504 | 232565 | 214696 | 156421 | 55156 | 10850 | 11292 | 14202 | 9459 |
| 2,3,4-TMP | 130898 | 154057 | 78328 | 193474 | 177280 | 170200 | 189045 | 178755 | 143591 | 20073 | 13805 | 11133 | |
| 2,3,3-TMP | 226272 | 270082 | 147284 | 345093 | 284288 | 290205 | 275290 | 240247 | 145093 | 7200 | | | |
| 2,3-DMHx | 94828 | 132906 | 59588 | 184603 | 148500 | 160840 | 177456 | 150849 | 102857 | 12580 | 9188 | | 6407 |
| 3,4-DMHx | 25059 | 40209 | 11373 | 52632 | 40609 | 39389 | 52832 | 77924 | 216613 | 100426 | 83922 | 62285 | 71338 |
| 1 DMHx= | | | | | | | | | | | | | |
| 2 DMHx= | 6873 | 9740 | 5642 | 11136 | 9034 | 9200 | 8424 | 7635 | 101112 | 245801 | 248776 | 197025 | 200878 |
| 3 DMHx= | | | | | | | | | | | | | |
| 4 DMHx= | | | | | | | | | | | | | |
| 5 DMHx= | 95718 | 141909 | 46791 | 164146 | 119685 | 126855 | 110096 | 99232 | 49935 | 5765 | | | |
| 6 DMHx= | | | | 5015 | | | | | 21510 | 95705 | 92119 | 73580 | 78212 |
| **C9+** | 403759 | 530939 | 120363 | 473318 | 630933 | 777290 | 529102 | 552930 | 583902 | 362034 | 173193 | 179232 | 179567 |
| **C5+** | 3576962 | 3685498 | 2866404 | 4543823 | 3622035 | 3623825 | 3257807 | 2782851 | 1782329 | 891825 | 632295 | 537457 | 545861 |
| Tot Peak Area | 44810042 | 40965438 | 27621424 | 26431143 | 25893575 | 52412645 | 31976287 | 43623831 | 33174329 | 31010945 | 37730375 | 46528837 | 46774741 |
| ***Feed Analysis*** | | Inj 1 | Inj 2 | Inj 3 | Inj 4 | Inj 5 | Avg | Mass % | | | | | |
| C3 | | 15360 | 16384 | 16393 | 16003 | 21731 | 17174 | 0 75 | | | | | |
| i-C4 | | 1601462 | 1965158 | 1969365 | 1928514 | 2717689 | 2036438 | 89 33 | Avg Mass I/O Ratio | | | 11 64 | |
| 1-C4= | | 138689 | 170060 | 170342 | 166441 | 227416 | 174590 | 7 66 | Avg Molar I/O Ratio | | | **11.236** | |
| n-C4 | | 40302 | 50295 | 50266 | 49358 | 67435 | 51531 | 2 26 | | | | | |
| **I/O Mass Ratio** | | 11 547 | 11 556 | 11 561 | 11 587 | 11 950 | **11.640** | | | | | | |

F31EMT

(EMT; Tcalc=425degC; Trxn=77degC; P=382psig; I/O=11.4; butene WHSV=2.65h-1; t=1h; mcat=2.78g)

| **Samp t [min]** | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 19 | 22 | 27 | 37 | 67 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **T.O.S. [min.]** | **2** | **3** | **4** | **5** | **6** | **7** | **8** | **9** | **10** | **12** | **15** | **20** | **30** | **60** |
| 1-C4= Disapp. [%] | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| t-2-C4= Prod. [%] | 0 | 0 | 0 | 0 | 0 | 0 | 9 | 17 | 23 | 33 | 34 | 34 | 39 | 39 |
| c-2-C4= Prod. [%] | 0 | 0 | 0 | 0 | 0 | 0 | 4 | 7 | 9 | 14 | 14 | 14 | 16 | 17 |
| **Butene Disapp. [%]** | **100** | **100** | **100** | **100** | **100** | **100** | **87** | **76** | **67** | **53** | **52** | **52** | **45** | **44** |
| n-Butane Change [%] | 5 | 9 | 7 | 5 | 6 | 7 | 8 | 4 | 5 | 3 | -1 | 4 | 3 | -5 |
| | | | | | | | | | | | | | | |
| ***C5+ Product Analysis [mass %]*** | | | | | | | | | | | | | | |
| C5-C7 | 23 | 29 | 25 | 23 | 23 | 20 | 13 | 8 | 4 | 2 | 0 | 1 | 0 | 0 |
| **C8** | **53** | **55** | **54** | **57** | **49** | **48** | **48** | **51** | **51** | **57** | **59** | **63** | **58** | **61** |
| C9+ | 24 | 16 | 21 | 19 | 28 | 31 | 39 | 41 | 45 | 42 | 41 | 36 | 42 | 39 |
| | | | | | | | | | | | | | | |
| ***C8 Distribution [mass %]*** | | | | | | | | | | | | | | |
| **TMP** | **61** | **61** | **60** | **57** | **57** | **52** | **47** | **17** | **6** | **0** | **0** | **0** | **0** | **0** |
| DMH | 24 | 26 | 26 | 30 | 28 | 33 | 36 | 50 | 44 | 36 | 30 | 31 | 26 | 24 |
| C8= | 15 | 13 | 14 | 13 | 15 | 16 | 16 | 33 | 49 | 64 | 70 | 69 | 74 | 76 |
| | | | | | | | | | | | | | | |
| ***TMP Distribution [%]*** | | | | | | | | | | | | | | |
| 2,2,4-TMP | 50 | 47 | 45 | 43 | 40 | 35 | 31 | 32 | 25 | 0 | 0 | 0 | 0 | 0 |
| 2,2,3-TMP | 13 | 9 | 8 | 7 | 5 | 3 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 2,3,4-TMP | 13 | 17 | 18 | 20 | 24 | 30 | 36 | 38 | 38 | 0 | 0 | 0 | 0 | 0 |
| 2,3,3-TMP | 24 | 27 | 28 | 29 | 30 | 32 | 31 | 30 | 37 | 0 | 0 | 0 | 0 | 0 |
| | | | | | | | | | | | | | | |
| ***Indicators [mass fraction]*** | | | | | | | | | | | | | | |
| **TMP** | **2.51** | **2.40** | **2.33** | **1.94** | **2.06** | **1.59** | **1.30** | **0.34** | **0.14** | **0.00** | **0.00** | **0.00** | **0.00** | **0.00** |
| **DMH** | | | | | | | | | | | | | | |
| TMP+DMH | 1.41 | 2.04 | 1.65 | 1.85 | 1.17 | 1.05 | 0.86 | 0.60 | 0.36 | 0.26 | 0.21 | 0.25 | 0.18 | 0.17 |
| C8= + C9+ | | | | | | | | | | | | | | |
| (2,2,3-+2,2,4-TMP) | 1.75 | 1.27 | 1.14 | 1.02 | 0.84 | 0.62 | 0.50 | 0.47 | 0.33 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| (2,3,4-+2,3,3-TMP) | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | |
| ***DMH Isomer Distribution [%]*** | | | | | | | | | | | | | | |
| 2,5-DMH | 15 | 13 | 13 | 11 | 11 | 6 | 4 | 7 | 8 | 3 | 0 | 0 | 0 | 0 |
| 2,4-DMH | 39 | 34 | 31 | 27 | 24 | 18 | 13 | 2 | 3 | 6 | 12 | 9 | 9 | 11 |
| 2,3-DMH | 36 | 41 | 41 | 38 | 44 | 37 | 41 | 20 | 25 | 13 | 11 | 12 | 11 | 6 |
| 3,4-DMH | 10 | 12 | 15 | 23 | 21 | 40 | 42 | 70 | 64 | 78 | 77 | 79 | 80 | 83 |

F31EMT

(EMT, Tcalc=425degC, Trxn=77degC, P=382psig, I/O=11 4, butene WHSV=2 65h-1, t=1h, mcat=2 78g)

| TOS [min] | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 12 | 15 | 20 | 30 | 60 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Propane | 358200 | 372360 | 357200 | 325420 | 355420 | 377460 | 284420 | 356180 | 313120 | 358320 | 297080 | 274600 | 279280 | 324320 |
| Isobutane | 39991780 | 42439780 | 40302000 | 36822840 | 42777880 | 46696960 | 36069200 | 42727240 | 33642340 | 44536160 | 29582320 | 35544940 | 27033580 | 29508300 |
| 1-butene | | | | | | | | | | | | | | |
| n-butane | 1075000 | 1140100 | 1081140 | 966400 | 1117860 | 1226700 | 941980 | 1071960 | 860020 | 1111120 | 713560 | 893240 | 683180 | 684440 |
| t-2-butene | | | | | | | 268280 | 603860 | 640740 | 1209160 | 836060 | 995660 | 867220 | 951060 |
| c-2-butene | | | | | | | 106400 | 242740 | 260140 | 497180 | 341040 | 415600 | 369260 | 414660 |
| **C5-C7** | **913154** | **807220** | **779742** | **645845** | **635510** | **525678** | **159891** | **80640** | **34501** | **12927** | **0** | **5630** | **0** | **0** |
| C5 | 323480 | 296820 | 276460 | 215060 | 229740 | 185960 | | | | | | | | |
| 2,3-DMB | 141619 | 134944 | 129434 | 104620 | 104331 | 84738 | 36659 | 14121 | 5232 | | | | | |
| 2,2-DMP | 60703 | 55643 | 52329 | 43199 | 43288 | 34831 | 16265 | 8602 | | | | | | |
| 3-MP | 55803 | 55566 | 53870 | 46782 | 48756 | 45208 | 25836 | 18460 | 12650 | 7627 | | 5630 | | |
| 2,4-DMP | 145507 | 114516 | 112842 | 95062 | 81864 | 64294 | 27817 | 10835 | | 5300 | | | | |
| 2,2,3-TMB | 12340 | 10724 | 11199 | 9840 | 9167 | 8060 | | | | | | | | |
| 2-MHx | 32095 | 23173 | 23233 | 20885 | 17909 | 14365 | 6716 | | | | | | | |
| 2,3-DMP | 109892 | 90805 | 94623 | 86474 | 78220 | 68618 | 34322 | 18857 | 9710 | | | | | |
| 3-MHx | 31715 | 25029 | 25752 | 23923 | 22235 | 19604 | 12276 | 9765 | 6909 | | | | | |
| **C8** | **2115219** | **1504014** | **1654590** | **1588327** | **1356299** | **1240630** | **572582** | **542311** | **470014** | **479709** | **413194** | **368367** | **423636** | **361131** |
| **2,2,4-TMP** | **648084** | **434704** | **448560** | **394911** | **313619** | **224262** | **83898** | **29767** | **7274** | | | | | |
| 2,5-DMHx | 79148 | 50329 | 54522 | 51730 | 40212 | 22863 | 8248 | 20135 | 17169 | 5136 | | | | |
| 2,2,3-TMP | 172398 | 81168 | 83595 | 66419 | 40599 | 20912 | 6513 | | | | | | | |
| 2,4-DMHx | 200173 | 129454 | 133082 | 128583 | 91841 | 72780 | 26602 | 5303 | 7220 | 10688 | 14621 | 9991 | 10308 | 9196 |
| 2,3,4-TMP | 165315 | 160990 | 163428 | 162269 | 187494 | 192721 | 97401 | 35154 | 11246 | | | | | |
| 2,3,3-TMP | 304510 | 245324 | 281992 | 267880 | 232841 | 205339 | 83385 | 28272 | 10704 | | | | | |
| 2,3-DMHx | 185094 | 155962 | 176201 | 180231 | 164521 | 149096 | 85990 | 55321 | 51181 | 22120 | 13880 | 14322 | 12027 | 5366 |
| 3,4-DMHx | 50664 | 47792 | 64986 | 109735 | 78658 | 159813 | 87994 | 191958 | 132686 | 133524 | 94641 | 91645 | 89602 | 71679 |
| 1 DMHx= | | | | | | | | | | | | | | |
| 2 DMHx= | 10020 | 7144 | 6968 | 6648 | 7028 | 8854 | 11572 | 55069 | 116257 | 173374 | 182041 | 164426 | 187753 | 165135 |
| 3 DMHx= | | | | | | | | | | | | | | |
| 4 DMHx= | | | | | | | | 10434 | 9150 | 9054 | 7838 | | | |
| 5 DMHx= | 136292 | 82411 | 93563 | 90125 | 76475 | 54859 | 10110 | 5154 | | | | 7576 | 7546 | 6411 |
| 6 DMHx= | 5864 | | 5682 | | | | | 23107 | 32445 | 77854 | 67045 | 52654 | 86643 | 81729 |
| 7 DMHx= | 34702 | 28217 | 41802 | 29622 | 40325 | 36906 | 8528 | 6112 | | | | | | |
| 8 DMHx= | 122955 | 80519 | 80209 | 80174 | 82686 | 92225 | 62341 | 76525 | 74682 | 47959 | 33128 | 27753 | 29757 | 21615 |
| **C9+** | 971842 | 441580 | 638711 | 540259 | 778878 | 809695 | 468654 | 431142 | 418975 | 354137 | 289998 | 212345 | 306983 | 226087 |
| **C5+** | 4000215 | 2752814 | 3073043 | 2774431 | 2770687 | 2576003 | 1201127 | 1054093 | 923490 | 846773 | 703192 | 586342 | 730619 | 587218 |
| Tot Peak Area | 45425195 | 46705054 | 44813383 | 40889091 | 47021847 | 50877123 | 38871407 | 46056073 | 36379710 | 48061533 | 32132212 | 38294782 | 29593879 | 32055338 |
| **FEED ANAL.** | | Inj 1 | Inj 2 | Inj 3 | Inj 4 | Inj 5 | Avg | Mass % | | | | | | |
| C3 | | 19221 | 18345 | 18081 | 18050 | 14811 | 17702 | 0 75 | | | | | | |
| i-C4 | | 2300990 | 2250098 | 2211863 | 2202486 | 1645529 | 2122193 | 89 41 | Average Mass I/O Ratio | | | | 11 77 | |
| 1-C4= | | 195299 | 191639 | 188427 | 187171 | 139374 | 180382 | 7 60 | Average Molar I/O Ratio | | | | **11.359** | |
| n-C4 | | 57688 | 56834 | 55575 | 55628 | 40695 | 53284 | 2 24 | | | | | | |
| **I/O Mass Ratio** | | 11 782 | 11 741 | 11 739 | 11 767 | 11 807 | **11.767** | | | | | | | |

Run F33Y
(Y; Tcalc=425degC; Trxn=100degC; P=382psig; I/O=11.5; butene WHVS=2.62h-1; t=1h; mcat=2.78g)

| T.O.S. [min.] | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 12 | 15 | 20 | 30 | 60 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1-C4= Disapp. [%] | 95 | 100 | 100 | 100 | 100 | 100 | 97 | 96 | 96 | 95 | 96 | 96 | 95 | 95 | 96 |
| t-2-C4= Prod. [%] | 0 | 0 | 0 | 0 | 5 | 25 | 31 | 34 | 37 | 37 | 40 | 42 | 41 | 44 | 46 |
| c-2-C4= Prod. [%] | 0 | 0 | 0 | 0 | 0 | 11 | 14 | 15 | 17 | 17 | 18 | 19 | 19 | 20 | 21 |
| **Butene Disapp. [%]** | **95** | **100** | **100** | **100** | **95** | **65** | **52** | **47** | **42** | **42** | **38** | **34** | **35** | **31** | **28** |
| n-Butane Change [%] | 7 | 11 | 9 | 8 | 8 | 6 | 2 | 2 | 5 | 3 | 4 | 3 | 3 | 4 | 3 |
| ***C5+ Product Analysis [mass %]*** | | | | | | | | | | | | | | | |
| C5-C7 | 50 | 54 | 54 | 50 | 34 | 18 | 10 | 7 | 4 | 3 | 1 | 1 | 1 | 0 | 1 |
| **C8** | **41** | **40** | **40** | **36** | **43** | **55** | **54** | **57** | **57** | **69** | **60** | **67** | **52** | **65** | **77** |
| C9+ | 9 | 6 | 6 | 14 | 23 | 28 | 37 | 36 | 39 | 28 | 38 | 32 | 47 | 35 | 22 |
| ***C8 Distribution [mass %]*** | | | | | | | | | | | | | | | |
| **TMP** | **61** | **60** | **60** | **59** | **62** | **38** | **7** | **6** | **2** | **0** | **0** | **0** | **0** | **0** | **0** |
| DMH | 32 | 34 | 34 | 37 | 30 | 42 | 39 | 44 | 35 | 38 | 32 | 31 | 24 | 26 | 25 |
| C8= | 6 | 6 | 6 | 4 | 8 | 20 | 54 | 51 | 63 | 62 | 68 | 69 | 76 | 74 | 75 |
| ***TMP Isomer Distribution [%]*** | | | | | | | | | | | | | | | |
| **2,2,4-TMP** | **56** | **58** | **57** | **54** | **34** | **33** | **48** | **56** | **100** | **0** | **0** | **0** | **0** | **0** | **0** |
| 2,2,3-TMP | 9 | 8 | 7 | 6 | 23 | 21 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 2,3,4-TMP | 13 | 12 | 15 | 17 | 22 | 26 | 52 | 23 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 2,3,3-TMP | 22 | 21 | 21 | 24 | 21 | 20 | 0 | 21 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| ***Indicators [mass fraction]*** | | | | | | | | | | | | | | | |
| **TMP** | **1.91** | **1.77** | **1.78** | **1.62** | **2.04** | **0.89** | **0.19** | **0.13** | **0.06** | **0.00** | **0.00** | **0.00** | **0.00** | **0.00** | **0.00** |
| **DMH** | | | | | | | | | | | | | | | |
| TMP+DMH | 3.36 | 4.39 | 4.44 | 2.34 | 1.46 | 1.14 | 0.38 | 0.43 | 0.28 | 0.37 | 0.24 | 0.27 | 0.14 | 0.20 | 0.24 |
| C8= + C9+ | | | | | | | | | | | | | | | |
| (2,2,3-+2,2,4-TMP) | 1.86 | 1.96 | 1.78 | 1.46 | 1.33 | 1.19 | 0.92 | 1.28 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| (2,3,4-+2,3,3-TMP) | | | | | | | | | | | | | | | |
| ***DMH Isomer Distribution [%]*** | | | | | | | | | | | | | | | |
| 2,5-DMH | 25 | 25 | 25 | 21 | 18 | 5 | 0 | 8 | 11 | 4 | 0 | 6 | 0 | 0 | 0 |
| 2,4-DMH | 47 | 48 | 49 | 45 | 0 | 2 | 9 | 5 | 9 | 8 | 9 | 9 | 16 | 16 | 11 |
| 2,3-DMH | 20 | 20 | 20 | 26 | 40 | 29 | 14 | 11 | 15 | 10 | 11 | 6 | 0 | 10 | 6 |
| 3,4-DMH | 8 | 7 | 6 | 8 | 42 | 64 | 78 | 76 | 65 | 78 | 80 | 79 | 84 | 74 | 82 |

Run F 33Y
(Y, Tcalc=425degC, Trxn=100degC, P=382psig, I/O=11 5, butene WHVS=2 62h-1, t=1h, mcat=2 78g)

| TOS [min] | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 12 | 15 | 20 | 30 | 60 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Propane | 540320 | 356580 | 337700 | 355240 | 337960 | 313960 | 330160 | 389260 | 258480 | 348300 | 318400 | 352740 | 306500 | 254680 | 348660 |
| Isobutane | 64065980 | 39902300 | 36616200 | 38121380 | 42295860 | 39815360 | 39660760 | 50658180 | 32694140 | 41528120 | 40578000 | 44935720 | 36484080 | 31389280 | 43431880 |
| 1-butene | 259340 | | | | | | 101980 | 147260 | 118480 | 153620 | 131060 | 158880 | 141440 | 116240 | 157400 |
| n-butane | 1716040 | 1090460 | 973040 | 997840 | 1120020 | 1021080 | 962980 | 1250020 | 822700 | 1015640 | 1007480 | 1106700 | 895800 | 777740 | 1069180 |
| t-2-butene | | | | | 168400 | 801680 | 988920 | 1429060 | 971100 | 1240660 | 1307220 | 1528240 | 1225240 | 1117980 | 1636740 |
| c-2-butene | | | | | | 347160 | 434620 | 639420 | 437660 | 558100 | 594660 | 703140 | 555560 | 513560 | 758420 |
| **C6-C7** | **2900631** | **1713984** | **1285352** | **1188307** | **1016128** | **201830** | **26434** | **62613** | **17617** | **12626** | **7240** | **7543** | **5403** | **0** | **6415** |
| C5 | 1200340 | 731620 | 532500 | 501300 | 363920 | | | | | | | | | | |
| 2,3-DMB | 510120 | 299805 | 226327 | 210816 | 179686 | 50227 | 7024 | 11752 | 5590 | | | | | | |
| 2,2-DMP | 248045 | 147649 | 112608 | 100742 | 84815 | 24746 | | 7066 | | | | | | | |
| 3-MP | 144163 | 85721 | 67982 | 64337 | 68419 | 26385 | 8293 | 11680 | 6363 | 5740 | | | | | |
| 2,4-DMP | 385863 | 215772 | 163709 | 145776 | 132133 | 38964 | 5875 | 8259 | 5664 | 6785 | 7240 | 7543 | 5403 | | 6415 |
| 2,2,3-TMB | 21917 | 11921 | 8736 | 8288 | 8512 | | | 10501 | | | | | | | |
| 2-MHx | 90672 | 51290 | 39714 | 34130 | 33407 | 10462 | | | | | | | | | |
| 2,3-DMP | 226107 | 128087 | 100240 | 92986 | 110083 | 37747 | 5242 | 7668 | | | | | | | |
| 3-MHx | 73404 | 42119 | 33536 | 29932 | 35153 | 13299 | | 5587 | | | | | | | |
| **C8** | **2379446** | **1259060** | **936909** | **863552** | **1272111** | **613280** | **147901** | **508397** | **262615** | **305397** | **348041** | **382277** | **198933** | **202600** | **410378** |
| **2,2,4-TMP** | **815319** | **438153** | **323399** | **274897** | **266776** | **77169** | **6143** | **16880** | **5321** | | | | | | |
| 2,5-DMHx | 187648 | 105582 | 80083 | 68147 | 67371 | 12384 | | 18105 | 9981 | 5061 | | 7058 | | | |
| 2,2,3-TMP | 134453 | 60647 | 38732 | 30092 | 180755 | 48615 | | | | | | | | | |
| 2,4-DMHx | 361597 | 204200 | 156246 | 141599 | | 5461 | 5000 | 10525 | 8459 | 9216 | 9804 | 10686 | 7316 | 8274 | 11409 |
| 2,3,4-TMP | 187033 | 93097 | 82471 | 86948 | 169368 | 59233 | 5562 | 6439 | | | | | | | |
| 2,3,3-TMP | 323715 | 161866 | 120535 | 121502 | 168019 | 46540 | | 5942 | | | | | | | |
| 2,3-DMHx | 154247 | 86558 | 63417 | 81535 | 154987 | 74960 | 7912 | 24476 | 13772 | 11939 | 12123 | 7193 | | 5405 | 6502 |
| 3,4-DMHx | 61401 | 30434 | 17554 | 25733 | 162479 | 166874 | 44818 | 169866 | 60047 | 90413 | 87877 | 94186 | 39854 | 39174 | 83268 |
| 1,DMHx= | | | | | | | | | | | | | | | |
| 2 DMHx= | 13645 | 8717 | 6436 | 7013 | 21845 | 72257 | 52598 | 180499 | 120972 | 142590 | 165243 | 186882 | 113837 | 114604 | 207043 |
| 3 DMHx= | | | | | | | | | | | | | | | |
| 4 DMHx= | | | | | | | | | | | | | | | |
| 5 DMHx= | 140388 | 69806 | 48036 | 26086 | 80511 | 26299 | 5208 | 10972 | 7938 | 7741 | 7948 | 7600 | 5198 | | 5789 |
| 6 DMHx= | | | | | | 23488 | 21660 | 65693 | 36125 | 38437 | 65046 | 68672 | 32728 | 35143 | 96367 |
| **C9+** | 508103 | 190414 | 144192 | 322037 | 696234 | 309852 | 101364 | 321545 | 178187 | 122584 | 222056 | 182179 | 180063 | 110761 | 114701 |
| **C5+** | 5788180 | 3163458 | 2366453 | 2373896 | 2984473 | 1124962 | 275699 | 892455 | 458419 | 440506 | 577337 | 571999 | 384399 | 313361 | 531494 |
| Tot. Peak Area | 72369860 | 44512798 | 40293393 | 41848356 | 46906713 | 43424202 | 42755119 | 55405655 | 35323319 | 44726846 | 43919497 | 48654279 | 39437459 | 33969281 | 47175354 |
| **FEED ANAL.** | | Inj 1 | Inj 2 | Inj 3 | Inj 4 | Inj 5 | Avg | Mass % | | | | | | | |
| C3 | | 17255 | 15767 | 15794 | 18541 | 20624 | 17596 | 0 73 | | | | | | | |
| i-C4 | | 2021376 | 1915354 | 2006636 | 2316989 | 2527123 | 2157496 | 89 56 | | Avg Mass I/O Ratio | | 11 93 | | | |
| 1-C4= | | 170077 | 162649 | 170031 | 193589 | 206897 | 180649 | 7 50 | | Avg Molar I/O Ratio | | **11.515** | | | |
| n-C4 | | 49671 | 48009 | 50371 | 57473 | 60507 | 53206 | 2 21 | | | | | | | |
| **I/O Mass Ratio** | | 11 885 | 11 776 | 11 802 | 11 969 | 12 214 | **11.929** | | | | | | | | |

Run F34EMT

(EMT; Tcalc=425degC; Trxn=100degC; P=382psig; I/O=11 5; butene WHSV=2.72h-1; t=1h; mcat=2.78g)

| Samp t [min] | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 18 | 21 | 26 | 36 | 66 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **T.O.S. [min.]** | **2** | **3** | **4** | **5** | **6** | **7** | **8** | **9** | **10** | **12** | **15** | **20** | **30** | **60** |
| 1-C4= Disapp. [%] | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 97 | 97 | 96 | 96 | 96 |
| t-2-C4= Prod. [%] | 0 | 0 | 0 | 0 | 0 | 8 | 15 | 22 | 22 | 30 | 33 | 42 | 39 | 34 |
| c-2-C4= Prod. [%] | 0 | 0 | 0 | 0 | 0 | 4 | 7 | 10 | 10 | 14 | 15 | 19 | 18 | 16 |
| **Butene Disapp. [%]** | **100** | **100** | **100** | **100** | **100** | **88** | **78** | **68** | **68** | **53** | **49** | **35** | **38** | **46** |
| n-Butane Change [%] | 12 | 10 | 12 | 11 | 10 | 8 | 6 | 6 | 7 | 4 | 4 | 4 | 4 | 4 |
| | | | | | | | | | | | | | | |
| ***C5+ Product Analysis [mass %]*** | | | | | | | | | | | | | | |
| C5-C7 | 40 | 46 | 41 | 35 | 34 | 30 | 25 | 18 | 18 | 11 | 2 | 1 | 1 | 3 |
| C8 | 44 | 43 | 46 | 47 | 45 | 42 | 43 | 48 | 48 | 57 | 57 | 70 | 65 | 67 |
| C9+ | 16 | 11 | 13 | 18 | 21 | 28 | 32 | 34 | 34 | 32 | 41 | 29 | 34 | 30 |
| | | | | | | | | | | | | | | |
| ***C8 Distribution [mass %]*** | | | | | | | | | | | | | | |
| **TMP** | **60** | **59** | **62** | **60** | **59** | **57** | **50** | **38** | **38** | **16** | **4** | **2** | **0** | **0** |
| DMH | 33 | 34 | 32 | 34 | 35 | 36 | 41 | 46 | 46 | 37 | 36 | 30 | 30 | 39 |
| C8= | 6 | 7 | 5 | 6 | 6 | 7 | 10 | 16 | 16 | 48 | 60 | 68 | 70 | 61 |
| | | | | | | | | | | | | | | |
| ***TMP Isomer Distribution [%]*** | | | | | | | | | | | | | | |
| **2,2,4-TMP** | **56** | **56** | **50** | **46** | **43** | **42** | **41** | **48** | **48** | **21** | **0** | **0** | **0** | **0** |
| 2,2,3-TMP | 14 | 13 | 11 | 9 | 8 | 6 | 4 | 0 | 0 | 31 | 0 | 0 | 0 | 0 |
| 2,3,4-TMP | 10 | 11 | 15 | 19 | 22 | 24 | 26 | 29 | 29 | 27 | 61 | 100 | 0 | 0 |
| 2,3,3-TMP | 20 | 20 | 24 | 26 | 27 | 27 | 28 | 23 | 23 | 20 | 39 | 0 | 0 | 0 |
| | | | | | | | | | | | | | | |
| ***Indicators [mass fraction]*** | | | | | | | | | | | | | | |
| **TMP** | **1.81** | **1.74** | **1.93** | **1.77** | **1.72** | **1.59** | **1.22** | **0.83** | **0.83** | **0.42** | **0.12** | **0.08** | **0.00** | **0.00** |
| **DMH** | | | | | | | | | | | | | | |
| TMP+DMH | 2.22 | 2.92 | 2.72 | 2.11 | 1.78 | 1.25 | 1.09 | 0.98 | 0.98 | 0.50 | 0.30 | 0.29 | 0.25 | 0.36 |
| C8= + C9+ | | | | | | | | | | | | | | |
| (2,2,3-+2,2,4-TMP) | 2.30 | 2.21 | 1.55 | 1.22 | 1.06 | 0.94 | 0.83 | 0.91 | 0.91 | 1.09 | 0.00 | 0.00 | 0.00 | 0.00 |
| (2,3,4-+2,3,3-TMP) | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | |
| ***DMH Isomer Distribution [%]*** | | | | | | | | | | | | | | |
| 2,5-DMH | 23 | 22 | 20 | 18 | 16 | 13 | 10 | 5 | 5 | 0 | 9 | 6 | 10 | 5 |
| 2,4-DMH | 47 | 46 | 44 | 41 | 38 | 31 | 25 | 19 | 19 | 7 | 7 | 9 | 11 | 7 |
| 2,3-DMH | 21 | 23 | 27 | 29 | 33 | 38 | 39 | 37 | 37 | 17 | 16 | 11 | 16 | 14 |
| 3,4-DMH | 8 | 9 | 9 | 12 | 13 | 19 | 27 | 39 | 39 | 76 | 68 | 74 | 63 | 74 |

Run F34EMT

(EMT, Tcalc=425degC, Trxn=100degC, P=382psig, I/O=11 5, butene WHSV=2 72h-1, t=1h, mcat=2 78g)

| TOS (min) | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 12 | 15 | 20 | 30 | 60 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Propane | 327220 | 344300 | 314280 | 291240 | 308260 | 322940 | 355240 | 273000 | 273000 | 335740 | 323900 | 330120 | 254920 | 303840 |
| Isobutane | 36467720 | 35571120 | 35950880 | 34354080 | 36487960 | 38593860 | 43249960 | 32720900 | 32720900 | 40404060 | 39851720 | 42788060 | 32031560 | 36717620 |
| 1-butene | | | | | | | | | | 101720 | 108660 | 140760 | 103260 | 104420 |
| n-butane | 1008740 | 957420 | 994200 | 967940 | 992400 | 1010220 | 1108160 | 829720 | 829720 | 993420 | 983040 | 1064820 | 797380 | 906320 |
| t-2-butene | | | | | | 260540 | 538180 | 582100 | 582100 | 974800 | 1047980 | 1457200 | 1024100 | 1020380 |
| c-2-butene | | | | | | 119120 | 246320 | 267160 | 267160 | 446780 | 484480 | 677120 | 476300 | 469680 |
| **C6-C7** | **1259623** | **1176169** | **1277735** | **1320623** | **984462** | **665422** | **449730** | **132915** | **132915** | **48106** | **14057** | **6911** | **5238** | **11545** |
| C5 | 566400 | 466580 | 475660 | 461020 | 358720 | 243460 | 157360 | | | | | | | |
| 2,3-DMB | 246122 | 198832 | 221387 | 227134 | 167840 | 113120 | 75033 | 32339 | 32339 | 8359 | | | | |
| 2,2-DMP | 120897 | 97648 | 103780 | 107604 | 79628 | 53843 | 36533 | 16376 | 16376 | 5983 | | | | |
| 3-MP | 74026 | 61104 | 69263 | 74529 | 58736 | 43259 | 33600 | 17242 | 17242 | 9935 | 8007 | | | 5789 |
| 2,4-DMP | 20639 | 164329 | 186580 | 199236 | 137619 | 87563 | 58035 | 25544 | 25544 | 5039 | 6050 | 6911 | 5238 | 5756 |
| 2,2,3-TMB | 15043 | 12341 | 14263 | 17129 | 12269 | 7726 | | | | 6878 | | | | |
| 2-MHx | 50792 | 40663 | 45082 | 49908 | 35181 | 22843 | 16619 | 7515 | 7515 | | | | | |
| 2,3-DMP | 125319 | 100510 | 122964 | 139521 | 101812 | 70471 | 53481 | 24329 | 24329 | 6778 | | | | |
| 3-MHx | 40385 | 33162 | 38756 | 44542 | 32647 | 23137 | 19069 | 9570 | 9570 | 5133 | | | | |
| **C8** | **1361705** | **1096337** | **1420202** | **1788327** | **1322250** | **923092** | **778389** | **356906** | **356906** | **244087** | **366942** | **434488** | **266856** | **307079** |
| **2,2,4-TMP** | **461385** | **361563** | **442909** | **490119** | **341446** | **222506** | **169224** | **64498** | **64498** | **7998** | | | | |
| 2,5-DMHx | 105904 | 82928 | 93209 | 106855 | 73163 | 44448 | 30758 | 8857 | 8857 | | 12057 | 8236 | 7576 | 5920 |
| 2,2,3-TMP | 111551 | 85613 | 95240 | 99944 | 63044 | 32387 | 15779 | | | 11800 | | | | |
| 2,4-DMHx | 215558 | 172770 | 201546 | 250273 | 171652 | 101169 | 78227 | 31162 | 31162 | 6239 | 8798 | 11235 | 8593 | 8700 |
| 2,3,4-TMP | 83146 | 74124 | 135912 | 204606 | 170054 | 128806 | 101700 | 39110 | 39110 | 10363 | 9260 | 9806 | | |
| 2,3,3-TMP | 166205 | 127990 | 211916 | 278265 | 210635 | 143065 | 108837 | 31476 | 31476 | 7756 | 5826 | | | |
| 2,3-DMHx | 94256 | 85781 | 121724 | 177295 | 150799 | 124699 | 122786 | 59698 | 59698 | 15416 | 20524 | 13751 | 12682 | 16218 |
| 3,4-DMHx | 38526 | 32492 | 42796 | 71353 | 60776 | 61363 | 84073 | 63718 | 63718 | 67678 | 89295 | 96390 | 49058 | 87855 |
| 1 DMHx= | | | | | | | | | | | | | | |
| 2 DMHx= | 10172 | 13984 | 8982 | 12192 | 13091 | 20554 | 18906 | 22234 | 22234 | 78738 | 130268 | 193907 | 118002 | 116208 |
| 3 DMHx= | | | | | | | | | | | | | | |
| 4 DMHx= | | | | | | | 7211 | 6739 | 6739 | | | | | |
| 5 DMHx= | 75002 | 58092 | 65968 | 95425 | 67590 | 44095 | 32828 | 8481 | 8481 | 8349 | 20897 | 8823 | 7467 | 9282 |
| 6 DMHx= | | | | | | | 18040 | 19932 | 19932 | 29750 | 70017 | 92340 | 53478 | 62896 |
| **C9+** | 489096 | 278818 | 419464 | 688627 | 617472 | 621498 | 569031 | 247774 | 247774 | 137343 | 260940 | 178458 | 135617 | 136860 |
| **C5+** | 3110424 | 2549324 | 3117401 | 3795577 | 2924174 | 2210012 | 1797130 | 736594 | 736594 | 429535 | 641939 | 619857 | 397711 | 455484 |
| Tot Peak Area | 40914104 | 39422164 | 40376761 | 39408837 | 40712794 | 42516692 | 47294990 | 35409474 | 35142314 | 43239275 | 42957239 | 46400817 | 34608931 | 39508064 |
| **FEED ANAL.** | | Inj 1 | Inj 2 | Inj 3 | Inj 4 | Inj 5 | Avg | Mass % | | | | | | |
| C3 | | 17905 | 17804 | 16496 | 15396 | 17313 | 16900 | 0 73 | | | | | | |
| i-C4 | | 2181826 | 2261972 | 2114054 | 1600860 | 2217005 | 2075143 | 89 56 | Average Mass I/O Ratio | | | | 11 94 | |
| 1-C4= | | 183171 | 189430 | 178225 | 134523 | 183445 | 173759 | 7 50 | Average Molar I/O Ratio | | | | **11.526** | |
| n-C4 | | 54240 | 55599 | 52928 | 38546 | 54316 | 51126 | 2 21 | | | | | | |
| **I/O Mass Ratio** | | 11 911 | 11 941 | 11 862 | 11 900 | 12 085 | **11.940** | | | | | | | |

Run F36Y
(Y; Tcalc=425degC; Trxn=49degC; P=382psig; I/O=11.5; butene WHSV=2.61h-1; t=1h; mcat=2.78g)

| Samp t [min] | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 19 | 22 | 27 | 37 | 67 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **T.O.S. [min.]** | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** | **9** | **10** | **12** | **15** | **20** | **30** | **60** |
| 1-C4= Disapp. [%] | 96 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 95 | 91 |
| t-2-C4= Prod. [%] | 0 | 0 | 0 | 0 | 4 | 11 | 19 | 26 | 31 | 32 | 34 | 35 | 38 | 36 | 35 |
| c-2-C4= Prod. [%] | 0 | 0 | 0 | 0 | 0 | 5 | 8 | 12 | 18 | 21 | 26 | 27 | 33 | 35 | 40 |
| **Butene Disapp. [%]** | **96** | **100** | **100** | **100** | **96** | **85** | **74** | **62** | **52** | **46** | **40** | **39** | **28** | **24** | **16** |
| n-Butane Change [%] | 6 | 8 | 8 | 9 | 3 | 0 | 1 | 1 | 5 | 3 | 4 | 2 | 8 | 0 | 1 |
| | | | | | | | | | | | | | | | |
| ***C5+ Product Analysis [mass %]*** | | | | | | | | | | | | | | | |
| C5-C7 | 43 | 32 | 27 | 25 | 19 | 10 | 6 | 3 | 1 | 0 | 0 | 0 | 0 | 0 | 0 |
| **C8** | **54** | **62** | **60** | **60** | **48** | **51** | **50** | **45** | **32** | **44** | **52** | **59** | **64** | **49** | **100** |
| C9+ | 3 | 5 | 13 | 15 | 33 | 39 | 44 | 53 | 67 | 56 | 48 | 41 | 36 | 51 | 0 |
| | | | | | | | | | | | | | | | |
| ***C8 Product Distribution [mass %]*** | | | | | | | | | | | | | | | |
| **TMP** | **77** | **69** | **64** | **61** | **62** | **56** | **44** | **16** | **6** | **2** | **2** | **3** | **2** | **2** | **0** |
| DMH | 19 | 24 | 26 | 28 | 28 | 30 | 34 | 42 | 37 | 31 | 26 | 18 | 22 | 17 | 12 |
| C8= | 5 | 7 | 10 | 12 | 11 | 13 | 21 | 42 | 57 | 67 | 72 | 80 | 77 | 81 | 88 |
| | | | | | | | | | | | | | | | |
| ***TMP Distribution [%]*** | | | | | | | | | | | | | | | |
| **2,2,4-TMP** | **32** | **33** | **33** | **33** | **30** | **25** | **21** | **17** | **0** | **0** | **0** | **0** | **0** | **0** | **0** |
| 2,2,3-TMP | 5 | 4 | 5 | 5 | 3 | 3 | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 2,3,4-TMP | 29 | 29 | 27 | 28 | 31 | 35 | 37 | 35 | 63 | 100 | 100 | 100 | 100 | 100 | 0 |
| 2,3,3-TMP | 34 | 34 | 34 | 34 | 36 | 37 | 38 | 48 | 37 | 0 | 0 | 0 | 0 | 0 | 0 |
| | | | | | | | | | | | | | | | |
| ***Indicators [mass fraction]*** | | | | | | | | | | | | | | | |
| **TMP** | **4.06** | **2.83** | **2.42** | **2.18** | **2.23** | **1.85** | **1.30** | **0.37** | **0.16** | **0.07** | **0.07** | **0.14** | **0.07** | **0.12** | **0.00** |
| **DMH** | | | | | | | | | | | | | | | |
| TMP+DMH | 9.28 | 6.10 | 2.80 | 2.46 | 1.12 | 0.96 | 0.71 | 0.36 | 0.16 | 0.17 | 0.17 | 0.13 | 0.18 | 0.10 | 0.14 |
| C8= + C9+ | | | | | | | | | | | | | | | |
| (2,2,3-+2,2,4-TMP) | 0.58 | 0.59 | 0.63 | 0.61 | 0.50 | 0.39 | 0.33 | 0.21 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| (2,3,4-+2,3,3-TMP) | | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | | |
| ***DMH Distribution [%]*** | | | | | | | | | | | | | | | |
| 2,5-DMH | 12 | 6 | 9 | 8 | 5 | 3 | 0 | 4 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 2,4-DMH | 27 | 21 | 25 | 22 | 13 | 9 | 6 | 4 | 5 | 9 | 10 | 17 | 10 | 12 | 28 |
| 2,3-DMH | 31 | 33 | 30 | 32 | 29 | 23 | 9 | 7 | 5 | 0 | 0 | 13 | 0 | 0 | 0 |
| 3,4-DMH | 30 | 41 | 36 | 38 | 53 | 64 | 84 | 86 | 90 | 91 | 90 | 70 | 90 | 88 | 72 |

Run F36Y
(Y, Tcalc=425degC, Trxn=49degC, P=382psig, I/O=11 5, butene WHSV=2 61h-1, t=1h, mcat=2 78g)

| TOS (min) | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 12 | 15 | 20 | 30 | 60 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Propane | 420180 | 326920 | 313920 | 295420 | 303980 | 352900 | 273960 | 309020 | 283560 | 310260 | 293200 | 257920 | 229480 | 327940 | 329440 |
| Isobutane | 55056580 | 39782080 | 38074460 | 36358860 | 35965880 | 40138180 | 32253900 | 38084240 | 36253780 | 39141200 | 36626560 | 31966380 | 25492060 | 41017160 | 41431860 |
| 1-butene | 171040 | | | | | | | | | | | | | 170920 | 293880 |
| n-butane | 1357080 | 1019980 | 975460 | 943600 | 879440 | 954740 | 771100 | 919240 | 906680 | 951920 | 896200 | 770400 | 657340 | 975880 | 989040 |
| t-2-butene | | | | | 110220 | 354520 | 483880 | 792820 | 910280 | 1018320 | 1013060 | 891680 | 797460 | 1177980 | 1175640 |
| c-2-butene | | | | | | 150400 | 205740 | 383580 | 518940 | 666120 | 759540 | 683240 | 691160 | 1172280 | 1321720 |
| **C5-C7** | **617416** | **585337** | **517313** | **480895** | **334056** | **164574** | **55130** | **21180** | **5124** | **0** | **0** | **0** | **0** | **0** | **0** |
| C5 | 250160 | 204580 | 194260 | 174600 | 112260 | | | | | | | | | | |
| 2,3-DMB | 115251 | 104675 | 87567 | 82312 | 58676 | 39571 | 14010 | 5150 | | | | | | | |
| 2,2-DMP | 32286 | 34308 | 29870 | 27868 | 19008 | 12735 | | | | | | | | | |
| 3-MP | 50713 | 50682 | 42869 | 41580 | 31585 | 25424 | 13217 | 8031 | 5124 | | | | | | |
| 2,4-DMP | 75536 | 78190 | 65933 | 60448 | 43776 | 30738 | 10659 | | | | | | | | |
| 2,2,3-TMB | 6586 | 5647 | | 5038 | | | | | | | | | | | |
| 2-MHx | 10440 | 12783 | 11971 | 10720 | 7488 | 5560 | | | | | | | | | |
| 2,3-DMP | 62675 | 75600 | 67326 | 62182 | 48688 | 40070 | 17244 | 8009 | | | | | | | |
| 3-MHx | 13769 | 18872 | 17517 | 16147 | 12575 | 10476 | | | | | | | | | |
| **C8** | **783236** | **1130748** | **1169139** | **1134000** | **866347** | **844301** | **438737** | **349021** | **320418** | **263991** | **305650** | **227407** | **366652** | **269682** | **159289** |
| **2,2,4-TMP** | **192372** | **256767** | **248773** | **224100** | **158949** | **117778** | **41926** | **9321** | | | | | | | |
| 2,5-DMHx | 17115 | 15682 | 28233 | 25622 | 11391 | 8858 | | 5573 | | | | | | | |
| 2,2,3-TMP | 28257 | 32200 | 40153 | 35361 | 18275 | 16472 | 6171 | | | | | | | | |
| 2,4-DMHx | 40063 | 57847 | 76848 | 68202 | 31571 | 23777 | 9198 | 5539 | 6529 | 7349 | 7710 | 6820 | 8366 | 5714 | 5530 |
| 2,3,4-TMP | 173255 | 223632 | 202564 | 192966 | 164573 | 164940 | 72926 | 19051 | 12382 | 5499 | 5450 | 5775 | 5590 | 5571 | |
| 2,3,3-TMP | 205356 | 264710 | 253607 | 235717 | 192522 | 175965 | 74180 | 25916 | 7264 | | | | | | |
| 2,3-DMHx | 45532 | 89928 | 92204 | 101303 | 69296 | 59353 | 14134 | 9649 | 5411 | | | 5206 | | | |
| 3,4-DMHx | 44844 | 111578 | 109652 | 120293 | 127041 | 164276 | 126895 | 127436 | 107146 | 73898 | 71285 | 27803 | 71647 | 40740 | 13882 |
| 1 DMHx= | | | | | | | | | | | | | | | |
| 2 DMHx= | | | 5586 | 5170 | | 10269 | 31197 | 75219 | 107195 | 123747 | 151923 | 140257 | 198033 | 163913 | 108355 |
| 3 DMHx= | | | | | | | | | | | | | | | |
| 4 DMHx= | | | | | | | | | | | | | | | |
| 5 DMHx= | 13425 | 32738 | 42942 | 42567 | 16796 | 20640 | 6408 | | | | | | | | |
| 6 DMHx= | | | | | | | | 17059 | 27193 | 30058 | 45064 | 28197 | 68585 | 48475 | |
| 7 DMHx= | 6953 | 11021 | 15771 | 18746 | 15765 | 14188 | 7535 | 5031 | | | | | | | 31522 |
| 8 DMHx= | 16064 | 34645 | 54806 | 63953 | 60168 | 67785 | 48167 | 49227 | 47298 | 23440 | 24218 | 13349 | 14431 | 5269 | |
| **C9+** | 44008 | 94188 | 255282 | 276833 | 599401 | 649038 | 391017 | 410761 | 666017 | 338151 | 278148 | 160135 | 205347 | 284145 | 0 |
| **C5+** | 1444660 | 1810273 | 1941734 | 1891728 | 1799804 | 1657913 | 884884 | 780972 | 991559 | 602142 | 583798 | 387542 | 571999 | 553827 | 159289 |
| Tot Peak Area | 58449540 | 42939253 | 41305574 | 39489608 | 39059324 | 43608653 | 34873464 | 41269872 | 39345859 | 42023842 | 39412818 | 34273922 | 27748339 | 44223707 | 44379149 |
| **FEED ANAL.** | | Inj 1 | Inj 2 | Inj 3 | Inj 4 | Inj 5 | Avg | Mass % | | | | | | | |
| **C3** | | 18825 | 15463 | 16619 | 15438 | | 16586 | 0 72 | | | | | | | |
| **i-C4** | | 2351338 | 1945098 | 2049751 | 1942401 | | 2072147 | 89 60 | | | | | | | |
| **1-C4=** | | 194645 | 163620 | 171701 | 163011 | | 173244 | 7 49 | | | | | | | |
| **n-C4** | | 56886 | 48049 | 50396 | 47864 | | 50799 | 2 20 | | | | | | | |
| **I/O Mass Ratio** | | 12 080 | 11 888 | 11 938 | 11 916 | | **11.955** | | | | | | | | |

Run F44PTY

(0.5%Pt/Y; Tcalc=325degC; Tred=425degC; Trxn=52degC; P=382psig; I/O=15.3; butene WHSV=2.0h-1; t=1h; mcat=2.78g)

| Samp t [min] | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 19 | 22 | 27 | 37 | 67 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **T.O.S. [min.]** | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** | **9** | **10** | **12** | **15** | **20** | **30** | **60** |
| 1-C4= Disapp. [%] | 90 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| t-2-C4= Prod. [%] | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 9 | 16 | 25 | 35 | 37 | 39 | 40 | 43 |
| c-2-C4= Prod. [%] | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 6 | 12 | 21 | 22 | 28 | 30 | 31 |
| **Butene Disapp. [%]** | **90** | **100** | **100** | **100** | **100** | **100** | **100** | **91** | **78** | **62** | **43** | **41** | **33** | **30** | **27** |
| n-Butane Change [%] | 11 | 9 | 9 | 9 | 8 | 7 | 9 | 6 | 6 | 5 | 4 | 4 | 4 | 2 | 3 |
| | | | | | | | | | | | | | | | |
| ***C5+ Product Analysis [mass %]*** | | | | | | | | | | | | | | | |
| C5-C7 | 25 | 30 | 27 | 27 | 26 | 27 | 16 | 14 | 11 | 6 | 0 | 0 | 0 | 0 | 0 |
| **C8** | **68** | **57** | **54** | **56** | **54** | **51** | **62** | **58** | **46** | **46** | **52** | **62** | **74** | **63** | **69** |
| C9+ | 7 | 13 | 19 | 18 | 20 | 22 | 22 | 28 | 43 | 48 | 48 | 38 | 26 | 37 | 31 |
| | | | | | | | | | | | | | | | |
| ***C8 Distribution [mass %]*** | | | | | | | | | | | | | | | |
| **TMP** | **80** | **76** | **76** | **76** | **75** | **73** | **66** | **59** | **56** | **22** | **0** | **0** | **0** | **0** | **0** |
| DMH | 18 | 20 | 21 | 22 | 20 | 23 | 31 | 37 | 36 | 46 | 28 | 29 | 23 | 21 | 15 |
| C8= | 3 | 4 | 3 | 2 | 5 | 4 | 3 | 4 | 8 | 31 | 72 | 71 | 77 | 79 | 85 |
| | | | | | | | | | | | | | | | |
| **TMP Distribution [%]** | | | | | | | | | | | | | | | |
| **2,2,4-TMP** | **33** | **32** | **32** | **31** | **31** | **32** | **33** | **33** | **30** | **35** | **0** | **0** | **0** | **0** | **0** |
| 2,2,3-TMP | 3 | 3 | 4 | 3 | 3 | 4 | 3 | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 2,3,4-TMP | 29 | 32 | 30 | 32 | 32 | 31 | 30 | 32 | 35 | 39 | 0 | 0 | 0 | 0 | 0 |
| 2,3,3-TMP | 35 | 33 | 34 | 34 | 34 | 33 | 34 | 32 | 35 | 26 | 0 | 0 | 0 | 0 | 0 |
| | | | | | | | | | | | | | | | |
| ***Indicators [mass fraction]*** | | | | | | | | | | | | | | | |
| **TMP** | **4.47** | **3.88** | **3.59** | **3.42** | **3.73** | **3.23** | **2.14** | **1.62** | **1.58** | **0.48** | **0.00** | **0.00** | **0.00** | **0.00** | **0.00** |
| **DMH** | | | | | | | | | | | | | | | |
| TMP+DMH | 7.36 | 3.73 | 2.50 | 2.86 | 2.28 | 2.05 | 2.53 | 1.86 | 0.93 | 0.51 | 0.17 | 0.21 | 0.20 | 0.15 | 0.11 |
| C8= + C9+ | | | | | | | | | | | | | | | |
| (2,2,3-+2,2,4-TMP) | 0.56 | 0.54 | 0.56 | 0.52 | 0.52 | 0.56 | 0.56 | 0.56 | 0.44 | 0.54 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| (2,3,4-+2,3,3-TMP) | | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | | |
| ***DMH Distribution [%]*** | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 12 | 15 | 20 | 30 | 60 |
| 2,5-DMH | 11 | 9 | 8 | 7 | 8 | 7 | 5 | 4 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 2,4-DMH | 19 | 14 | 20 | 12 | 13 | 19 | 9 | 11 | 9 | 7 | 12 | 14 | 13 | 16 | 21 |
| 2,3-DMH | 36 | 44 | 39 | 36 | 38 | 35 | 30 | 29 | 14 | 8 | 0 | 0 | 0 | 0 | 0 |
| 3,4-DMH | 34 | 34 | 34 | 45 | 42 | 38 | 57 | 56 | 76 | 85 | 88 | 86 | 87 | 84 | 79 |

Run F44PTY
(0 5%Pt/Y, Tcalc=325degC, Tred=425degC, Trxn=52degC, P=382psig, I/O=15 3, butene WHSV=2 0h-1, t=1h, mcat=2 78g)

| TOS (min) | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 12 | 15 | 20 | 30 | 60 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Propane | 161760 | 230040 | 233580 | 238720 | 256900 | 308420 | 233500 | 280500 | 254480 | 260220 | 254400 | 218900 | 266880 | 290480 | 269380 |
| Isobutane | 21947360 | 29346600 | 29005500 | 29052280 | 30746440 | 36755640 | 28294180 | 33262060 | 30648940 | 31344200 | 30721500 | 26324020 | 31814400 | 35371140 | 32876880 |
| 1-butene | 137580 | | | | | | | | | | | | | | |
| n-butane | 553140 | 732660 | 728980 | 731600 | 762620 | 902720 | 706460 | 808980 | 742220 | 749460 | 731840 | 627080 | 753920 | 822820 | 774300 |
| t-2-butene | | | | | | | | 173840 | 299380 | 488540 | 665280 | 595600 | 761680 | 854760 | 862540 |
| c-2-butene | | | | | | | | | 117180 | 232420 | 398940 | 351900 | 540060 | 652880 | 615360 |
| **C5-C7** | **115561** | **291602** | **304935** | **306193** | **320813** | **328341** | **144370** | **125173** | **62824** | **26491** | **0** | **0** | **0** | **0** | **0** |
| C5 | | 112420 | 114100 | 112720 | 117700 | 126940 | | | | | | | | | |
| 2,3-DMB | 35745 | 52733 | 55659 | 55181 | 57418 | 59184 | 40395 | 33489 | 17086 | 7536 | | | | | |
| 2,2-DMP | 9609 | 14647 | 15671 | 16236 | 17674 | 18053 | 13025 | 11398 | 5599 | | | | | | |
| 3-MP | 14957 | 22882 | 24209 | 25142 | 26416 | 27799 | 21260 | 19092 | 12219 | 6704 | | | | | |
| 2,4-DMP | 27809 | 40835 | 42951 | 42617 | 44265 | 42882 | 30614 | 25252 | 12230 | 5430 | | | | | |
| 2,2,3-TMB | | | | | | | | | | | | | | | |
| 2-MHx | | 5432 | 5679 | 6267 | 6264 | 5960 | | | | | | | | | |
| 2,3-DMP | 22391 | 34894 | 37869 | 39212 | 41387 | 38390 | 31323 | 28166 | 15690 | 6821 | | | | | |
| 3-MHx | 5050 | 7759 | 8797 | 8818 | 9689 | 9133 | 7753 | 7776 | | | | | | | |
| **C8** | **321947** | **556060** | **615653** | **638657** | **674933** | **615541** | **542036** | **510619** | **264727** | **222681** | **149439** | **128180** | **179349** | **172494** | **183089** |
| **2,2,4-TMP** | **84161** | **135210** | **149359** | **149906** | **158345** | **144775** | **117640** | **99896** | **45288** | **17436** | | | | | |
| 2,5-DMHx | 6332 | 9481 | 10166 | 10488 | 10633 | 9774 | 7727 | 7256 | | | | | | | |
| 2,2,3-TMP | 8076 | 13988 | 16985 | 15350 | 16082 | 16812 | 11016 | 9942 | | | | | | | |
| 2,4-DMHx | 10651 | 14987 | 25334 | 16674 | 17391 | 26891 | 14387 | 21001 | 8687 | 7289 | 5118 | 5166 | 5565 | 5730 | 5769 |
| 2,3,4-TMP | 74283 | 135406 | 141422 | 155723 | 160319 | 139897 | 109114 | 96036 | 52456 | 19566 | | | | | |
| 2,3,3-TMP | 89564 | 140401 | 158229 | 162696 | 172620 | 148748 | 120325 | 98500 | 51520 | 12981 | | | | | |
| 2,3-DMHx | 20878 | 47842 | 50599 | 50823 | 51607 | 49405 | 50262 | 53695 | 13544 | 8567 | | | | | |
| 3,4-DMHx | 19490 | 37128 | 43681 | 63614 | 56545 | 53424 | 94906 | 105360 | 72116 | 87466 | 36577 | 31537 | 35696 | 31007 | 21185 |
| 1 DMHx= | | | | | | | | | | | | | | | |
| 2 DMHx= | | | | | 5573 | | 5629 | 8556 | 15075 | 54038 | 83555 | 72583 | 104375 | 110493 | 121701 |
| 3 DMHx= | | | | | | | | | | | | | | | |
| 4 DMHx= | | | | | | | | | | | | | | | |
| 5 DMHx= | 8512 | 21617 | 19878 | 13383 | 25818 | 25815 | 11030 | 11377 | 6041 | 15338 | | | | | |
| 6 DMHx= | | | | | | | | | | | 24189 | 18894 | 33713 | 25264 | 34434 |
| **C9+** | 34050 | 121713 | 218120 | 205605 | 251022 | 262039 | 190688 | 243649 | 242115 | 230359 | 135226 | 79569 | 63280 | 101521 | 82116 |
| **C5+** | 471558 | 969375 | 1138708 | 1150455 | 1246768 | 1205921 | 877094 | 879441 | 569666 | 479531 | 284665 | 207749 | 242629 | 274015 | 265205 |
| Tot Peak Area | 23271398 | 31278675 | 31106768 | 31173055 | 33012728 | 39172701 | 30111234 | 35404821 | 32514686 | 33321951 | 32657685 | 27973349 | 33839509 | 37613215 | 35048305 |
| ***Feed Analysis*** | Inj 1 | Inj 2 | Inj 3 | | | | Avg | Mass % | | | | | | | |
| **C3** | 15664 | 14410 | 14483 | | | | 14852 | 0 75 | | | | | | | |
| **i-C4** | 1883271 | 1734893 | 1782403 | | | | 1800189 | 91 35 | | | | | | | |
| **1-C4=** | 118726 | 110123 | 111245 | | | | 113365 | 5 75 | | | | | | | |
| **n-C4** | 44300 | 41321 | 41265 | | | | 42295 | 2 15 | | | | | | | |
| **I/O Mass Ratio** | 15 862 | 15 754 | 16 022 | | | | 15 880 | | | | | | | | |
| **Average I/O Molar Ratio** | | **15.329** | | | | | | | | | | | | | |

Run F45Pt1EMTr
(recalcined 0.1%Pt/EMT; Tcalc=325degC; Tred=425degC; Trxn=52degC; P=382psig; I/O=15.2; butene WHSV=2.02h-1; t=1h; mcat=2.78g)

| Samp t [min] | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 22 | 25 | 30 | 40 | 70 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **T.O.S. [min.]** | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** | **9** | **10** | **12** | **15** | **20** | **30** | **60** |
| 1-C4= Disapp. [%] | 57 | 93 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| t-2-C4= Prod. [%] | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 11 | 22 | 31 | 40 | 47 |
| c-2-C4= Prod. [%] | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 9 | 12 | 17 | 23 |
| **Butene Disapp. [%]** | **57** | **93** | **100** | **100** | **100** | **100** | **100** | **100** | **100** | **100** | **89** | **69** | **57** | **43** | **30** |
| n-Butane Change [%] | 7 | 6 | 9 | 10 | 9 | 9 | 9 | 9 | 9 | 7 | 6 | 5 | 3 | 3 | 3 |
| | | | | | | | | | | | | | | | |
| ***C5+ Product Analysis [mass %]*** | | | | | | | | | | | | | | | |
| C5-C7 | 39 | 26 | 27 | 26 | 26 | 26 | 26 | 27 | 17 | 21 | 14 | 11 | 2 | 0 | 0 |
| **C8** | **60** | **57** | **62** | **63** | **62** | **62** | **62** | **58** | **68** | **58** | **65** | **63** | **50** | **54** | **82** |
| C9+ | 2 | 17 | 10 | 11 | 13 | 12 | 12 | 15 | 15 | 21 | 21 | 26 | 48 | 46 | 18 |
| | | | | | | | | | | | | | | | |
| ***C8 Product Distribution [mass %]*** | | | | | | | | | | | | | | | |
| **TMP** | **84** | **80** | **79** | **78** | **77** | **76** | **76** | **76** | **69** | **67** | **70** | **61** | **16** | **0** | **0** |
| DMH | 12 | 14 | 15 | 17 | 18 | 19 | 18 | 18 | 26 | 27 | 25 | 24 | 36 | 29 | 17 |
| C8= | 3 | 6 | 5 | 6 | 5 | 6 | 6 | 6 | 5 | 6 | 5 | 15 | 48 | 71 | 83 |
| | | | | | | | | | | | | | | | |
| ***TMP Isomer Distribution [%]*** | | | | | | | | | | | | | | | |
| **2,2,4-TMP** | **49** | **43** | **42** | **41** | **40** | **41** | **40** | **39** | **40** | **37** | **34** | **30** | **28** | **0** | **0** |
| 2,2,3-TMP | 19 | 24 | 22 | 21 | 18 | 18 | 18 | 16 | 10 | 9 | 7 | 5 | 0 | 0 | 0 |
| 2,3,4-TMP | 11 | 12 | 13 | 14 | 16 | 16 | 16 | 17 | 21 | 23 | 26 | 30 | 34 | 0 | 0 |
| 2,3,3-TMP | 21 | 22 | 23 | 24 | 26 | 26 | 26 | 27 | 28 | 31 | 33 | 35 | 38 | 0 | 0 |
| | | | | | | | | | | | | | | | |
| ***Indicators [mass fraction]*** | | | | | | | | | | | | | | | |
| **TMP** | **6.79** | **5.63** | **5.19** | **4.66** | **4.24** | **4.09** | **4.11** | **4.17** | **2.64** | **2.50** | **2.79** | **2.57** | **0.44** | **0.00** | **0.00** |
| **DMH** | | | | | | | | | | | | | | | |
| TMP+DMH | 16.51 | 2.61 | 4.35 | 4.11 | 3.67 | 3.78 | 3.71 | 2.92 | 3.55 | 2.27 | 2.62 | 1.51 | 0.36 | 0.19 | 0.17 |
| C8= + C9+ | | | | | | | | | | | | | | | |
| (2,2,3-+2,2,4-TMP) | 2.12 | 1.99 | 1.82 | 1.65 | 1.39 | 1.43 | 1.37 | 1.23 | 1.01 | 0.86 | 0.70 | 0.54 | 0.39 | 0.00 | 0.00 |
| (2,3,4-+2,3,3-TMP) | | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | | |
| ***DMH Isomer Distribution [%]*** | | | | | | | | | | | | | | | |
| 2,5-DMH | 19 | 21 | 19 | 17 | 15 | 15 | 15 | 15 | 10 | 9 | 9 | 6 | 0 | 0 | 0 |
| 2,4-DMH | 12 | 11 | 11 | 10 | 10 | 10 | 10 | 11 | 23 | 22 | 17 | 10 | 8 | 13 | 21 |
| 2,3-DMH | 52 | 54 | 55 | 55 | 48 | 46 | 49 | 48 | 35 | 36 | 37 | 29 | 12 | 0 | 0 |
| 3,4-DMH | 17 | 14 | 15 | 18 | 27 | 29 | 25 | 26 | 32 | 33 | 37 | 55 | 80 | 87 | 79 |

Run F45P11EM1r

(recalcined 0 1%Pt/EM1, Tcalc=325degC, Tred=425degC, Trxn=52degC, P=382psig, I/O=15 2, butene WHSV=2 02h-1, t=1h, mcat=2 78g)

| TOS (min) | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 12 | 15 | 20 | 30 | 60 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Propane | 205040 | 222220 | 247820 | 229320 | 255620 | 251280 | 258080 | 264620 | 234160 | 268580 | 263520 | 269720 | 268560 | 254240 | 260780 |
| Isobutane | 32681960 | 29698100 | 30616180 | 27626420 | 30141100 | 29451640 | 30130680 | 31000340 | 27534860 | 31379080 | 31326440 | 32078780 | 32129000 | 30872580 | 31779840 |
| 1-butene | 883920 | 131980 | | | | | | | | | | | | | |
| n-butane | 821920 | 745620 | 787880 | 713740 | 771620 | 754140 | 770560 | 784360 | 696580 | 785920 | 768340 | 781000 | 764740 | 738500 | 757380 |
| t-2-butene | | | | | | | | | | | 213480 | 441840 | 611180 | 766140 | 918860 |
| c-2-butene | | | | | | | | | | | | 180180 | 239900 | 321520 | 458440 |
| **C6-C7** | **272837** | **396821** | **423872** | **379626** | **387250** | **372893** | **363661** | **334210** | **181146** | **284497** | **126111** | **69221** | **6828** | **0** | **0** |
| C5 | 107300 | 146820 | 154440 | 138180 | 141020 | 135100 | 131560 | 126520 | | 103740 | | | | | |
| 2,3-DMB | 44523 | 61491 | 65360 | 58302 | 59110 | 57125 | 56179 | 52751 | 44292 | 43622 | 30600 | 17615 | | | |
| 2,2-DMP | 15990 | 23087 | 24795 | 22339 | 22413 | 21922 | 21664 | 20036 | 16545 | 16237 | 11224 | 6230 | | | |
| 3-MP | 18586 | 26711 | 29357 | 27071 | 27856 | 27525 | 27670 | 25800 | 22798 | 23218 | 17387 | 11540 | 5828 | | |
| 2,4-DMP | 46453 | 67825 | 70530 | 61950 | 61641 | 57910 | 56180 | 48374 | 43873 | 42468 | 29917 | 16743 | | | |
| 2,2,3-TMB | | 5930 | 6210 | 5711 | 5883 | 6026 | 5422 | 5027 | | | | | | | |
| 2-MHx | 6367 | 10220 | 11409 | 9922 | 10245 | 9940 | 8949 | 7806 | 7336 | 7120 | | | | | |
| 2,3-DMP | 27351 | 44056 | 49220 | 44943 | 46825 | 45902 | 44631 | 37995 | 36838 | 38222 | 28290 | 17093 | | | |
| 3-MHx | 6267 | 10681 | 12551 | 11408 | 12257 | 11443 | 11406 | 9901 | 9464 | 9870 | 7693 | | | | |
| **C8** | **423906** | **862460** | **962783** | **903229** | **931214** | **896151** | **880725** | **718407** | **738828** | **810604** | **583436** | **385500** | **191436** | **183080** | **187185** |
| **2,2,4-TMP** | **174487** | **296623** | **324115** | **290693** | **288728** | **276371** | **268572** | **213382** | **206074** | **204787** | **139860** | **71662** | **8628** | | |
| 2,5-DMHx | 10167 | 25291 | 28217 | 25842 | 25572 | 25371 | 25099 | 19648 | 19187 | 19273 | 12607 | 5325 | | | |
| 2,2,3-TMP | 68858 | 164487 | 168943 | 145240 | 126068 | 123680 | 116996 | 86382 | 51371 | 48562 | 28514 | 11446 | | | |
| 2,4-DMHx | 6578 | 14114 | 15600 | 14480 | 16039 | 15959 | 16262 | 13792 | 44643 | 47543 | 25116 | 9159 | 5244 | 6807 | 6655 |
| 2,3,4-TMP | 38684 | 80653 | 96277 | 95787 | 112507 | 105689 | 109192 | 95023 | 109095 | 123292 | 105334 | 70197 | 10361 | | |
| 2,3,3-TMP | 76142 | 150828 | 174585 | 169159 | 186117 | 173764 | 172781 | 149396 | 144738 | 170087 | 135957 | 82597 | 11489 | | |
| 2,3-DMHx | 27291 | 66274 | 80718 | 83323 | 80963 | 75726 | 80194 | 62920 | 67218 | 79796 | 54111 | 26822 | 8627 | | |
| 3,4-DMHx | 8708 | 17113 | 22753 | 26778 | 45655 | 48824 | 40719 | 34028 | 62939 | 72008 | 54944 | 50600 | 55852 | 46798 | 25643 |
| 1 DMHx= | | | | | | | | | | | | | | | |
| 2 DMHx= | | | | | | | | | | | 10118 | 35719 | 73246 | 102613 | 115155 |
| 3 DMHx= | | | | | | | | | | | | | | | |
| 4 DMHx= | | | | | | | | | | | | | | | |
| 5 DMHx= | 12990 | 48177 | 51575 | 51927 | 49565 | 50767 | 50910 | 43836 | 33563 | 38701 | 16885 | 9503 | | | |
| 6 DMHx= | | | | | | | | | | 6455 | | 12580 | 17991 | 26862 | 39732 |
| **C9+** | 11892 | 263684 | 157784 | 155428 | 190686 | 172807 | 172713 | 187344 | 165106 | 292332 | 185175 | 159742 | 184962 | 157003 | 40747 |
| **C5+** | 708634 | 1522965 | 1544439 | 1438483 | 1509150 | 1440851 | 1417099 | 1239961 | 1085080 | 1387333 | 893722 | 614463 | 382226 | 340083 | 227932 |
| Tot Peak Area | 35301474 | 32320885 | 33196319 | 30007963 | 32677490 | 31897911 | 32576419 | 33289281 | 29550680 | 33820913 | 33465502 | 34185803 | 34155706 | 32971543 | 33944792 |
| **FEED ANAL.** | | Inj 1 | Inj 2 | Inj 3 | Inj 4 | Inj 5 | Avg | Mass % | | | | | | | |
| **C3** | | 13716 | 12728 | 12663 | 13895 | 14434 | 13487 | 0 75 | | | | | | | |
| **i-C4** | | 1645782 | 1551900 | 1552553 | 1716830 | 1790705 | 1651554 | 91 28 | | | | | | | |
| **1-C4=** | | 104396 | 99235 | 99322 | 108681 | 113424 | 105012 | 5 80 | | | | | | | |
| **n-C4** | | 39107 | 37152 | 37183 | 40487 | 42433 | 39272 | 2 17 | | | | | | | |
| **I/O Mass Ratio** | | 15 765 | 15 639 | 15 632 | 15 797 | 15 788 | 15 724 | | | | | | | | |

Run F48Pt5EMTr
(recalcined 0.5%Pt/EMT; tcalc=325degC; Tred=425degC; Trxn=52degC; P=382psig; t/O=15.2; butene WHVS=2.03h-1; t=1; mcat=2.78g)

| Samp t [min] | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 20 | 23 | 28 | 38 | 68 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| T.O.S. [min.] | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 12 | 15 | 20 | 30 | 60 |
| 1-C4= Disapp. [%] | 54 | 88 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| t-2-C4= Prod. [%] | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 9 | 20 | 33 | 38 | 43 | 46 |
| c-2-C4= Prod. [%] | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 7 | 14 | 15 | 19 | 24 |
| Butene Disapp. [%] | 54 | 88 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 91 | 73 | 53 | 47 | 38 | 30 |
| n-Butane Change [%] | 6 | 6 | 9 | 7 | 7 | 8 | 8 | 8 | 10 | 9 | 9 | 7 | 1 | 1 | 3 |
| | | | | | | | | | | | | | | | |
| *C5+ Product Analysis* | | | | | | | | | | | | | | | |
| C5-C7 | 42 | 29 | 28 | 27 | 28 | 16 | 20 | 13 | 11 | 11 | 4 | 0 | 0 | 0 | 0 |
| C8 | 58 | 63 | 63 | 63 | 58 | 66 | 56 | 57 | 57 | 56 | 44 | 55 | 55 | 58 | 69 |
| C9+ | 0 | 8 | 9 | 10 | 14 | 18 | 24 | 30 | 32 | 33 | 52 | 45 | 45 | 42 | 31 |
| | | | | | | | | | | | | | | | |
| *C8 Product Distribution* | | | | | | | | | | | | | | | |
| TMP | 91 | 81 | 79 | 79 | 76 | 71 | 70 | 70 | 66 | 61 | 29 | 3 | 0 | 0 | 0 |
| DMH | 7 | 14 | 15 | 16 | 18 | 24 | 25 | 26 | 30 | 34 | 55 | 35 | 26 | 29 | 18 |
| C8= | 3 | 5 | 6 | 5 | 6 | 5 | 5 | 4 | 4 | 4 | 16 | 62 | 74 | 71 | 82 |
| | | | | | | | | | | | | | | | |
| *TMP Isomer Distribution* | | | | | | | | | | | | | | | |
| 2,2,4-TMP | 46 | 40 | 41 | 39 | 39 | 39 | 35 | 32 | 27 | 25 | 31 | 0 | 0 | 0 | 0 |
| 2,2,3-TMP | 19 | 22 | 14 | 18 | 16 | 9 | 8 | 5 | 5 | 4 | 0 | 0 | 0 | 0 | 0 |
| 2,3,4-TMP | 10 | 13 | 16 | 16 | 17 | 22 | 25 | 30 | 33 | 34 | 35 | 0 | 0 | 0 | 0 |
| 2,3,3-TMP | 25 | 25 | 29 | 27 | 29 | 31 | 33 | 34 | 35 | 37 | 34 | 100 | 0 | 0 | 0 |
| | | | | | | | | | | | | | | | |
| *Indicators [mass fraction]* | | | | | | | | | | | | | | | |
| TMP | 13.59 | 6.92 | 6.28 | 4.96 | 4.12 | 2.99 | 2.86 | 2.73 | 2.24 | 1.80 | 0.62 | 0.09 | 0.00 | 0.00 | 0.00 |
| DMH | | | | | | | | | | | | | | | |
| TMP+DMH | 36.44 | 5.35 | 4.48 | 4.32 | 3.19 | 2.84 | 2.00 | 1.65 | 1.58 | 1.51 | 0.62 | 0.26 | 0.17 | 0.20 | 0.14 |
| C8= + C9+ | | | | | | | | | | | | | | | |
| (2,2,3-+2,2,4-TMP) | 1.86 | 1.64 | 1.22 | 1.33 | 1.20 | 0.90 | 0.74 | 0.57 | 0.48 | 0.40 | 0.45 | 0.00 | 0.00 | 0.00 | 0.00 |
| (2,3,4-+2,3,3-TMP) | | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | | |
| *DMH Isomer Distribution* | | | | | | | | | | | | | | | |
| 2,5-DMH | 39 | 19 | 16 | 17 | 15 | 10 | 10 | 5 | 6 | 4 | 0 | 0 | 0 | 0 | 0 |
| 2,4-DMH | 0 | 11 | 8 | 10 | 10 | 20 | 23 | 16 | 11 | 6 | 0 | 10 | 13 | 11 | 20 |
| 2,3-DMH | 61 | 52 | 56 | 51 | 49 | 47 | 38 | 40 | 32 | 27 | 14 | 10 | 0 | 9 | 0 |
| 3,4-DMH | 0 | 19 | 21 | 22 | 27 | 23 | 29 | 39 | 52 | 62 | 86 | 80 | 87 | 80 | 80 |

Run F48P15EMTr
(recalcined 0 5%Pt/EMT, tcalc=325degC, Tred=425degC, Trxn=52degC, P=382psig, I/O=15 2, butene WHVS=2 03h-1, t=1, mcat=2 78g)

| TOS [min] | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 12 | 15 | 20 | 30 | 60 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Propane | 233640 | 257900 | 262280 | 279480 | 286440 | 236100 | 276700 | 280980 | 278700 | 279380 | 238340 | 260820 | 279980 | 292340 | 274340 |
| Isobutane | 35347900 | 33655200 | 31863940 | 33327000 | 33959980 | 27167860 | 32286960 | 33219700 | 33386400 | 33729640 | 28741480 | 31417920 | 33969020 | 35969980 | 34592420 |
| 1-butene | 1027760 | 263000 | | | | | | | | | | | | | |
| n-butane | 879840 | 842180 | 817200 | 839940 | 862180 | 689940 | 823560 | 843900 | 854280 | 856340 | 724260 | 784140 | 800180 | 854420 | 835560 |
| t-2-butene | | | | | | | | | | 182380 | 346060 | 647060 | 793020 | 951540 | 989760 |
| c-2-butene | | | | | | | | | | | 123220 | 262660 | 316440 | 427900 | 508420 |
| **C6-C7** | **249912** | **383169** | **387176** | **392688** | **442940** | **183966** | **288851** | **165973** | **120268** | **83356** | **13644** | **0** | **0** | **0** | **0** |
| C5 | 100920 | 138320 | 135720 | 142580 | 129700 | | 103360 | | | | | | | | |
| 2,3-DMB | 40058 | 60843 | 61461 | 61015 | 55675 | 43085 | 44792 | 38618 | 28030 | 18393 | | | | | |
| 2,2-DMP | 13196 | 20711 | 21750 | 21994 | 20448 | 15969 | 15974 | 13397 | 10340 | 7387 | | | | | |
| 3-MP | 17549 | 27165 | 28484 | 29538 | 28276 | 22553 | 23741 | 22155 | 18436 | 15074 | 7527 | | | | |
| 2,4-DMP | 42484 | 67047 | 65628 | 62030 | 55679 | 44600 | 42681 | 35976 | 25585 | 15155 | | | | | |
| 2,2,3-TMB | | 5954 | 6140 | 6449 | 6357 | | | 5044 | | | | | | | |
| 2-MHx | 5057 | 8871 | 9455 | 9430 | 88678 | 7512 | 7277 | 5983 | | | | | | | |
| 2,3-DMP | 25277 | 44178 | 47462 | 48537 | 46360 | 40210 | 41523 | 36177 | 29888 | 20996 | 6117 | | | | |
| 3-MHx | 5371 | 10070 | 11076 | 11315 | 11767 | 10057 | 9503 | 8623 | 7989 | 6351 | | | | | |
| **C8** | **344342** | **827014** | **874264** | **919014** | **912160** | **769439** | **796462** | **721493** | **634721** | **440800** | **154392** | **161023** | **219230** | **246126** | **182133** |
| **2,2,4-TMP** | **142919** | **267550** | **281609** | **282208** | **266091** | **211781** | **194096** | **159399** | **115060** | **68111** | **14015** | | | | |
| 2,5-DMHx | 8988 | 21521 | 20465 | 24521 | 24430 | 18933 | 18684 | 8827 | 10699 | 5487 | | | | | |
| 2,2,3-TMP | 60127 | 149005 | 97569 | 130505 | 109593 | 47030 | 42922 | 24727 | 21166 | 9768 | | | | | |
| 2,4-DMHx | | 12316 | 10346 | 15186 | 16433 | 36437 | 45567 | 29368 | 20302 | 9689 | | 5753 | 7422 | 7957 | 6249 |
| 2,3,4-TMP | 31817 | 84964 | 109477 | 113384 | 115240 | 119358 | 138453 | 149942 | 138519 | 92793 | 15537 | | | | |
| 2,3,3-TMP | 77310 | 169678 | 201625 | 197840 | 197817 | 166781 | 183344 | 171342 | 146258 | 100171 | 15286 | 5026 | | | |
| 2,3-DMHx | 13985 | 58583 | 72859 | 74196 | 81992 | 85604 | 74350 | 74114 | 59557 | 41236 | 11812 | 5437 | | 6376 | |
| 3,4-DMHx | | 21041 | 27114 | 32323 | 44496 | 41313 | 57274 | 72907 | 97065 | 93883 | 73721 | 45095 | 49575 | 57745 | 25795 |
| 1 DMHx= | | | | | | | | | | | | | | | |
| 2 DMHx= | | | | | | | | | | 9250 | 24021 | 80596 | 123359 | 137017 | 122792 |
| 3 DMHx= | | | | | | | | | | | | | | | |
| 4 DMHx= | | | | | | | | | | | | | | | |
| 5 DMHx= | 9196 | 42356 | 53200 | 48851 | 49295 | 42202 | 41772 | 30867 | 26105 | 10412 | | | | | |
| 6 DMHx= | | | | | 6773 | | | | | | | 19116 | 38874 | 37031 | 27297 |
| **C9+** | 0 | 104410 | 130114 | 152380 | 211942 | 213975 | 336438 | 388738 | 358589 | 260067 | 185331 | 133370 | 179014 | 180029 | 81097 |
| **C5+** | 594254 | 1314583 | 1391554 | 1464282 | 1567042 | 1167400 | 1421751 | 1276204 | 1113578 | 784223 | 353367 | 294393 | 398244 | 426155 | 263230 |
| Tot Peak Area | 38083394 | 36332863 | 34334974 | 35910702 | 36675642 | 29261300 | 34808971 | 35620784 | 35632958 | 35831963 | 30403507 | 33404333 | 36240444 | 38494435 | 36955310 |
| FEED ANAL. | Inj 1,2 | Inj 3,4 | Inj 5,6 | Inj 7,8 | Inj 9,10 | Inj 11,12 | Avg | Mass % | | | | | | | |
| C3 | 13246 | 13275 | 14345 | 13714 | 12612 | 12581 | 13295 | 0 75 | | | | | | | |
| i-C4 | 1604909 | 1635118 | 1763578 | 1668810 | 1519776 | 1531788 | 1620663 | 91 26 | | | | | | | |
| 1-C4= | 102450 | 103575 | 111656 | 106264 | 97260 | 97740 | 103157 | 5 81 | | | | | | | |
| n-C4 | 38628 | 38802 | 42080 | 40136 | 36619 | 36774 | 38840 | 2 19 | | | | | | | |
| I/O Mass Ratio | 15 665 | 15 787 | 15 795 | 15 704 | 15 626 | 15 672 | 15 708 | | | | | | | | |

Run F49Pt5EMT

(0.5%Pt/EMT; Tcalc=325degC; Tred=425degC; Trxn=51degC; P=382psig; I/O=15.2; butene WHSV=2.02h-1; t=1h; mcat=2.78g)

| Samp t [min] | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 21 | 24 | 29 | 39 | 69 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **T.O.S. [min.]** | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** | **9** | **10** | **12** | **15** | **20** | **30** | **60** |
| 1-C4= Disapp. [%] | 82 | 94 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| t-2-C4= Prod. [%] | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 15 | 24 | 30 | 37 | 42 |
| c-2-C4= Prod. [%] | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 10 | 13 | 18 | 26 |
| **Butene Disapp. [%]** | **82** | **94** | **100** | **100** | **100** | **100** | **100** | **100** | **100** | **100** | **85** | **67** | **56** | **45** | **32** |
| n-Butane Change [%] | 9 | 9 | 7 | 6 | 9 | 9 | 9 | 9 | 9 | 8 | 6 | 7 | 5 | 4 | 6 |
| | | | | | | | | | | | | | | | |
| ***C5+ Product Analysis [mass %]*** | | | | | | | | | | | | | | | |
| C5-C7 | 43 | 27 | 26 | 18 | 28 | 25 | 23 | 20 | 13 | 11 | 7 | 5 | 2 | 0 | 0 |
| **C8** | **57** | **64** | **61** | **61** | **58** | **61** | **62** | **61** | **58** | **53** | **44** | **37** | **53** | **57** | **62** |
| C9+ | 0 | 9 | 13 | 20 | 14 | 14 | 15 | 19 | 30 | 36 | 49 | 57 | 45 | 43 | 38 |
| | | | | | | | | | | | | | | | |
| ***C8 Distribution [mass %]*** | | | | | | | | | | | | | | | |
| **TMP** | **94** | **80** | **77** | **75** | **79** | **76** | **74** | **70** | **72** | **68** | **62** | **50** | **20** | **4** | **0** |
| DMH | 6 | 16 | 19 | 18 | 19 | 19 | 21 | 25 | 24 | 28 | 28 | 28 | 35 | 27 | 20 |
| C8= | 0 | 5 | 5 | 6 | 2 | 5 | 5 | 4 | 5 | 4 | 10 | 22 | 45 | 69 | 80 |
| | | | | | | | | | | | | | | | |
| ***TMP Isomer Distribution [%]*** | | | | | | | | | | | | | | | |
| **2,2,4-TMP** | **27** | **32** | **37** | **30** | **38** | **35** | **34** | **32** | **31** | **28** | **29** | **29** | **39** | **0** | **0** |
| 2,2,3-TMP | 8 | 16 | 12 | 17 | 17 | 16 | 8 | 8 | 6 | 6 | 5 | 5 | 0 | 0 | 0 |
| 2,3,4-TMP | 24 | 21 | 20 | 20 | 18 | 21 | 26 | 28 | 29 | 31 | 30 | 31 | 28 | 0 | 0 |
| 2,3,3-TMP | 41 | 32 | 32 | 33 | 27 | 29 | 32 | 32 | 34 | 34 | 36 | 35 | 33 | 100 | 0 |
| | | | | | | | | | | | | | | | |
| ***Indicators [mass fraction]*** | | | | | | | | | | | | | | | |
| **TMP** | **15.59** | **5.09** | **4.14** | **4.11** | **4.24** | **3.99** | **3.49** | **2.77** | **3.00** | **2.41** | **2.21** | **1.76** | **0.57** | **0.15** | **0.00** |
| **DMH** | | | | | | | | | | | | | | | |
| TMP+DMH | n.a. | 5.23 | 3.61 | 2.37 | 3.69 | 3.39 | 3.29 | 2.71 | 1.71 | 1.33 | 0.75 | 0.45 | 0.42 | 0.21 | 0.15 |
| C8= + C9+ | | | | | | | | | | | | | | | |
| (2,2,3-+2,2,4-TMP) | 0.55 | 0.90 | 0.93 | 0.91 | 1.21 | 1.02 | 0.72 | 0.66 | 0.58 | 0.52 | 0.52 | 0.50 | 0.64 | 0.00 | 0.00 |
| (2,3,4-+2,3,3-TMP) | | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | | |
| ***DMH Isomer Distribution [%]*** | | | | | | | | | | | | | | | |
| 2,5-DMH | 0 | 14 | 11 | 13 | 15 | 13 | 10 | 8 | 7 | 5 | 6 | 10 | 0 | 0 | 0 |
| 2,4-DMH | 0 | 9 | 7 | 8 | 9 | 8 | 21 | 21 | 9 | 8 | 4 | 0 | 7 | 12 | 18 |
| 2,3-DMH | 100 | 47 | 62 | 55 | 47 | 53 | 41 | 35 | 37 | 30 | 25 | 17 | 17 | 0 | 0 |
| 3,4-DMH | 0 | 31 | 20 | 24 | 29 | 25 | 28 | 36 | 47 | 57 | 65 | 73 | 75 | 88 | 82 |

Run F49f15EMT
(0.5%Pt/EMT, Tcalc=325degC, Tred=425degC, Trxn=51degC, P=382psig, I/O=15.2, butene WHSV=2.02h-1, t=1h, mcat=2.78g)

| TOS [min] | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 12 | 15 | 20 | 30 | 60 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Propane | 273780 | 237320 | 245840 | 248980 | 236540 | 271240 | 264000 | 268980 | 270700 | 237040 | 240280 | 268380 | 282500 | 276680 | 253240 |
| Isobutane | 46688840 | 31206720 | 30605060 | 29856800 | 28496380 | 32436580 | 31486840 | 32055300 | 32200720 | 28486780 | 29135780 | 32558440 | 34143860 | 33462540 | 31220120 |
| 1-butene | 500150 | 125280 | | | | | | | | | | | | | |
| n-butane | 1157040 | 791800 | 766480 | 745960 | 724180 | 822540 | 803760 | 819560 | 816680 | 718600 | 721620 | 808860 | 828060 | 807120 | 765420 |
| t-2-butene | | | | | | | | | | | 273740 | 480460 | 638160 | 762220 | 814200 |
| c-2-butene | | | | | | | | | | | | 193540 | 278680 | 376980 | 493900 |
| **C6-C7** | **92485** | **338637** | **343037** | **272129** | **307669** | **338941** | **315956** | **308586** | **171858** | **119706** | **82053** | **40668** | **6122** | **0** | **0** |
| C5 | | 125520 | 125500 | 109040 | 115740 | 123120 | 115960 | 104260 | | | | | | | |
| 2,3-DMB | 30859 | 53148 | 54665 | 38554 | 49760 | 52445 | 49776 | 48248 | 41135 | 28637 | 26400 | 10498 | | | |
| 2,2-DMP | 9431 | 17550 | 18546 | 13079 | 18163 | 18808 | 17019 | 16859 | 14886 | 10148 | 5045 | | | | |
| 3-MP | 12665 | 24426 | 25383 | 17971 | 23880 | 25833 | 24647 | 25202 | 22590 | 17864 | 11369 | 8931 | 6122 | | |
| 2,4-DMP | 24462 | 55401 | 56043 | 41907 | 47811 | 52256 | 49553 | 48164 | 39855 | 28118 | 15874 | 9840 | | | |
| 2,2,3-TMB | | 5511 | 5892 | | | 5572 | | 5826 | | | | | | | |
| 2-MHx | | 7341 | 4818 | 7027 | 7324 | 8039 | 7408 | 7386 | 6426 | | | | | | |
| 2,3-DMP | 15068 | 40650 | 42319 | 36142 | 36262 | 42059 | 41569 | 42349 | 37555 | 27251 | 18364 | 11399 | | | |
| 3-MHx | | 9090 | 9871 | 8409 | 8729 | 10809 | 10023 | 10292 | 9411 | 7687 | 5001 | | | | |
| **C8** | **121345** | **812877** | **802328** | **917316** | **647490** | **833053** | **843268** | **922367** | **778282** | **600816** | **516688** | **278120** | **206964** | **182699** | **162366** |
| **2,2,4-TMP** | **30859** | **205764** | **225916** | **209764** | **196348** | **219506** | **210435** | **206209** | **170696** | **116926** | **93075** | **39747** | **16116** | | |
| 2,5-DMHx | | 17362 | 16749 | 21895 | 17628 | 20829 | 18787 | 19020 | 12080 | 8543 | 8499 | 7642 | | | |
| 2,2,3-TMP | 9553 | 100442 | 71026 | 118585 | 85565 | 98682 | 50410 | 51837 | 33177 | 23436 | 16045 | 6597 | | | |
| 2,4-DMHx | | 11114 | 9952 | 13801 | 11248 | 13276 | 38081 | 48512 | 17502 | 13395 | 5797 | | 5174 | 6088 | 5952 |
| 2,3,4-TMP | 27022 | 134523 | 123103 | 134618 | 91229 | 131756 | 162167 | 181756 | 161628 | 128168 | 96290 | 43505 | 11594 | | |
| 2,3,3-TMP | 46598 | 206290 | 195541 | 227122 | 141360 | 180669 | 201093 | 209077 | 191887 | 140059 | 115540 | 48863 | 13611 | 7349 | |
| 2,3-DMHx | 7313 | 59654 | 92422 | 92284 | 56857 | 83841 | 72669 | 82829 | 68788 | 50065 | 36229 | 13325 | 12586 | | |
| 3,4-DMHx | | 38864 | 29545 | 39926 | 35718 | 40083 | 49398 | 83633 | 87462 | 97128 | 94403 | 57765 | 54313 | 42642 | 27268 |
| 1,DMHx= | | | | | | | | | | | | | | | |
| 2 DMHx= | | | | | | | | | | | 29741 | 42405 | 69466 | 99418 | 106130 |
| 3 DMHx= | | | | | | | | | | | | | | | |
| 4 DMHx= | | | | | | | | | | | | | | | |
| 5 DMHx= | | 38864 | 38074 | 54023 | 11537 | 44411 | 40228 | 40494 | 35072 | 24095 | 20069 | 5108 | | | |
| 6 DMHx= | | | | 5297 | | | | | | | | 13163 | 24104 | 27102 | 23006 |
| **C9+** | | 109145 | 173517 | 303007 | 160597 | 188479 | 203613 | 284741 | 398640 | 409512 | 574289 | 424391 | 174847 | 137775 | 98347 |
| **C5+** | 213830 | 1260659 | 1318882 | 1492451 | 1115756 | 1360473 | 1362836 | 1515694 | 1348780 | 1130032 | 1172030 | 743179 | 387933 | 320374 | 260703 |
| Tot Peak Area | 48833640 | 33621779 | 32936262 | 32344191 | 30572856 | 34890833 | 33917436 | 34659534 | 34636880 | 30572452 | 31543450 | 34859319 | 36280513 | 35628934 | 33313683 |
| ***Feed Analysis*** | | Inj 1 | Inj 2 | Inj 3 | Inj 4 | Inj 5 | Avg | Mass % | | | | | | | |
| C3 | | 14792 | 12812 | 12812 | 13590 | | 13502 | 0.76 | | Avg Mass I/O Ratio | | 15.78 | | | |
| i-C4 | | 1817472 | 1538912 | 1533629 | 1626039 | | 1629013 | 91.29 | | Avg Molar I/O Ratio | | **15.234** | | | |
| 1-C4= | | 114233 | 97992 | 97647 | 102892 | | 103191 | 5.78 | | | | | | | |
| n-C4 | | 42715 | 36818 | 36575 | 38643 | | 38688 | 2.17 | | | | | | | |
| **I/O Mass Ratio** | | 15.910 | 15.704 | 15.706 | 15.803 | | 15.781 | | | | | | | | |

Run F50Pt5EMTr
(recalcined 0 5 % Pt/EMT; Tcalc=325degC; Tred=425degC; Trxn=50degC; P=382psig; I/O=15 0; butene WHSV=2 05h-1; t=1h; mcat=2 78g)

| Samp t [min] | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 22 | 25 | 30 | 40 | 70 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| T.O.S. [min.] | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 11 | 14 | 19 | 29 | 59 |
| 1-C4= Disapp. [%] | 82 | 94 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| t-2-C4= Prod. [%] | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 8 | 8 | 31 | 33 | 44 |
| c-2-C4= Prod. [%] | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 13 | 13 | 21 |
| Butene Disapp. [%] | 82 | 94 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 92 | 92 | 68 | 63 | 35 |
| n-Butane Change [%] | 7 | 5 | 7 | 8 | 8 | 8 | 9 | 8 | 10 | 7 | 8 | 9 | 6 | 8 |
| | | | | | | | | | | | | | | |
| *C5+ Product Analysis [%]* | | | | | | | | | | | | | | |
| C5-C7 | 29 | 27 | 24 | 25 | 26 | 25 | 29 | 25 | 16 | 10 | 7 | 2 | 0 | 0 |
| C8 | 57 | 57 | 55 | 57 | 59 | 60 | 58 | 62 | 67 | 55 | 51 | 62 | 50 | 62 |
| C9+ | 14 | 16 | 21 | 18 | 15 | 15 | 13 | 13 | 17 | 34 | 42 | 36 | 50 | 38 |
| | | | | | | | | | | | | | | |
| *C8 Distribution [mass %]* | | | | | | | | | | | | | | |
| TMP | 86 | 80 | 77 | 77 | 77 | 78 | 78 | 74 | 72 | 66 | 50 | 24 | 3 | 0 |
| DMH | 10 | 14 | 17 | 17 | 17 | 17 | 17 | 22 | 22 | 28 | 33 | 29 | 37 | 24 |
| C8= | 3 | 6 | 6 | 6 | 6 | 5 | 4 | 4 | 5 | 6 | 17 | 47 | 60 | 76 |
| | | | | | | | | | | | | | | |
| *TMP Isomer Distribution [%]* | | | | | | | | | | | | | | |
| 2,2,4-TMP | 64 | 43 | 42 | 41 | 40 | 38 | 38 | 38 | 36 | 29 | 30 | 43 | 0 | 0 |
| 2,2,3-TMP | 20 | 23 | 22 | 19 | 18 | 16 | 13 | 9 | 8 | 7 | 6 | 0 | 0 | 0 |
| 2,3,4-TMP | 6 | 12 | 12 | 14 | 15 | 18 | 20 | 23 | 25 | 31 | 31 | 27 | 0 | 0 |
| 2,3,3-TMP | 21 | 22 | 24 | 26 | 26 | 28 | 29 | 30 | 31 | 34 | 34 | 30 | 100 | 0 |
| | | | | | | | | | | | | | | |
| *Indicators [mass fraction]* | | | | | | | | | | | | | | |
| TMP | 8.51 | 5.74 | 4.59 | 4.39 | 4.49 | 4.48 | 4.56 | 3.30 | 3.28 | 2.34 | 1.62 | 0.84 | 0.09 | 0.00 |
| DMH | | | | | | | | | | | | | | |
| TMP+DMH | 3.44 | 2.74 | 2.17 | 2.57 | 3.00 | 3.14 | 3.52 | 3.81 | 3.12 | 1.39 | 0.82 | 0.51 | 0.25 | 0.18 |
| C8= + C9+ | | | | | | | | | | | | | | |
| (2,2,3-+2,2,4-TMP) | 2.83 | 1.93 | 1.77 | 1.53 | 1.41 | 1.18 | 1.05 | 0.90 | 0.81 | 0.55 | 0.55 | 0.77 | 0.00 | 0.00 |
| (2,3,4-+2,3,3-TMP) | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | |
| *DMH Isomer Distribution [%]* | | | | | | | | | | | | | | |
| 2,5-DMH | 32 | 2 | 18 | 17 | 17 | 16 | 15 | 11 | 11 | 6 | 0 | 0 | 0 | 0 |
| 2,4-DMH | 0 | 13 | 10 | 11 | 10 | 11 | 10 | 28 | 22 | 13 | 6 | 0 | 9 | 15 |
| 2,3-DMH | 45 | 63 | 55 | 52 | 53 | 48 | 50 | 38 | 42 | 32 | 21 | 15 | 9 | 0 |
| 3,4-DMH | 23 | 21 | 17 | 20 | 20 | 25 | 25 | 24 | 26 | 49 | 73 | 85 | 82 | 85 |

F50Pt5EMTr

(recalcined 0 5%Pt/EMT, Tcalc=325degC, Tred=425degC, Trxn=50degC, P=382psig, I/O=15 0, butene WHSV=2 05h-1, t=1h, mcat=2 78g)

| TOS (min) | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 11 | 14 | 19 | 29 | 59 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Propane | 161720 | 220480 | 238620 | 211080 | 245660 | 246320 | 255140 | 262420 | 228100 | 257780 | 261800 | 241600 | 261040 | 235580 |
| Isobutane | 20991300 | 29803780 | 30242220 | 26166440 | 29633460 | 29206760 | 30033160 | 30895760 | 26847720 | 30959800 | 32054440 | 28907460 | 31596960 | 28667920 |
| 1-butene | 232360 | 112880 | | | | | | | | | | | | |
| n-butane | 525940 | 745560 | 769720 | 676680 | 760500 | 746400 | 772040 | 790580 | 693940 | 785900 | 805320 | 738340 | 786860 | 728840 |
| t-2-butene | | | | | | | | | | 164340 | 156760 | 555300 | 653960 | 793740 |
| c-2-butene | | | | | | | | | | | | 238420 | 265140 | 379860 |
| **C6-C7** | **138248** | **390610** | **387622** | **341706** | **363223** | **332852** | **358422** | **321256** | **164663** | **113123** | **47609** | **5618** | **0** | **0** |
| C5 | | 143560 | 143220 | 123560 | 131860 | 123440 | 120980 | 119480 | | | | | | |
| 2,3-DMB | 46091 | 59767 | 59995 | 52488 | 56081 | 51815 | 51405 | 50484 | 40072 | 27041 | 12448 | | | |
| 2,2-DMP | 13612 | 23217 | 23042 | 19719 | 21072 | 19141 | 18943 | 18627 | 14518 | 10326 | | | | |
| 3-MP | 15488 | 28223 | 29095 | 25279 | 27376 | 25602 | 25343 | 25086 | 20849 | 16404 | 10400 | 5618 | | |
| 2,4-DMP | 34964 | 63381 | 63069 | 54563 | 57153 | 52375 | 79798 | 48843 | 39400 | 25869 | 11592 | | | |
| 2,2,3-TMB | | 5349 | | 5421 | 5635 | | 5276 | | | | | | | |
| 2-MHx | 5394 | 10377 | 10725 | 8954 | 9232 | 8453 | 7632 | 7826 | 6474 | | | | | |
| 2,3-DMP | 22699 | 45262 | 47264 | 41351 | 43742 | 42012 | 39295 | 40976 | 34494 | 26517 | 13069 | | | |
| 3-MHx | | 11374 | 11112 | 10371 | 11072 | 10014 | 9750 | 9934 | 8846 | 6966 | | | | |
| **C8** | **274488** | **834233** | **878980** | **779160** | **821029** | **706646** | **717647** | **782320** | **606580** | **607672** | **345164** | **170769** | **177870** | **173699** |
| **2,2,4-TMP** | **127660** | **284029** | **286917** | **245232** | **263798** | **232473** | **213466** | **219443** | **181618** | **116406** | **50884** | **18111** | | |
| 2,5-DMHx | 9042 | 2641 | 26889 | 22780 | 23582 | 21338 | 18228 | 19467 | 16274 | 10428 | | | | |
| 2,2,3-TMP | 47426 | 154138 | 146259 | 115718 | 116589 | 99300 | 73979 | 52758 | 41190 | 26751 | 9988 | | | |
| 2,4-DMHx | | 15218 | 14862 | 14683 | 14484 | 14981 | 12798 | 48385 | 32882 | 23118 | 6846 | | 5952 | 6492 |
| 2,3,4-TMP | 13227 | 78076 | 82614 | 82887 | 95089 | 108079 | 109961 | 132832 | 122499 | 124216 | 52655 | 11102 | | |
| 2,3,3-TMP | 48714 | 148747 | 162511 | 152706 | 167679 | 172930 | 165074 | 170423 | 152427 | 135136 | 58351 | 12555 | 5687 | |
| 2,3-DMHx | 12533 | 73214 | 81403 | 70694 | 75276 | 66191 | 61977 | 65499 | 63335 | 54556 | 23301 | 7349 | 5692 | |
| 3,4-DMHx | 6311 | 24827 | 24771 | 27852 | 27605 | 34206 | 30306 | 41045 | 39335 | 83637 | 83089 | 42153 | 53910 | 36056 |
| 1 DMHx= | | | | | | | | | | | | | | |
| 2 DMHx= | | | | | | | | | | 11561 | 41347 | 62651 | 77213 | 105786 |
| 3 DMHx= | | | | | | | | | | | | | | |
| 4 DMHx= | | | | | | | | | | | | | | |
| 5 DMHx= | 9375 | 53343 | 52634 | 46598 | 46927 | 37148 | 31858 | 32468 | 37020 | 22764 | 6822 | | | |
| 6 DMHx= | | | | | | | | | | | 11881 | 16848 | 29416 | 25365 |
| **C9+** | 67776 | 231554 | 328904 | 238869 | 211067 | 201182 | 163050 | 164280 | 171494 | 377789 | 289651 | 100395 | 175782 | 107346 |
| **C6+** | 480512 | 1456297 | 1595286 | 1359725 | 1395319 | 1320680 | 1239119 | 1267856 | 1022727 | 1098484 | 682324 | 276782 | 353652 | 281045 |
| Tot Peak Area | 22391832 | 32338997 | 32845846 | 28413925 | 32034939 | 31520160 | 32299459 | 33216616 | 28792487 | 33266304 | 33960644 | 30719482 | 33652472 | 30707125 |
| **FEED ANAL.** | | Inj 1 | Inj 2 | Inj 3 | Inj 4 | Inj 5 | Avg | Mass % | | | | | | |
| **C3** | | 13260 | 11768 | 12041 | 12105 | 11226 | 12080 | 0 75 | | | | | | |
| **i-C4** | | 1612474 | 1430884 | 1464755 | 1463586 | 1355949 | 1465530 | 91 19 | | | | | | |
| **1-C4=** | | 102785 | 92194 | 94199 | 94030 | 87728 | 94187 | 5 86 | | | | | | |
| **n-C4** | | 38501 | 34610 | 35385 | 35362 | 32879 | 35347 | 2 20 | | | | | | |
| **I/O Mass Ratio** | | 15 688 | 15 520 | 15 550 | 15 565 | 15 456 | 15 556 | | | | | | | |

Run F54Y
(Y; Tcalc=425degC; Trxn=50degC; P=382psig; I/O=15.2; butene WHSV=2.03h-1; t=1h; mcat=2.78g)

| Samp t [min] | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 22 | 25 | 30 | 40 | 70 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **T.O.S. [min.]** | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** | **9** | **10** | **12** | **15** | **20** | **30** | **60** |
| 1-C4= Disapp. [%] | 88 | 95 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 97 | 95 |
| t-2-C4= Prod. [%] | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 5 | 16 | 35 | 35 | 37 | 40 | 42 | 44 |
| c-2-C4= Prod. [%] | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 7 | 14 | 17 | 19 | 28 | 23 | 35 |
| **Butene Disapp. [%]** | **88** | **95** | **100** | **100** | **100** | **100** | **100** | **95** | **77** | **51** | **48** | **44** | **32** | **32** | **16** |
| n-Butane Change [%] | 13 | 15 | 13 | 14 | 14 | 14 | 17 | 17 | 16 | 11 | 10 | 10 | 8 | 9 | 9 |
| | | | | | | | | | | | | | | | |
| ***C5+ Product Analysis [mass %]*** | | | | | | | | | | | | | | | |
| C5-C7 | 34 | 31 | 31 | 30 | 29 | 24 | 12 | 8 | 4 | 2 | 0 | 0 | 0 | 0 | 0 |
| **C8** | **55** | **53** | **55** | **54** | **55** | **53** | **54** | **47** | **45** | **42** | **41** | **44** | **54** | **60** | **71** |
| C9+ | 11 | 16 | 14 | 16 | 16 | 23 | 34 | 45 | 51 | 56 | 59 | 56 | 46 | 40 | 29 |
| | | | | | | | | | | | | | | | |
| ***C8 Distribution [mass %]*** | | | | | | | | | | | | | | | |
| **TMP** | **75** | **74** | **72** | **71** | **69** | **68** | **65** | **63** | **47** | **42** | **15** | **7** | **2** | **2** | **2** |
| DMH | 20 | 21 | 22 | 23 | 25 | 27 | 30 | 32 | 42 | 37 | 36 | 26 | 25 | 26 | 21 |
| C8= | 5 | 5 | 5 | 6 | 6 | 5 | 5 | 5 | 11 | 21 | 49 | 67 | 73 | 72 | 77 |
| | | | | | | | | | | | | | | | |
| ***TMP Isomer Distribution [%]*** | | | | | | | | | | | | | | | |
| **2,2,4-TMP** | **39** | **40** | **41** | **41** | **43** | **42** | **37** | **33** | **28** | **25** | **23** | **20** | **0** | **0** | **0** |
| 2,2,3-TMP | 6 | 7 | 7 | 7 | 6 | 6 | 5 | 5 | 5 | 5 | 0 | 0 | 0 | 0 | 0 |
| 2,3,4-TMP | 23 | 21 | 21 | 20 | 20 | 21 | 25 | 29 | 34 | 34 | 51 | 51 | 100 | 100 | 100 |
| 2,3,3-TMP | 31 | 32 | 31 | 31 | 31 | 31 | 32 | 33 | 33 | 36 | 26 | 30 | 0 | 0 | 0 |
| | | | | | | | | | | | | | | | |
| ***Indicators [mass fraction]*** | | | | | | | | | | | | | | | |
| **TMP** | **3.69** | **3.53** | **3.25** | **3.05** | **2.81** | **2.51** | **2.14** | **1.97** | **1.12** | **1.14** | **0.42** | **0.27** | **0.08** | **0.07** | **0.08** |
| **DMH** | | | | | | | | | | | | | | | |
| TMP+DMH | 3.95 | 2.69 | 3.14 | 2.68 | 2.71 | 1.97 | 1.39 | 0.94 | 0.72 | 0.51 | 0.26 | 0.17 | 0.17 | 0.20 | 0.19 |
| C8= + C9+ | | | | | | | | | | | | | | | |
| (2,2,3-+2,2,4-TMP) | 0.83 | 0.89 | 0.94 | 0.93 | 0.96 | 0.92 | 0.74 | 0.61 | 0.49 | 0.43 | 0.30 | 0.25 | 0.00 | 0.00 | 0.00 |
| (2,3,4-+2,3,3-TMP) | | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | | |
| ***DMH Isomer Distribution [%]*** | | | | | | | | | | | | | | | |
| 2,5-DMH | 14 | 14 | 13 | 13 | 13 | 11 | 11 | 8 | 5 | 4 | 0 | 0 | 0 | 0 | 0 |
| 2,4-DMH | 35 | 35 | 32 | 33 | 31 | 26 | 28 | 21 | 12 | 0 | 4 | 7 | 10 | 10 | 11 |
| 2,3-DMH | 32 | 39 | 38 | 40 | 41 | 37 | 37 | 31 | 25 | 20 | 12 | 5 | 5 | 5 | 7 |
| 3,4-DMH | 19 | 13 | 16 | 14 | 15 | 26 | 24 | 40 | 58 | 76 | 84 | 88 | 85 | 84 | 81 |

Run F54Y

(Y, Tcalc=425degC, Trxn=50degC, P=382psig, I/O=15 2, butene WHSV=2 03h-1, t=1h, mcat=2 78g)

| TOS [min] | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 12 | 15 | 20 | 30 | 60 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Propane | 327840 | 375180 | 422900 | 453160 | 394040 | 463580 | 428320 | 434040 | 434820 | 390100 | 390100 | 449020 | 400220 | 464400 | 467620 |
| Isobutane | 43783560 | 45678920 | 49516540 | 51564260 | 44943920 | 52177140 | 47976060 | 48681540 | 48820360 | 45503980 | 45503980 | 51313800 | 46583280 | 53668880 | 54140940 |
| 1-butene | 318460 | 134720 | | | | | | | | | | | | 102640 | 159280 |
| n-butane | 1165800 | 1245760 | 1328740 | 1399860 | 1219600 | 1403580 | 1293760 | 1307580 | 1310200 | 1174800 | 1174800 | 1313580 | 1179980 | 1370600 | 1376840 |
| t-2-butene | | | | | | | | 139040 | 469020 | 986840 | 990820 | 1175560 | 1168700 | 1400920 | 1464220 |
| c-2-butene | | | | | | | | | 209440 | 394740 | 482220 | 606180 | 802420 | 784100 | 1193340 |
| **C5-C7** | **563236** | **703775** | **825339** | **863777** | **748672** | **843918** | **137302** | **64117** | **30012** | **15488** | **0** | **0** | **0** | **0** | **0** |
| C5 | 219500 | 267800 | 305100 | 322760 | 273300 | 220580 | | | | | | | | | |
| 2,3-DMB | 102590 | 126179 | 147727 | 153225 | 131649 | 116283 | 36897 | 17210 | 9814 | 7755 | | | | | |
| 2,2-DMP | 31152 | 41788 | 51776 | 54702 | 48221 | 39631 | 5147 | 5106 | | | | | | | |
| 3-MP | 39183 | 50946 | 61362 | 64567 | 57143 | 52532 | 21510 | 11640 | 5033 | | | | | | |
| 2,4-DMP | 84517 | 101021 | 118432 | 120042 | 104634 | 88899 | 43807 | 10954 | 5147 | | | | | | |
| 2,2,3-TMB | 5986 | 7153 | 7720 | 8311 | 7004 | 7020 | | | | | | | | | |
| 2-MHx | 11518 | 15239 | 18749 | 19822 | 18070 | 14726 | | | | | | | | | |
| 2,3-DMP | 56279 | 75096 | 90992 | 95332 | 85675 | 83246 | 29941 | 19207 | 10018 | 7733 | | | | | |
| 3-MHx | 12511 | 18553 | 23481 | 25016 | 22976 | 21001 | | | | | | | | | |
| **C8** | **905823** | **1228420** | **1486447** | **1560884** | **1412202** | **1399628** | **614218** | **376681** | **337660** | **326244** | **338144** | **358213** | **347816** | **446817** | **347902** |
| **2,2,4-TMP** | **265247** | **362940** | **444035** | **458751** | **417343** | **399290** | **148590** | **78314** | **44433** | **34161** | **11658** | **6010** | | | |
| 2,5-DMHx | 26047 | 35862 | 43189 | 46689 | 44009 | 41693 | 20390 | 9643 | 7090 | 5030 | | | | | |
| 2,2,3-TMP | 41458 | 62387 | 76646 | 76791 | 63635 | 57041 | 20077 | 11870 | 7940 | 6830 | | | | | |
| 2,4-DMHx | 64374 | 88690 | 107435 | 118964 | 109436 | 98550 | 51900 | 25307 | 17015 | | 5100 | 6513 | 8694 | 11830 | 8239 |
| 2,3,4-TMP | 157617 | 193674 | 220865 | 226806 | 197094 | 199650 | 100400 | 68820 | 53945 | 46445 | 25855 | 12776 | 6955 | 7563 | 6073 |
| 2,3,3-TMP | 213036 | 286404 | 334457 | 346307 | 302317 | 294714 | 128511 | 78311 | 52370 | 49177 | 13180 | 7510 | | | |
| 2,3-DMHx | 58929 | 99638 | 127521 | 146507 | 141491 | 140242 | 68585 | 37362 | 35460 | 24068 | 14597 | 5060 | 4347 | 6199 | 5267 |
| 3,4-DMHx | 34118 | 32365 | 53397 | 51887 | 53797 | 98545 | 44484 | 48220 | 82257 | 91242 | 102182 | 81570 | 73992 | 98270 | 59066 |
| 1 DMHx= | | | | | | | | | | | | | | | |
| 2 DMHx= | | 5596 | 6401 | 6720 | 6544 | 6316 | 6609 | 11386 | 27626 | 51776 | 142015 | 164325 | 180153 | 224540 | 195758 |
| 3 DMHx= | | | | | | | | | | | | | | | |
| 4 DMHx= | | | | | | | | | | | | | | | |
| 5 DMHx= | 44997 | 60864 | 72501 | 81462 | 76536 | 63587 | 24672 | 7448 | 9514 | 11211 | 9778 | 9107 | | 5212 | |
| 6 DMHx= | | | | | | | | | | 5314 | 13779 | 66342 | 73675 | 93203 | 73499 |
| **C9+** | 173110 | 365964 | 369087 | 460696 | 406742 | 606711 | 389010 | 360660 | 382659 | 433658 | 486249 | 455454 | 296223 | 297878 | 140965 |
| **C5+** | 1642169 | 2298159 | 2680873 | 2885357 | 2567616 | 2650257 | 1140530 | 801458 | 750321 | 774390 | 824393 | 813667 | 644039 | 744695 | 488867 |
| Tot Peak Area | 47237829 | 49732739 | 53949053 | 56302637 | 49125176 | 56694557 | 50838670 | 51363658 | 51784721 | 48830110 | 48884093 | 55065627 | 49976219 | 57752135 | 58097767 |
| ***Feed Analysis*** | Inj 1 | Inj 2 | Inj 3 | Inj 4 | Inj 5 | Avg | Mass % | | | | | | | | |
| C3 | 13410 | 11768 | 11827 | 12319 | 12778 | 12420 | 0 74 | | | | | | | | |
| i-C4 | 1654456 | 1448580 | 1435022 | 1519065 | 1586500 | 1528725 | 91 29 | | Avg Mass I/O ratio | | 15 76 | | | | |
| 1-C4= | 104348 | 92411 | 91529 | 96376 | 100114 | 96956 | 5 79 | | Avg Molar I/O ratio | | **16.217** | | | | |
| n-C4 | 39121 | 34822 | 34529 | 36118 | 37695 | 36457 | 2 18 | | | | | | | | |
| **I/O Mass Ratio** | 15 855 | 15 675 | 15 678 | 15 762 | 15 847 | 15 764 | | | | | | | | | |

Run F55Yr
(recalcined Y; Tcalc=425degC; Trxn=50degC; P=382psig; I/O=14.4; butene WHSV=2.13h-1; t=1h; mcat=2.78g)

| Samp t [min] | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 21 | 24 | 29 | 39 | 69 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **T.O.S. [min.]** | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** | **9** | **10** | **12** | **15** | **20** | **30** | **60** |
| 1-C4= Disapp. [%] | 67 | 95 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 96 | 97 | 95 |
| t-2-C4= Prod. [%] | 0 | 0 | 0 | 0 | 0 | 4 | 16 | 25 | 30 | 33 | 35 | 37 | 38 | 40 | 40 |
| c-2-C4= Prod. [%] | 0 | 0 | 0 | 0 | 0 | 0 | 6 | 11 | 14 | 16 | 17 | 22 | 25 | 28 | 36 |
| **Butene Disapp. [%]** | **67** | **95** | **100** | **100** | **100** | **96** | **78** | **64** | **56** | **52** | **48** | **41** | **33** | **29** | **19** |
| n-Butane Change [%] | -1 | 6 | 6 | 6 | 6 | 5 | 4 | 2 | 3 | 2 | 3 | 1 | 1 | 2 | 0 |
| | | | | | | | | | | | | | | | |
| ***C5+ Product Analysis [mass %]*** | | | | | | | | | | | | | | | |
| C5-C7 | 33 | 31 | 28 | 26 | 23 | 13 | 8 | 3 | 1 | 0 | 0 | 0 | 0 | 0 | 0 |
| **C8** | **33** | **56** | **57** | **56** | **55** | **57** | **51** | **40** | **52** | **58** | **61** | **61** | **63** | **69** | **74** |
| C9+ | 33 | 14 | 15 | 18 | 23 | 30 | 41 | 57 | 48 | 42 | 39 | 39 | 37 | 31 | 26 |
| | | | | | | | | | | | | | | | |
| ***C8 Distribution [mass %]*** | | | | | | | | | | | | | | | |
| **TMP** | **78** | **73** | **68** | **63** | **59** | **53** | **37** | **9** | **5** | **0** | **1** | **1** | **5** | **2** | **0** |
| DMH | 18 | 22 | 28 | 32 | 37 | 42 | 50 | 54 | 43 | 40 | 32 | 26 | 24 | 22 | 18 |
| C8= | 4 | 5 | 4 | 4 | 4 | 5 | 13 | 37 | 53 | 60 | 67 | 73 | 71 | 76 | 82 |
| | | | | | | | | | | | | | | | |
| ***TMP Isomer Distribution [%]*** | | | | | | | | | | | | | | | |
| **2,2,4-TMP** | **46** | **36** | **35** | **35** | **33** | **26** | **20** | **24** | **0** | **0** | **0** | **0** | **70** | **0** | **0** |
| 2,2,3-TMP | 5 | 4 | 5 | 5 | 4 | 3 | 6 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 2,3,4-TMP | 15 | 25 | 27 | 28 | 31 | 37 | 40 | 38 | 67 | 0 | 100 | 100 | 30 | 100 | 0 |
| 2,3,3-TMP | 34 | 34 | 33 | 33 | 32 | 34 | 35 | 37 | 33 | 0 | 0 | 0 | 0 | 0 | 0 |
| | | | | | | | | | | | | | | | |
| ***Indicators [mass fraction]*** | | | | | | | | | | | | | | | |
| **TMP** | **4.35** | **3.34** | **2.43** | **1.95** | **1.58** | **1.28** | **0.74** | **0.17** | **0.11** | **0.00** | **0.04** | **0.06** | **0.20** | **0.07** | **0.00** |
| **DMH** | | | | | | | | | | | | | | | |
| TMP+DMH | 0.92 | 3.26 | 3.19 | 2.68 | 2.10 | 1.66 | 0.92 | 0.35 | 0.33 | 0.30 | 0.25 | 0.20 | 0.22 | 0.20 | 0.15 |
| C8= + C9+ | | | | | | | | | | | | | | | |
| (2,2,3-+2,2,4-TMP) | 1.04 | 0.69 | 0.67 | 0.66 | 0.58 | 0.41 | 0.34 | 0.32 | 0.00 | 0.00 | 0.00 | 0.00 | 2.37 | 0.00 | 0.00 |
| (2,3,4-+2,3,3-TMP) | | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | | |
| ***DMH Isomer Distribution [%]*** | | | | | | | | | | | | | | | |
| 2,5-DMH | 15 | 7 | 9 | 8 | 6 | 3 | 2 | 4 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 2,4-DMH | 25 | 26 | 23 | 21 | 17 | 11 | 0 | 4 | 6 | 11 | 14 | 10 | 15 | 11 | 18 |
| 2,3-DMH | 31 | 44 | 34 | 32 | 29 | 25 | 19 | 6 | 5 | 5 | 0 | 5 | 6 | 6 | 0 |
| 3,4-DMH | 29 | 23 | 34 | 40 | 48 | 62 | 79 | 86 | 89 | 84 | 86 | 85 | 79 | 82 | 82 |

Run F55Yr
(recalcined Y, Tcalc=425degC, Trxn=50degC, P=382psig, I/O=14 4, butene WHSV=2 13h-1, t=1h, mcat=2 78g)

| TOS (min) | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 12 | 15 | 20 | 30 | 60 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Propane | 320720 | 368780 | 425440 | 465520 | 408040 | 445700 | 414700 | 418220 | 417840 | 369700 | 419740 | 433340 | 418420 | 433980 | 439060 |
| Isobutane | 42651600 | 46679680 | 50878960 | 53981680 | 47231620 | 51340520 | 47796660 | 48756760 | 48681260 | 43773320 | 48786720 | 50847660 | 49027220 | 50808180 | 51050560 |
| 1-butene | 900280 | 163760 | | | | | | | | | | | 112340 | 115040 | 163740 |
| n-butane | 1043820 | 1236540 | 1340720 | 1433240 | 1249540 | 1339020 | 1231640 | 1243420 | 1241200 | 1111460 | 1246500 | 1276540 | 1241020 | 1292040 | 1275820 |
| t-2-butene | | | | | | 131360 | 487140 | 800300 | 955220 | 925400 | 1105420 | 1235700 | 1224040 | 1324120 | 1330980 |
| c-2-butene | | | | | | | 183620 | 340640 | 439880 | 440960 | 533500 | 727100 | 797140 | 918600 | 1212780 |
| **C5-C7** | **212566** | **526444** | **565215** | **565468** | **389538** | **184131** | **76434** | **23564** | **6089** | **0** | **0** | **0** | **0** | **0** | **0** |
| C5 | 102220 | 197800 | 205720 | 203640 | 138580 | | | | | | | | | | |
| 2,3-DMB | 39667 | 94371 | 100686 | 98763 | 68484 | 46724 | 16310 | 5516 | | | | | | | |
| 2,2-DMP | 10320 | 29103 | 32415 | 33065 | 22644 | 15041 | 5924 | | | | | | | | |
| 3-MP | 14907 | 41599 | 47097 | 49088 | 37057 | 29948 | 16174 | 9173 | 6089 | | | | | | |
| 2,4-DMP | 26199 | 70720 | 72237 | 69200 | 46170 | 30019 | 10182 | | | | | | | | |
| 2,2,3-TMB | | 5883 | 6572 | 6483 | | | | | | | | | | | |
| 2-MHx | | 10217 | 11340 | 11867 | 5291 | 5284 | | | | | | | | | |
| 2,3-DMP | 19253 | 62722 | 72189 | 74984 | 57482 | 45570 | 21310 | 8875 | | | | | | | |
| 3-MHx | | 14029 | 16959 | 18378 | 13830 | 11545 | 6534 | | | | | | | | |
| **C8** | **214103** | **952429** | **1151732** | **1197986** | **937700** | **819825** | **519976** | **375289** | **357990** | **319045** | **426691** | **430342** | **418107** | **401083** | **312857** |
| **2,2,4-TMP** | **77159** | **254509** | **289253** | **266064** | **179660** | **113452** | **37672** | **8225** | | | | | **14097** | | |
| 2,5-DMHx | 5806 | 15634 | 27671 | 29578 | 20972 | 10233 | 5507 | 7763 | | | | | | | |
| 2,2,3-TMP | 7926 | 31228 | 42296 | 35118 | 23320 | 14646 | 10979 | | | | | | | | |
| 2,4-DMHx | 9667 | 53203 | 75342 | 80321 | 57870 | 36737 | | 7148 | 8904 | 13846 | 18617 | 11450 | 15342 | 9948 | 10250 |
| 2,3,4-TMP | 24508 | 177150 | 209746 | 209442 | 170671 | 161767 | 76075 | 12936 | 11132 | | 5827 | 6074 | 5936 | 6174 | |
| 2,3,3-TMP | 57122 | 234573 | 258204 | 247017 | 177298 | 148183 | 67511 | 12649 | 5586 | | | | | | |
| 2,3-DMHx | 11904 | 91035 | 110277 | 123932 | 101165 | 84645 | 48033 | 12798 | 7479 | 6421 | | 5393 | 5654 | 5656 | |
| 3,4-DMHx | 10925 | 48670 | 107660 | 154166 | 169491 | 210857 | 204858 | 176324 | 136217 | 107768 | 117711 | 93179 | 80216 | 72922 | 46372 |
| 1 DMHx= | | | | | | | | | | | | | | | |
| 2 DMHx= | | | 5534 | 5856 | | 5849 | 44279 | 102294 | 138148 | 145000 | 196195 | 221412 | 213122 | 214806 | 183460 |
| 3 DMHx= | | | | | | 5303 | | | | | | | | | |
| 4 DMHx= | | | | | | | 5005 | | | | | | | | |
| 5 DMHx= | 9086 | 46427 | 45749 | 46492 | 37253 | 28153 | 7957 | 6199 | 6063 | 5157 | 5900 | | | | |
| 6 DMHx= | | | | | | | 12100 | 28953 | 44461 | 40853 | 82441 | 92834 | 83740 | 91577 | 72775 |
| **C9+** | 213797 | 231355 | 293560 | 374453 | 391211 | 430112 | 421097 | 536184 | 329691 | 231822 | 275222 | 275888 | 249175 | 177426 | 109216 |
| **C5+** | 640466 | 1710228 | 2010507 | 2137907 | 1718449 | 1434068 | 1017507 | 935037 | 693770 | 550867 | 701913 | 706230 | 667282 | 578509 | 422073 |
| Tot Peak Area | 45556886 | 50158988 | 54655627 | 58018347 | 50607649 | 54690668 | 51131267 | 52494377 | 51989290 | 46730747 | 52260293 | 54499470 | 52690322 | 54551869 | 54682233 |
| ***Feed Analysis*** | | Inj 1 | Inj 2 | Inj 3 | Inj 4 | Inj 5 | Avg | Mass % | | | | | | | |
| C3 | | 23244 | 20507 | 20590 | 23135 | 19165 | 21328 | 0 78 | | | | | | | |
| t-C4 | | 2702502 | 2368125 | 2377076 | 2716082 | 2195844 | 2471926 | 90 81 | | Avg Mass I/O Ratio | | 14 93 | | | |
| 1-C4= | | 180012 | 159003 | 159551 | 180978 | 147917 | 165492 | 6 08 | | Avg Molar I/O Ratio | | **14.414** | | | |
| n-C4 | | 68691 | 60613 | 60879 | 69202 | 57071 | 63291 | 2 33 | | | | | | | |
| **I/O Mass Ratio** | | 15 013 | 14 894 | 14 899 | 15 008 | 14 845 | 14 932 | | | | | | | | |

Run F56Pt5Y
(0.5%Pt/Y; Tcalc=325degC; Tred=425degC, Trxn=53degC; P=382psig; I/O=14.5; butene WHSV=2.12h-1; t=1h; mcat=2.78g)

| Samp t [min] | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 22 | 25 | 30 | 40 | 70 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| T.O.S. [min | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 12 | 15 | 20 | 30 | 60 |
| 1-C4= Disap | 89 | 96 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 96 |
| t-2-C4= Pro | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 5 | 12 | 23 | 32 | 36 | 39 | 37 | 42 |
| c-2-C4= Pro | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 4 | 9 | 15 | 19 | 24 | 17 | 33 |
| Butene Dis | 89 | 96 | 100 | 100 | 100 | 100 | 100 | 95 | 84 | 68 | 54 | 44 | 38 | 45 | 21 |
| n-Butane Ch | 6 | 7 | 8 | 8 | 8 | 6 | 8 | 8 | 7 | 5 | 3 | 5 | 5 | 6 | 3 |
| ***C5+ Product Analysis [mass %]*** | | | | | | | | | | | | | | | |
| C5-C7 | 33 | 27 | 27 | 27 | 26 | 18 | 23 | 22 | 12 | 6 | 1 | 2 | 0 | 0 | 0 |
| C8 | 60 | 56 | 56 | 56 | 56 | 58 | 55 | 55 | 57 | 53 | 49 | 56 | 58 | 62 | 71 |
| C9+ | 8 | 17 | 16 | 17 | 18 | 25 | 22 | 23 | 31 | 42 | 50 | 42 | 42 | 38 | 29 |
| ***C8 Distribution [mass %]*** | | | | | | | | | | | | | | | |
| TMP | 71 | 69 | 68 | 66 | 64 | 61 | 62 | 61 | 53 | 31 | 7 | 0 | 0 | 0 | 0 |
| DMH | 24 | 26 | 27 | 29 | 30 | 33 | 33 | 34 | 42 | 48 | 39 | 32 | 27 | 24 | 21 |
| C8= | 4 | 5 | 5 | 5 | 5 | 6 | 5 | 5 | 5 | 21 | 54 | 68 | 73 | 76 | 79 |
| ***TMP Isomer Distribution [%]*** | | | | | | | | | | | | | | | |
| 2,2,4-TMP | 33 | 33 | 36 | 40 | 39 | 32 | 33 | 32 | 28 | 26 | 33 | 0 | 0 | 0 | 0 |
| 2,2,3-TMP | 5 | 5 | 5 | 5 | 5 | 5 | 4 | 3 | 3 | 7 | 0 | 0 | 0 | 0 | 0 |
| 2,3,4-TMP | 30 | 30 | 27 | 24 | 25 | 29 | 30 | 32 | 37 | 38 | 33 | 0 | 0 | 0 | 0 |
| 2,3,3-TMP | 33 | 32 | 32 | 32 | 31 | 34 | 33 | 33 | 32 | 30 | 34 | 0 | 0 | 0 | 0 |
| ***Indicators [mass fraction]*** | | | | | | | | | | | | | | | |
| TMP | 2.91 | 2.68 | 2.55 | 2.32 | 2.12 | 1.83 | 1.87 | 1.79 | 1.26 | 0.64 | 0.19 | 0.00 | 0.00 | 0.00 | 0.00 |
| DMH | | | | | | | | | | | | | | | |
| TMP+DMH | 5.57 | 2.71 | 2.73 | 2.70 | 2.58 | 1.95 | 2.18 | 1.99 | 1.63 | 0.78 | 0.29 | 0.22 | 0.19 | 0.18 | 0.17 |
| C8= + C9+ | | | | | | | | | | | | | | | |
| (2,2,3-+2,2,4 | 0.61 | 0.62 | 0.69 | 0.80 | 0.78 | 0.57 | 0.59 | 0.54 | 0.45 | 0.46 | 0.50 | 0.00 | 0.00 | 0.00 | 0.00 |
| (2,3,4-+2,3,3-TMP) | | | | | | | | | | | | | | | |
| ***DMH Isomer Distribution [%]*** | | | | | | | | | | | | | | | |
| 2,5-DMH | 9 | 9 | 9 | 10 | 9 | 7 | 7 | 4 | 3 | 0 | 0 | 0 | 0 | 0 | 0 |
| 2,4-DMH | 25 | 24 | 23 | 23 | 24 | 20 | 20 | 14 | 7 | 3 | 7 | 9 | 12 | 14 | 13 |
| 2,3-DMH | 31 | 34 | 36 | 38 | 35 | 34 | 30 | 30 | 25 | 17 | 6 | 0 | 0 | 0 | 0 |
| 3,4-DMH | 35 | 34 | 32 | 29 | 32 | 39 | 44 | 52 | 66 | 81 | 87 | 91 | 88 | 86 | 87 |

Run F56Pt5Y

(0.5%Pt/Y; Tcalc=325degC; Tred=425degC; Trxn=53degC; P=382psig; I/O=14.5; butene WHSV=2.12h-1; t=1h; mcat=2.78g)

| TOS [min] | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 12 | 15 | 20 | 30 | 60 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Propane | 404400 | 366520 | 394520 | 369160 | 410160 | 390060 | 400420 | 395400 | 357420 | 406480 | 412360 | 394220 | 363820 | 378240 | 366540 |
| Isobutane | 57199780 | 45357980 | 46707220 | 43325420 | 47532040 | 43567720 | 45842180 | 45688180 | 41796620 | 47482740 | 48680820 | 46112780 | 42375460 | 44040500 | 42635440 |
| 1-butene | 413880 | 132580 | | | | | | | | | | | | | 113340 |
| n-butane | 1498280 | 1207680 | 1259340 | 1170240 | 1278900 | 1150340 | 1224300 | 1219000 | 1094600 | 1228960 | 1239040 | 1195020 | 1101540 | 1149780 | 1090140 |
| t-2-butene | | | | | | | | 140560 | 323080 | 712860 | 1003020 | 1084060 | 1056700 | 1059240 | 1161520 |
| c-2-butene | | | | | | | | | 118320 | 277420 | 457640 | 573780 | 653680 | 494080 | 912540 |
| | | | | | | | | | | | | | | | |
| C5-C7 | 556515 | 539028 | 599602 | 543093 | 584883 | 390477 | 439326 | 353183 | 116644 | 45627 | 6683 | 14479 | 0 | 0 | 0 |
| C5 | 218000 | 199860 | 220780 | 209000 | 212620 | 161440 | 159620 | 126840 | | | | | | | |
| 2,3-DMB | 101486 | 96387 | 105382 | 99216 | 100333 | 60047 | 76994 | 60923 | 29771 | 11394 | | | | | |
| 2,2-DMP | 27008 | 29845 | 35420 | 35682 | 36191 | 20236 | 25049 | 19717 | 9971 | | | | | | |
| 3-MP | 41644 | 42080 | 47575 | 16203 | 47571 | 27430 | 38164 | 32826 | 20156 | 12048 | 6683 | | | | |
| 2,4-DMP | 78026 | 74338 | 80868 | 76124 | 76708 | 46308 | 56597 | 44401 | 20667 | 8219 | | | | | |
| 2,2,3-TMB | 6603 | 6136 | 6442 | 5755 | 6195 | | | | | | | | | | |
| 2-MHx | 10030 | 10613 | 12911 | 13255 | 13528 | 8944 | 8765 | 6739 | | | | 14479 | | | |
| 2,3-DMP | 60490 | 64710 | 72410 | 69576 | 72468 | 52057 | 59356 | 49138 | 28156 | 13866 | | | | | |
| 3-MHx | 13228 | 15059 | 17814 | 18282 | 19269 | 14015 | 14781 | 12599 | 7823 | | | | | | |
| | | | | | | | | | | | | | | | |
| C8 | 1009727 | 1107310 | 1233127 | 1140591 | 1244649 | 1270624 | 1072006 | 874114 | 539613 | 414016 | 335162 | 323373 | 286669 | 286856 | 287726 |
| 2,2,4-TMP | 237474 | 266122 | 302241 | 299778 | 311550 | 244068 | 218670 | 167806 | 80968 | 31300 | 8106 | | | | |
| 2,5-DMHx | 22964 | 24990 | 31134 | 32337 | 34610 | 31730 | 23925 | 12696 | 6812 | | | | | | |
| 2,2,3-TMP | 33576 | 37900 | 40303 | 35972 | 39431 | 37506 | 29245 | 18398 | 8208 | 8728 | | | | | |
| 2,4-DMHx | 62000 | 68816 | 74858 | 76371 | 89857 | 84846 | 69589 | 41866 | 14818 | 5359 | 8705 | 9650 | 8458 | 9498 | 7033 |
| 2,3,4-TMP | 212934 | 226574 | 226255 | 179916 | 200298 | 226230 | 201727 | 171445 | 104558 | 48171 | 7894 | | | | |
| 2,3,3-TMP | 234825 | 247414 | 268836 | 238121 | 248389 | 266306 | 217035 | 175002 | 92665 | 38452 | 6242 | | | | |
| 2,3-DMHx | 76469 | 95871 | 118544 | 123163 | 133003 | 142810 | 106315 | 88301 | 55976 | 32895 | 8069 | | | | |
| 3,4-DMHx | 85899 | 96391 | 104562 | 93660 | 119829 | 164507 | 156658 | 155176 | 149280 | 160419 | 113084 | 93811 | 63764 | 58996 | 47908 |
| 1:DMHx= | | | | | | | | | | | | | | | |
| 2:DMHx= | | 5234 | 5407 | 5460 | 6012 | 6424 | 5535 | 13939 | 12754 | 67107 | 131652 | 160016 | 150619 | 155719 | 150766 |
| 3:DMHx= | | | | | | | | | | | | | | | |
| 4:DMHx= | | | | | | | | | | | | | | | |
| 5:DMHx= | 43586 | 47998 | 60987 | 55813 | 61670 | 66397 | 43306 | 29486 | 13574 | 5705 | 5510 | | | | |
| 6:DMHx= | | | | | | | | | | 15879 | 43901 | 59896 | 42728 | 62642 | 62019 |
| | | | | | | | | | | | | | | | |
| C9+ | 129851 | 335036 | 361507 | 339175 | 388638 | 541250 | 421066 | 373402 | 288498 | 326523 | 343213 | 241857 | 194327 | 172903 | 110742 |
| | | | | | | | | | | | | | | | |
| Tot. Peak Area | 61212433 | 49046134 | 50555316 | 46887679 | 51439270 | 47310671 | 49399297 | 49043839 | 44516375 | 50617105 | 52020298 | 49365789 | 45357416 | 47087518 | 45745448 |
| | | | | | | | | | | | | | | | |
| ***Feed Analysis*** | | Inj.1 | Inj.2 | Inj. 3 | Inj. 4 | Inj. 5 | Avg. | Mass % | | | | | | | |
| C3 | | 23750 | 21795 | 20975 | 22051 | 22712 | 22257 | 0.78 | | | | | | | |
| i-C4 | | 2785000 | 2536799 | 2428342 | 2566129 | 2663070 | 2595868 | 90.87 | | | | | | | |
| 1-C4= | | 184293 | 169142 | 162319 | 170686 | 176690 | 172626 | 6.04 | | | | | | | |
| n-C4 | | 70126 | 64442 | 61846 | 65064 | 67457 | 65787 | 2.30 | | | | | | | |
| I/O Mass Ratio | | 15.112 | 14.998 | 14.960 | 15.034 | 15.072 | 15.035 | | | | | | | | |

Run F58Pt5Yr

(recalcined 0.5%Pt/Y; Tcalc=325degC; Tred=425degC; Trxn=52degC; P=382psig; I/O=14.5; butene WHSV=2.11h-1; t=1h; mcat=2.78g)

| Samp t [min] | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 21 | 30 | 40 | 70 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **T.O.S. [min.]** | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** | **9** | **11** | **20** | **30** | **60** |
| 1-C4= Disapp. [%] | 80 | 91 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 96 | 95 | 94 |
| t-2-C4= Prod. [%] | 0 | 0 | 0 | 0 | 0 | 0 | 11 | 25 | 31 | 34 | 36 | 37 | 37 |
| c-2-C4= Prod. [%] | 0 | 0 | 0 | 0 | 0 | 0 | 5 | 13 | 19 | 20 | 30 | 33 | 38 |
| **Butene Disapp. [%]** | **80** | **91** | **100** | **100** | **100** | **100** | **84** | **61** | **50** | **46** | **30** | **26** | **19** |
| n-Butane Change [%] | 2 | 4 | 8 | 8 | 7 | 7 | 6 | 4 | 4 | 5 | 5 | 4 | 4 |
| | | | | | | | | | | | | | |
| ***C5+ Product Analysis [mass %]*** | | | | | | | | | | | | | |
| C5-C7 | 17 | 32 | 33 | 27 | 23 | 21 | 10 | 4 | 0 | 0 | 0 | 0 | 0 |
| C8 | 27 | 53 | 54 | 56 | 54 | 54 | 48 | 49 | 54 | 54 | 65 | 66 | 68 |
| C9+ | 57 | 15 | 13 | 17 | 23 | 25 | 41 | 47 | 46 | 46 | 35 | 34 | 32 |
| | | | | | | | | | | | | | |
| ***C8 Distribution*** | | | | | | | | | | | | | |
| TMP | 75 | 74 | 73 | 67 | 62 | 56 | 35 | 16 | 4 | 0 | 2 | 2 | 0 |
| DMH | 20 | 22 | 23 | 28 | 33 | 40 | 59 | 51 | 41 | 31 | 23 | 21 | 18 |
| C8= | 5 | 5 | 4 | 5 | 5 | 4 | 6 | 33 | 55 | 69 | 75 | 77 | 82 |
| | | | | | | | | | | | | | |
| ***TMP Isomer Distribution [%]*** | | | | | | | | | | | | | |
| **2,2,4-TMP** | **39** | **39** | **39** | **36** | **36** | **34** | **38** | **29** | **0** | **#DIV/0!** | **0** | **0** | **#DIV/0!** |
| 2,2,3-TMP | 5 | 5 | 5 | 5 | 4 | 4 | 4 | 0 | 0 | #DIV/0! | 0 | 0 | #DIV/0! |
| 2,3,4-TMP | 25 | 24 | 24 | 26 | 28 | 31 | 6 | 48 | 50 | #DIV/0! | 100 | 100 | #DIV/0! |
| 2,3,3-TMP | 31 | 32 | 32 | 32 | 32 | 31 | 52 | 23 | 50 | #DIV/0! | 0 | 0 | #DIV/0! |
| | | | | | | | | | | | | | |
| ***Indicators [mass fraction]*** | | | | | | | | | | | | | |
| **TMP** | **3.74** | **3.41** | **3.19** | **2.38** | **1.85** | **1.39** | **0.59** | **0.32** | **0.10** | **0.00** | **0.07** | **0.07** | **0.00** |
| **DMH** | | | | | | | | | | | | | |
| TMP+DMH | 0.43 | 2.86 | 3.48 | 2.70 | 1.99 | 1.89 | 1.03 | 0.52 | 0.32 | 0.20 | 0.19 | 0.18 | 0.14 |
| C8= + C9+ | | | | | | | | | | | | | |
| (2,2,3-+2,2,4-TMP) | 0.78 | 0.79 | 0.79 | 0.71 | 0.68 | 0.61 | 0.74 | 0.41 | 0.00 | #DIV/0! | 0.00 | 0.00 | #DIV/0! |
| (2,3,4-+2,3,3-TMP) | | | | | | | | | | | | | |
| | | | | | | | | | | | | | |
| ***DMH Isomer Distribution [%]*** | | | | | | | | | | | | | |
| 2,5-DMH | 13 | 12 | 11 | 9 | 7 | 5 | 2 | 5 | 0 | 0 | 0 | 0 | 0 |
| 2,4-DMH | 28 | 28 | 29 | 24 | 17 | 15 | 5 | 4 | 7 | 9 | 12 | 12 | 14 |
| 2,3-DMH | 38 | 43 | 40 | 34 | 34 | 28 | 21 | 8 | 11 | 0 | 0 | 0 | 0 |
| 3,4-DMH | 21 | 17 | 20 | 32 | 42 | 51 | 72 | 83 | 81 | 91 | 88 | 88 | 86 |

Run F58Pt5Yr

(recalcined 0 5%Pt/Y, Tcalc=325degC, Tred=425degC, Trxn=52degC, P=382psig, I/O=14 5, butene WHSV=2 11h-1, t=1h, mcat=2 78g)

| TOS (min) | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 11 | 20 | 30 | 60 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Propane | 263380 | 353280 | 432120 | 386840 | 418260 | 412640 | 401700 | 393680 | 349920 | 407100 | 401600 | 421760 | 421320 |
| Isobutane | 40702260 | 48204500 | 53386480 | 46654840 | 49222980 | 48206280 | 47267860 | 46180760 | 41947820 | 48611380 | 47621320 | 49842240 | 50211860 |
| 1-butene | 542420 | 271820 | | | | | | | | | 122860 | 145760 | 190640 |
| n-butane | 1053900 | 1246800 | 1420460 | 1249660 | 1309020 | 1271340 | 1231460 | 1194020 | 1074880 | 1259600 | 1237700 | 1280280 | 1286480 |
| t-2-butene | | | | | | | 339580 | 757360 | 842380 | 1063420 | 1107280 | 1180560 | 1198560 |
| c-2-butene | | | | | | | 142640 | 400660 | 500000 | 630220 | 920560 | 1053900 | 1229900 |
| **C6-C7** | **360061** | **529180** | **629922** | **551399** | **487649** | **336926** | **101050** | **24237** | **0** | **0** | **0** | **0** | **0** |
| C5 | 145040 | 209520 | 243680 | 200820 | 175040 | 113180 | | | | | | | |
| 2,3-DMB | 64191 | 93187 | 112268 | 96064 | 82373 | 57923 | 23753 | | | | | | |
| 2,2-DMP | 19186 | 29681 | 36511 | 32880 | 29574 | 20382 | 8542 | 6623 | | | | | |
| 3-MP | 26324 | 39234 | 49704 | 45682 | 43489 | 34088 | 19259 | 8544 | | | | | |
| 2,4-DMP | 51786 | 71626 | 82475 | 72213 | 59575 | 39648 | 15340 | | | | | | |
| 2,2,3-TMB | | 5866 | 6602 | 5980 | 5155 | | | | | | | | |
| 2-MHx | 7358 | 10598 | 12296 | 12001 | 11039 | 7558 | | | | | | | |
| 2,3-DMP | 37623 | 56352 | 69542 | 68783 | 64161 | 50637 | 26518 | 9070 | | | | | |
| 3-MHx | 8553 | 13116 | 16844 | 16976 | 17243 | 13510 | 7638 | | | | | | |
| **C8** | **579317** | **880620** | **1026566** | **1167690** | **1114756** | **877739** | **469497** | **336990** | **251953** | **339461** | **328896** | **320461** | **276218** |
| **2,2,4-TMP** | **168294** | **261456** | **288735** | **284233** | **247695** | **184034** | **62958** | **16789** | | | | | |
| 2,5-DMHx | 15565 | 23596 | 26234 | 29103 | 27222 | 18659 | 6384 | 8583 | | | | | |
| 2,2,3-TMP | 20784 | 34145 | 41004 | 39271 | 29071 | 20252 | 7125 | | | | | | |
| 2,4-DMHx | 32025 | 52961 | 68503 | 79390 | 64838 | 54362 | 13805 | 6714 | 7494 | 9823 | 9039 | 8431 | 6894 |
| 2,3,4-TMP | 107301 | 156264 | 181381 | 205894 | 192432 | 150384 | 9188 | 26141 | 5339 | | 5006 | 5059 | |
| 2,3,3-TMP | 136235 | 206997 | 236813 | 251615 | 216434 | 152788 | 85287 | 12703 | 5438 | | | | |
| 2,3-DMHx | 43879 | 81720 | 93028 | 113116 | 124861 | 98378 | 58891 | 13272 | 11633 | | | | |
| 3,4-DMHx | 24057 | 31948 | 46783 | 106469 | 154406 | 179890 | 198654 | 143069 | 83656 | 96613 | 66700 | 59172 | 42206 |
| 1 DMHx= | | | | | | | | | | | | | |
| 2 DMHx= | | | | 5315 | 5997 | 6247 | 15531 | 85358 | 112797 | 172359 | 174527 | 178653 | 167007 |
| 3 DMHx= | | | | | | | | | | | | | |
| 4 DMHx= | | | | | | | | | | | | | |
| 5 DMHx= | 31177 | 41533 | 43085 | 53284 | 51800 | 32745 | 11774 | | | 5084 | | | |
| 6 DMHx= | | | | | | | | 25361 | 25596 | 55582 | 73623 | 69136 | 60111 |
| **C9+** | 1233587 | 251580 | 239078 | 352438 | 473420 | 405745 | 399991 | 320643 | 212506 | 288523 | 174719 | 166119 | 127881 |
| **C6+** | 2172965 | 1661380 | 1894566 | 2071527 | 2075825 | 1620410 | 970538 | 681870 | 464459 | 627984 | 503614 | 486570 | 404099 |
| Tot Peak Area | 44734925 | 51737780 | 57133626 | 50362867 | 53026085 | 51510670 | 50353778 | 49608350 | 44679459 | 51969484 | 50994374 | 53357170 | 53712959 |
| **FEED ANAL.** | | Inj 1 | Inj 2 | Inj 3 | Inj 4 | Inj 5 | Avg | Mass % | | | | | |
| **C3** | | 19802 | 17684 | 17521 | 17871 | 21791 | 18934 | 0 77 | | | | | |
| **i-C4** | | 2335882 | 2078799 | 2057617 | 2085319 | 2587354 | 2228994 | 90 88 | | | | | |
| **1-C4=** | | 154819 | 139163 | 137731 | 139332 | 170376 | 148284 | 6 05 | | | | | |
| **n-C4** | | 58952 | 53118 | 52472 | 53123 | 65221 | 56577 | 2 31 | | | | | |
| **I/O Mass Ratio** | | 15 088 | 14 938 | 14 939 | 14 967 | 15 186 | 15 024 | | | | | | |

Run F60P15EMTr
(recalcined 0 5%Pt/EMT, Tcalc=325degC, Tred=425degC, P=382psig, I/O=14 5, butene WHSV=2 1h-1, t=1h, mcat=1h)

| Samp t (min) | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 21 | 24 | 29 | 39 | 69 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **T.O.S. (min.)** | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** | **9** | **10** | **12** | **15** | **20** | **30** | **60** |
| 1-C4= Disapp (%) | 86 | 98 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| t-2-C4= Prod (%) | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 4 | 17 | 33 | 38 | 42 | 47 |
| c-2-C4= Prod (%) | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 6 | 14 | 15 | 19 | 25 |
| **Butene Disapp. (%)** | **86** | **98** | **100** | **100** | **100** | **100** | **100** | **100** | **100** | **96** | **77** | **52** | **47** | **39** | **28** |
| n-Butane Change (%) | 0 | 6 | 4 | 6 | 7 | 7 | 7 | 6 | 6 | 6 | 5 | 2 | 1 | 1 | 3 |
| | | | | | | | | | | | | | | | |
| ***C5+ Product Analysis (mass %*** | 86 | 98 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 96 | 77 | 52 | 47 | 39 | 28 |
| C5-C7 | 24 | 21 | 20 | 23 | 22 | 22 | 21 | 21 | 18 | 10 | 8 | 2 | 0 | 0 | 0 |
| **C8** | **57** | **53** | **44** | **55** | **53** | **55** | **56** | **58** | **52** | **49** | **59** | **55** | **38** | **46** | **60** |
| C9+ | 19 | 25 | 36 | 22 | 25 | 23 | 23 | 21 | 31 | 41 | 33 | 43 | 62 | 54 | 40 |
| | | | | | | | | | | | | | | | |
| ***C8 Distribution (mass %)*** | | | | | | | | | | | | | | | |
| **TMP** | **71** | **77** | **77** | **74** | **74** | **67** | **66** | **66** | **65** | **62** | **44** | **7** | **0** | **0** | **0** |
| DMH | 19 | 16 | 16 | 19 | 19 | 26 | 27 | 28 | 29 | 33 | 42 | 41 | 33 | 25 | 22 |
| C8= | 11 | 7 | 7 | 7 | 7 | 7 | 7 | 6 | 6 | 5 | 15 | 53 | 67 | 75 | 78 |
| | | | | | | | | | | | | | | | |
| ***TMP Distribution (%)*** | | | | | | | | | | | | | | | |
| **2,2,4-TMP** | **31** | **41** | **41** | **42** | **42** | **43** | **40** | **38** | **34** | **30** | **23** | **24** | **0** | **0** | **0** |
| 2,2,3-TMP | 26 | 23 | 21 | 20 | 19 | 11 | 9 | 8 | 7 | 5 | 4 | 0 | 0 | 0 | 0 |
| 2,3,4-TMP | 15 | 12 | 13 | 14 | 14 | 18 | 21 | 23 | 27 | 31 | 37 | 35 | 0 | 0 | 0 |
| 2,3,3-TMP | 28 | 23 | 24 | 25 | 25 | 28 | 30 | 31 | 33 | 34 | 36 | 40 | 0 | 0 | 0 |
| | | | | | | | | | | | | | | | |
| ***Indicators (mass fraction)*** | | | | | | | | | | | | | | | |
| **TMP** | **3.80** | **4.89** | **4.88** | **3.97** | **3.84** | **2.58** | **2.45** | **2.36** | **2.19** | **1.86** | **1.04** | **0.16** | **0.00** | **0.00** | **0.00** |
| **DMH** | | | | | | | | | | | | | | | |
| TMP+DMH | 2 00 | 1 68 | 1 06 | 1 93 | 1 71 | 1 86 | 1 96 | 2 21 | 1 44 | 1 07 | 1 20 | 0 36 | 0 14 | 0 13 | 0 15 |
| C8= + C9+ | | | | | | | | | | | | | | | |
| (2,2,3-+2,2,4-TMP) | 1 34 | 1 82 | 1 69 | 1 60 | 1 53 | 1 17 | 0 96 | 0 84 | 0 68 | 0 54 | 0 36 | 0 32 | 0 00 | 0 00 | 0 00 |
| (2,3,4-+2,3,3-TMP) | | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | | |
| ***DMH Isomer Distribution*** | | | | | | | | | | | | | | | |
| 2,5-DMH | 16 | 18 | 18 | 15 | 15 | 11 | 10 | 9 | 8 | 4 | 0 | 4 | 0 | 0 | 0 |
| 2,4-DMH | 10 | 11 | 10 | 10 | 10 | 27 | 23 | 20 | 20 | 15 | 5 | 6 | 9 | 12 | 21 |
| 2,3-DMH | 52 | 50 | 57 | 51 | 54 | 40 | 37 | 36 | 34 | 32 | 26 | 10 | 9 | 5 | 0 |
| 3,4-DMH | 22 | 21 | 14 | 24 | 21 | 22 | 30 | 35 | 39 | 50 | 69 | 80 | 82 | 82 | 79 |

Run F60Pt5EM1r
(recalcined 0 5%Pt/EMT, Tcalc=325degC, Tred=425degC, P=382psig, I/O=14 5, butene WHSV=2 1h-1, t=1h, mcat=1h)

| TOS [min] | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 12 | 15 | 20 | 30 | 60 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Propane | 374640 | 341060 | 387240 | 420040 | 363440 | 401660 | 393900 | 412620 | 402600 | 347500 | 391200 | 389220 | 391240 | 404200 | 385880 |
| Isobutane | 40068500 | 42955320 | 46407180 | 49057180 | 42296300 | 46365640 | 45548080 | 47565680 | 46992460 | 41313180 | 46276340 | 46743240 | 46483440 | 48616260 | 46761380 |
| 1-butene | 369740 | 61360 | | | | | | | | | | | | | |
| n-butane | 999560 | 1146940 | 1228300 | 1309320 | 1134560 | 1236360 | 1211140 | 1253640 | 1241600 | 1082560 | 1190780 | 1169800 | 1165420 | 1215940 | 1191020 |
| t-2-butene | | | | | | | | | | 114540 | 512640 | 1006200 | 1145200 | 1343880 | 1427560 |
| c-2-butene | | | | | | | | | | | 181080 | 430580 | 451820 | 593260 | 767160 |
| **C5-C7** | **434339** | **566034** | **660066** | **674471** | **560254** | **581848** | **506766** | **484028** | **410854** | **184203** | **77406** | **11772** | **0** | **0** | **0** |
| C5 | 309140 | 231060 | 241700 | 244080 | 200140 | 199460 | 181480 | 171360 | 143740 | | | | | | |
| 2,3-DMB | 25031 | 97771 | 103375 | 105126 | 86968 | 86991 | 77903 | 75163 | 62356 | 41156 | 15091 | | | | |
| 2,2-DMP | 8820 | 35723 | 38661 | 39849 | 33807 | 33334 | 29118 | 27636 | 22724 | 15538 | 6900 | | | | |
| 3-MP | 11509 | 42939 | 46918 | 49344 | 42452 | 43236 | 39852 | 39026 | 34954 | 26175 | 16103 | 6692 | | | |
| 2,4-DMP | 36567 | 104937 | 107890 | 106095 | 84888 | 83881 | 74127 | 69883 | 57420 | 36348 | 12204 | | | | |
| 2,2,3-TMB | | | 10095 | 10166 | 8676 | 9106 | 8428 | 8480 | 7501 | 5402 | | | | | |
| 2-MHx | 6572 | 8198 | 16470 | 17386 | 15280 | 15244 | 12997 | 12063 | 9953 | 6904 | | | | | |
| 2,3-DMP | 29258 | 27563 | 76886 | 82014 | 69944 | 72015 | 66245 | 64383 | 57625 | 41801 | 19926 | 5080 | | | |
| 3-MHx | 7442 | 17843 | 18071 | 20411 | 18099 | 18581 | 16616 | 16034 | 14581 | 10879 | 7182 | | | | |
| **C8** | **1052983** | **1408495** | **1488277** | **1602601** | **1338078** | **1417666** | **1327023** | **1300702** | **1212966** | **915988** | **545047** | **394845** | **394768** | **390378** | **332917** |
| **2,2,4-TMP** | **229417** | **448921** | **477354** | **494067** | **412699** | **409261** | **352097** | **324976** | **284309** | **170883** | **54620** | **6320** | | | |
| 2,5-DMHx | 31151 | 40020 | 42640 | 45626 | 39558 | 40582 | 34428 | 31644 | 27001 | 12095 | | 6585 | | | |
| 2,2,3-TMP | 196611 | 250806 | 246800 | 237610 | 183774 | 101408 | 78708 | 66517 | 51590 | 27447 | 8428 | | | | |
| 2,4-DMHx | 19453 | 23301 | 24411 | 29186 | 26617 | 99282 | 82332 | 72860 | 70156 | 44117 | 11373 | 9096 | 11579 | 12088 | 15696 |
| 2,3,4-TMP | 109181 | 133822 | 150052 | 162664 | 140403 | 165865 | 183412 | 197466 | 209494 | 173741 | 88383 | 9137 | | | |
| 2,3,3-TMP | 208542 | 249947 | 278057 | 295689 | 248927 | 268798 | 264012 | 267151 | 257651 | 191350 | 86009 | 10518 | | | |
| 2,3-DMHx | 102121 | 111813 | 135444 | 152740 | 137559 | 145133 | 133534 | 130391 | 121817 | 96382 | 58635 | 16571 | 11704 | 5111 | |
| 3,4-DMHx | 43017 | 46633 | 33747 | 72125 | 52913 | 81801 | 107889 | 128319 | 138371 | 150150 | 158308 | 128470 | 105221 | 79824 | 57866 |
| 1,DMHx= | | | | | | | | | | | | | | | |
| 2 DMHx= | 6741 | 5067 | 5854 | 6176 | 5919 | 6333 | 5315 | 5448 | | 5216 | 49264 | 140513 | 174201 | 201034 | 183271 |
| 3 DMHx= | | | | | | | | | | | | | | | |
| 4 DMHx= | | | | | | | | | | | 5977 | | | | |
| 5 DMHx= | 98249 | 86456 | 87131 | 98812 | 83394 | 92927 | 78839 | 69915 | 66195 | 44627 | 11403 | 7750 | 7778 | 6227 | |
| 6 DMHx= | 8500 | 11709 | 6787 | 7906 | 6315 | 6276 | 6457 | 6015 | 6382 | | 12647 | 59885 | 84285 | 86094 | 76084 |
| **C9+** | 355352 | 674717 | 1208445 | 658425 | 630434 | 599856 | 541817 | 471184 | 716930 | 760203 | 307865 | 312799 | 631695 | 464593 | 225822 |
| **C5+** | 1842674 | 2649246 | 3356788 | 2935497 | 2528766 | 2579370 | 2375606 | 2255914 | 2340750 | 1860394 | 930318 | 719416 | 1026463 | 854971 | 558739 |
| Tot Peak Area | 43655114 | 47153926 | 51379508 | 53722037 | 46323066 | 50583030 | 49528726 | 51487854 | 50977410 | 44718174 | 49301278 | 50027876 | 50211763 | 52435251 | 50324579 |
| **FEED ANAL.** | | Inj 1 | Inj 2 | Inj 3 | Inj 4 | Inj 5 | Avg | Mass % | | | | | | | |
| **C3** | | 19739 | 17977 | 18117 | 19444 | 18544 | 18764 | 0 76 | | | | | | | |
| **i-C4** | | 2358899 | 2158938 | 2184557 | 2315452 | 2199961 | 2243561 | 90 91 | | | | | | | |
| **1-C4=** | | 156271 | 143946 | 145473 | 153193 | 146296 | 149036 | 6 04 | | | | | | | |
| **n-C4** | | 59308 | 54680 | 55408 | 58135 | 55576 | 56621 | 2 29 | | | | | | | |
| **I/O Mass Ratio** | | 15 095 | 14 998 | 15 017 | 15 115 | 15 038 | 15 052 | | | | | | | | |

Run F62Pt1EMT

(0.1%Pt/EMT; Tcalc=325degC; Tred=425degC; Trxn=50degC; P=382psig; I/O=14.6; butene WHSV=2.10h-1; t=1h; mcat=2.78g)

| T.O.S. [min.] | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 12 | 15 | 20 | 30 | 60 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1-C4= Disapp. [%] | 88 | 96 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 97 |
| t-2-C4= Prod. [%] | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 8 | 13 | 20 | 27 | 33 | 39 | 43 |
| c-2-C4= Prod. [%] | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 5 | 7 | 11 | 14 | 20 | 28 |
| **Butene Disapp. [%]** | **88** | **96** | **100** | **100** | **100** | **100** | **100** | **100** | **92** | **82** | **73** | **61** | **54** | **41** | **26** |
| n-Butane Change [%] | 7 | 8 | 7 | 9 | 9 | 8 | 5 | 8 | 8 | 8 | 9 | 7 | 5 | 3 | 5 |
| ***C5+ Product Analysis [mass %]*** | | | | | | | | | | | | | | | |
| C5-C7 | 26 | 24 | 24 | 24 | 24 | 22 | 19 | 19 | 16 | 10 | 7 | 5 | 4 | 0 | 0 |
| **C8** | **64** | **60** | **63** | **62** | **62** | **61** | **60** | **56** | **53** | **54** | **48** | **41** | **53** | **66** | **66** |
| C9+ | 10 | 16 | 13 | 14 | 14 | 17 | 22 | 24 | 31 | 36 | 46 | 53 | 43 | 34 | 34 |
| ***C8 Distribution [mass %]*** | | | | | | | | | | | | | | | |
| **TMP** | **80** | **78** | **78** | **77** | **75** | **73** | **68** | **67** | **65** | **65** | **52** | **39** | **20** | **6** | **0** |
| DMH | 15 | 16 | 16 | 17 | 19 | 21 | 26 | 28 | 29 | 29 | 33 | 33 | 37 | 26 | 22 |
| C8= | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 5 | 6 | 6 | 15 | 28 | 43 | 68 | 78 |
| ***TMP Isomer Distribution [%]*** | | | | | | | | | | | | | | | |
| **2,2,4-TMP** | **36** | **36** | **36** | **35** | **36** | **34** | **35** | **34** | **31** | **29** | **28** | **29** | **36** | **34** | **0** |
| 2,2,3-TMP | 20 | 19 | 18 | 17 | 16 | 14 | 9 | 8 | 8 | 6 | 5 | 5 | 8 | 0 | 0 |
| 2,3,4-TMP | 15 | 17 | 18 | 19 | 20 | 22 | 25 | 27 | 29 | 31 | 32 | 30 | 18 | 32 | 0 |
| 2,3,3-TMP | 28 | 28 | 29 | 29 | 29 | 29 | 31 | 32 | 33 | 34 | 34 | 36 | 38 | 34 | 0 |
| ***Indicators [mass fraction]*** | | | | | | | | | | | | | | | |
| **TMP** | **5.47** | **4.95** | **4.75** | **4.44** | **3.89** | **3.57** | **2.58** | **2.41** | **2.23** | **2.22** | **1.58** | **1.17** | **0.56** | **0.22** | **0.00** |
| **DMH** | | | | | | | | | | | | | | | |
| TMP+DMH | 4.27 | 2.94 | 3.55 | 3.32 | 3.25 | 2.77 | 2.22 | 1.95 | 1.45 | 1.30 | 0.75 | 0.46 | 0.46 | 0.27 | 0.17 |
| C8= + C9+ | | | | | | | | | | | | | | | |
| (2,2,3-+2,2,4-TMP) | 1.32 | 1.22 | 1.15 | 1.09 | 1.06 | 0.95 | 0.78 | 0.72 | 0.62 | 0.53 | 0.51 | 0.52 | 0.79 | 0.51 | 0.00 |
| (2,3,4-+2,3,3-TMP) | | | | | | | | | | | | | | | |
| ***DMH Isomer Distribution [%]*** | | | | | | | | | | | | | | | |
| 2,5-DMH | 17 | 15 | 14 | 14 | 12 | 11 | 9 | 8 | 7 | 5 | 3 | 7 | 4 | 0 | 0 |
| 2,4-DMH | 10 | 9 | 9 | 8 | 9 | 8 | 22 | 18 | 19 | 8 | 6 | 4 | 6 | 11 | 14 |
| 2,3-DMH | 55 | 52 | 50 | 48 | 44 | 43 | 35 | 33 | 32 | 34 | 28 | 12 | 16 | 12 | 0 |
| 3,4-DMH | 18 | 24 | 27 | 30 | 35 | 38 | 35 | 40 | 43 | 54 | 63 | 77 | 74 | 77 | 86 |

Run F62Pt1EMT
(0 1%Pt/EMT, Tcalc=325degC, Tred=425degC, Trxn=50degC, P=382psig, I/O=14 6, butene WHSV=2 10h-1, t=1h, mcat=2 78g)

| TOS [min] | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 12 | 15 | 20 | 30 | 60 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Propane | 336640 | 324240 | 355740 | 402220 | 369620 | 406220 | 396560 | 398000 | 390420 | 341760 | 377020 | 392120 | 393620 | 410120 | 385940 |
| Isobutane | 46751160 | 41206520 | 43426980 | 48349480 | 43888940 | 47775760 | 42920260 | 46595600 | 46149260 | 40931440 | 44892640 | 47087760 | 46999960 | 49623300 | 46985040 |
| 1-butene | 373280 | 115300 | | | | | | | | | | | | | 104400 |
| n-butane | 1248100 | 1111840 | 1156020 | 1303580 | 1184560 | 1283620 | 1128080 | 1244400 | 1235120 | 1091900 | 1203640 | 1233540 | 1205320 | 1246480 | 1202520 |
| t-2-butene | | | | | | | | | 240380 | 349660 | 578260 | 830000 | 987500 | 1235580 | 1302200 |
| c-2-butene | | | | | | | | | | 123760 | 213080 | 348280 | 415960 | 628260 | 832540 |
| **C5-C7** | **604160** | **548605** | **566519** | **614296** | **537475** | **539325** | **471356** | **426002** | **338135** | **151248** | **106227** | **62798** | **31744** | **0** | **0** |
| C5 | 221960 | 196980 | 204340 | 225940 | 189100 | 188700 | 157280 | 150980 | 117580 | | | | | | |
| 2,3-DMB | 95071 | 87195 | 89585 | 96690 | 84836 | 84676 | 72387 | 65206 | 50236 | 34644 | 23970 | 13418 | 7793 | | |
| 2,2-DMP | 31921 | 29635 | 30750 | 33328 | 30072 | 30485 | 26516 | 24124 | 18409 | 12861 | 9298 | 5622 | | | |
| 3-MP | 40594 | 37894 | 39496 | 43341 | 39684 | 40892 | 36363 | 33908 | 28318 | 20870 | 17005 | 11095 | 8321 | | |
| 2,4-DMP | 103948 | 94202 | 95465 | 99814 | 86766 | 84708 | 74752 | 63150 | 49824 | 34190 | 22940 | 12957 | 7399 | | |
| 2,2,3-TMB | 10074 | 9094 | 9300 | 9970 | 9203 | 9175 | 8750 | 7474 | 6266 | | | | | | |
| 2-MHx | 13927 | 12900 | 13316 | 14076 | 13219 | 13471 | 12682 | 10517 | 8538 | 5823 | | | | | |
| 2,3-DMP | 70986 | 66095 | 68873 | 74133 | 68418 | 70320 | 66311 | 56163 | 47385 | 33574 | 24822 | 14504 | 8231 | | |
| 3-MHx | 15679 | 14610 | 15394 | 17004 | 16177 | 16898 | 16315 | 14480 | 11579 | 9286 | 7192 | 5202 | | | |
| **C8** | **1472946** | **1380453** | **1460729** | **1556248** | **1421220** | **1526402** | **1491462** | **1260374** | **1116148** | **803933** | **686689** | **486382** | **407407** | **376220** | **310596** |
| **2,2,4-TMP** | **428535** | **392968** | **404381** | **424400** | **381322** | **383486** | **356949** | **281558** | **221344** | **150985** | **101367** | **66667** | **29973** | **7334** | |
| 2,5-DMHx | 36215 | 32907 | 34211 | 36525 | 33202 | 35331 | 34196 | 27142 | 22029 | 11328 | 6315 | 11424 | 5399 | | |
| 2,2,3-TMP | 239338 | 201855 | 204144 | 200154 | 165554 | 160883 | 86866 | 68547 | 55873 | 29180 | 19690 | 9159 | 6733 | | |
| 2,4-DMHx | 20566 | 19873 | 21078 | 22706 | 23669 | 25088 | 86419 | 64127 | 60879 | 18123 | 14208 | 6604 | 9287 | 10475 | 9433 |
| 2,3,4-TMP | 181798 | 182624 | 201598 | 224561 | 209460 | 246062 | 252215 | 223499 | 209466 | 162072 | 113891 | 57253 | 15154 | 6998 | |
| 2,3,3-TMP | 325301 | 303800 | 327661 | 348927 | 307278 | 329536 | 315551 | 263896 | 236393 | 179636 | 123670 | 67786 | 31338 | 7495 | |
| 2,3-DMHx | 118733 | 113643 | 120664 | 129663 | 121373 | 135294 | 135393 | 115911 | 102992 | 79811 | 62541 | 19744 | 23599 | 11952 | |
| 3,4-DMHx | 39227 | 51916 | 63633 | 80976 | 95051 | 117806 | 135900 | 139905 | 138140 | 125907 | 143896 | 124131 | 111145 | 77072 | 59477 |
| 1 DMHx= | | | | | | | | | | | 5410 | | | | |
| 2 DMHx= | 5454 | 5174 | 5314 | 5703 | 5245 | 6080 | 6089 | | 14606 | 13617 | 60006 | 91957 | 132253 | 172658 | 172471 |
| 3 DMHx= | | | | | | | | | | | | | | | |
| 4 DMHx= | | | | | | | | | | | 5929 | 6489 | 6882 | | |
| 5 DMHx= | 71934 | 69698 | 71685 | 77719 | 72631 | 80108 | 76554 | 60444 | 49131 | 33274 | 13866 | 8259 | | 6710 | |
| 6 DMHx= | 5845 | 5995 | 6360 | 6914 | 6435 | 6728 | 6330 | 5345 | 5295 | | 14900 | 26919 | 35644 | 75526 | 69215 |
| **C9+** | 241869 | 360748 | 304703 | 351866 | 326427 | 424856 | 542585 | 542677 | 653973 | 533962 | 684303 | 624755 | 329009 | 197249 | 162089 |
| **C5+** | 2318975 | 2289806 | 2331951 | 2524410 | 2285122 | 2490583 | 2505403 | 2219053 | 2108256 | 1489143 | 1475219 | 1172935 | 768160 | 573469 | 472685 |
| Tot Peak Area | 51028155 | 45047706 | 47270691 | 52579690 | 47728242 | 51956183 | 46950303 | 50457053 | 50123436 | 44203903 | 48526779 | 50716355 | 50354560 | 53088949 | 50452785 |

| ***Feed Analysis*** | Inj 1 | Inj 2 | Inj 3 | Inj 4 | Inj 5 | Avg | Mass % |
|---|---|---|---|---|---|---|---|
| C3 | 18701 | 19299 | 18708 | 19540 | 19552 | 19160 | 0 76 |
| i-C4 | 2265871 | 2319728 | 2239606 | 2341678 | 2356598 | 2304696 | 90 96 |
| 1-C4= | 149502 | 153130 | 147983 | 153898 | 155376 | 151978 | 6 00 |
| n-C4 | 56982 | 58357 | 56340 | 58049 | 59201 | 57786 | 2 28 |
| **I/O Mass Ratio** | 15 156 | 15 149 | 15 134 | 15 216 | 15 167 | 15 164 | |

Avg Mass I/O Ratio 15 16
Avg Molar I/O Ratio **14.638**

Run F63Pt1EMTr

(recalcined 0.1%Pt/EMT; Tcalc=325degC; Tred=425degC; Trxn=50degC; P=382psig; I/O=14.8; butene WHSV=2.10h-1; t=1h; mcat=2.78g)

| Samp t [min] | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 21 | 24 | 29 | 39 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| T.O.S. [min.] | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 12 | 15 | 20 | 30 |
| 1-C4= Disapp. [%] | 82 | 95 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| t-2-C4= Prod. [%] | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 6 | 12 | 17 | 24 | 36 | 36 | 41 |
| c-2-C4= Prod. [%] | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 4 | 6 | 9 | 15 | 15 | 18 |
| Butene Disapp. [%] | 82 | 95 | 100 | 100 | 100 | 100 | 100 | 94 | 84 | 77 | 67 | 49 | 49 | 42 |
| n-Butane Change [%] | 7 | 8 | 8 | 8 | 8 | 8 | 7 | 6 | 5 | 5 | 4 | 2 | 3 | 2 |
| | | | | | | | | | | | | | | |
| *C5+ Product Analysis [mass %]* | | | | | | | | | | | | | | |
| C5-C7 | 29 | 26 | 25 | 24 | 22 | 21 | 19 | 16 | 10 | 7 | 6 | 19 | 1 | 0 |
| C8 | 64 | 59 | 62 | 63 | 63 | 63 | 61 | 55 | 52 | 47 | 48 | 39 | 56 | 62 |
| C9+ | 7 | 15 | 13 | 13 | 14 | 17 | 20 | 29 | 39 | 45 | 46 | 42 | 43 | 38 |
| | | | | | | | | | | | | | | |
| *C8 Product Distribution [mass %]* | | | | | | | | | | | | | | |
| TMP | 82 | 80 | 80 | 77 | 75 | 69 | 68 | 64 | 62 | 52 | 37 | 19 | 8 | 5 |
| DMH | 14 | 15 | 15 | 18 | 20 | 25 | 27 | 31 | 33 | 35 | 38 | 39 | 29 | 26 |
| C8= | 4 | 5 | 5 | 6 | 6 | 6 | 5 | 6 | 5 | 13 | 25 | 42 | 63 | 70 |
| | | | | | | | | | | | | | | |
| *TMP Isomer Distribution [%]* | | | | | | | | | | | | | | |
| 2,2,4-TMP | 38 | 36 | 35 | 35 | 34 | 34 | 32 | 29 | 28 | 28 | 27 | 52 | 29 | 36 |
| 2,2,3-TMP | 20 | 19 | 17 | 15 | 14 | 8 | 7 | 7 | 6 | 5 | 5 | 6 | 0 | 0 |
| 2,3,4-TMP | 15 | 16 | 18 | 20 | 22 | 25 | 28 | 31 | 33 | 33 | 33 | 16 | 34 | 30 |
| 2,3,3-TMP | 26 | 28 | 29 | 30 | 30 | 32 | 33 | 33 | 34 | 34 | 35 | 26 | 37 | 34 |
| | | | | | | | | | | | | | | |
| *Indicators [mass fraction]* | | | | | | | | | | | | | | |
| TMP | 5.88 | 5.52 | 5.43 | 4.30 | 3.82 | 2.72 | 2.46 | 2.08 | 1.85 | 1.49 | 0.95 | 0.48 | 0.26 | 0.18 |
| DMH | | | | | | | | | | | | | | |
| TMP+DMH | 6.17 | 3.00 | 3.63 | 3.73 | 3.33 | 2.92 | 2.50 | 1.62 | 1.19 | 0.80 | 0.62 | 0.39 | 0.26 | 0.23 |
| C8= + C9+ | | | | | | | | | | | | | | |
| (2,2,3-+2,2,4-TMP) | 1.41 | 1.24 | 1.12 | 1.01 | 0.94 | 0.75 | 0.65 | 0.56 | 0.50 | 0.48 | 0.47 | 1.38 | 0.42 | 0.57 |
| (2,3,4-+2,3,3-TMP) | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | |
| *DMH Distribution [%]* | | | | | | | | | | | | | | |
| 2,5-DMH | 17 | 16 | 15 | 12 | 11 | 8 | 7 | 6 | 4 | 3 | 4 | 12 | 0 | 0 |
| 2,4-DMH | 11 | 10 | 10 | 8 | 8 | 22 | 21 | 17 | 12 | 6 | 3 | 5 | 10 | 11 |
| 2,3-DMH | 55 | 55 | 56 | 47 | 44 | 35 | 34 | 32 | 32 | 30 | 23 | 22 | 9 | 11 |
| 3,4-DMH | 18 | 19 | 19 | 33 | 36 | 35 | 38 | 45 | 52 | 61 | 69 | 61 | 81 | 78 |

Run F63Pt1EMTr
(recalcined 0 1%Pt/EMT, Tcalc=325degC, Tred=425degC, Trxn=50degC, P=382psig, I/O=14 8, butene WHSV=2 10h-1, t=1h, mcat=2 78g)

| TOS (min) | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 12 | 15 | 20 | 30 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Propane | 329280 | 326580 | 326560 | 399480 | 349580 | 387940 | 374400 | 386260 | 383140 | 332560 | 369240 | 371320 | 377640 | 389840 |
| Isobutane | 47388180 | 41947620 | 40154900 | 47969000 | 41627960 | 45798360 | 44060660 | 46206300 | 45824720 | 40176160 | 44563920 | 44911800 | 45657980 | 47656520 |
| 1-butene | 536820 | 138040 | | | | | | | | | | | | |
| n-butane | 1249380 | 1121380 | 1066100 | 1273240 | 1109360 | 1210920 | 1155800 | 1194520 | 1174360 | 1022260 | 1125200 | 1125080 | 1139000 | 1180120 |
| t-2-butene | | | | | | | | 169660 | 345360 | 426460 | 690080 | 1047220 | 1055340 | 1233100 |
| c-2-butene | | | | | | | | | 123900 | 156480 | 261260 | 429860 | 438940 | 542420 |
| | | | | | | | | | | | | | | |
| **C6-C7** | **670621** | **590684** | **612171** | **680906** | **477834** | **465833** | **386793** | **299458** | **138622** | **86814** | **59690** | **221962** | **6426** | **0** |
| C5 | 212080 | 241740 | 189660 | 213340 | 171800 | 166280 | 136220 | 103880 | | | | | | |
| 2,3-DMB | 90408 | 87346 | 80908 | 90964 | 74073 | 71551 | 58528 | 43972 | 30756 | 18929 | 11947 | 53534 | | |
| 2,2-DMP | 29848 | 29103 | 27483 | 31305 | 26235 | 25396 | 20954 | 16244 | 11988 | 7935 | 5419 | 5791 | | |
| 3-MP | 38260 | 37695 | 35669 | 41744 | 35849 | 36226 | 31703 | 27193 | 21569 | 15516 | 11944 | 53376 | 5426 | |
| 2,4-DMP | 99094 | 94474 | 85012 | 93620 | 74367 | 69692 | 55247 | 40549 | 27601 | 16624 | 10368 | 38087 | | |
| 2,2,3-TMB | 9382 | 8805 | 8416 | 9584 | 8275 | 8377 | 7102 | 5089 | | | | 5709 | | |
| 2-MHx | 12337 | 12187 | 11374 | 12791 | 11351 | 11027 | 9224 | 7209 | 5228 | | | | | |
| 2,3-DMP | 65130 | 65040 | 61161 | 71479 | 61522 | 62422 | 53792 | 43775 | 32190 | 20941 | 14413 | 38510 | | |
| 3-MHx | 14082 | 14294 | 12488 | 15979 | 14362 | 14862 | 13023 | 11547 | 9190 | 6869 | 5599 | 26855 | | |
| | | | | | | | | | | | | | | |
| **C8** | **1277890** | **1351389** | **1276878** | **1530313** | **1380244** | **1394883** | **1219201** | **1047668** | **751013** | **568380** | **500007** | **480224** | **359645** | **373172** |
| **2,2,4-TMP** | **399366** | **394968** | **362398** | **408780** | **346242** | **330127** | **262293** | **192985** | **128926** | **80431** | **49320** | **45091** | **8043** | **6481** |
| 2,5-DMHx | 29681 | 30813 | 28534 | 33081 | 29291 | 29265 | 24117 | 18554 | 10474 | 5154 | 8546 | 21127 | | |
| 2,2,3-TMP | 211654 | 205496 | 178800 | 179935 | 145756 | 80357 | 60997 | 45096 | 25780 | 13316 | 9106 | 5375 | | |
| 2,4-DMHx | 19057 | 20085 | 18927 | 22949 | 22511 | 76841 | 68727 | 55596 | 28898 | 12687 | 6296 | 8630 | 10042 | 10593 |
| 2,3,4-TMP | 157296 | 178037 | 187235 | 231568 | 221183 | 243003 | 231807 | 206009 | 150608 | 96940 | 60796 | 13643 | 9239 | 5267 |
| 2,3,3-TMP | 275891 | 305597 | 294915 | 352365 | 303681 | 307264 | 268045 | 222470 | 157091 | 99928 | 63609 | 22811 | 10130 | 5988 |
| 2,3-DMHx | 97611 | 108886 | 105785 | 126766 | 117506 | 124265 | 114273 | 102357 | 80679 | 58675 | 44718 | 39883 | 9578 | 10765 |
| 3,4-DMHx | 31200 | 36564 | 35166 | 89764 | 97045 | 122991 | 127844 | 144129 | 129280 | 118865 | 132354 | 110353 | 84819 | 74690 |
| 1 DMHx= | | | | | | | | | | | | | | |
| 2 DMHx= | | | | 5280 | 5030 | 5182 | 5071 | 12485 | 14743 | 43862 | 83052 | 132072 | 153332 | 175726 |
| 3 DMHx= | | | | | | | | | | | | | | |
| 4 DMHx= | | | | | | | | | | | | | | |
| 5 DMHx= | 55514 | 65098 | 59718 | 73026 | 66187 | 69144 | 56027 | 47987 | 24534 | 5380 | 14819 | 6428 | 6825 | 6309 |
| 6 DMHx= | | 5845 | 5400 | 6799 | 5812 | 6444 | | | | 23142 | 27391 | 54811 | 67837 | 77383 |
| | | | | | | | | | | | | | | |
| **C9+** | 142548 | 355451 | 268587 | 302205 | 308169 | 369231 | 402703 | 547543 | 559857 | 532538 | 476389 | 491936 | 274240 | 228748 |
| | | | | | | | | | | | | | | |
| **C6+** | 1991059 | 2297524 | 2057636 | 2413324 | 2146247 | 2229947 | 2007697 | 1894669 | 1449392 | 1177732 | 1036086 | 1174022 | 639511 | 601920 |
| | | | | | | | | | | | | | | |
| Tot Peak Area | 51494719 | 45831144 | 43605196 | 52055044 | 45233147 | 49627167 | 47598557 | 49851409 | 49176972 | 43135172 | 47784526 | 48629442 | 48869471 | 51061500 |
| | | | | | | | | | | | | | | |
| **FEED ANAL.** | | Inj 1 | Inj 2 | Inj 3 | Inj 4 | Inj 5 | Avg | Mass % | | | | | | |
| **C3** | | 21125 | 18919 | 18506 | 19673 | 20417 | 19728 | 0 74 | | | | | | |
| **i-C4** | | 2583099 | 2311216 | 2260896 | 2404147 | 2507648 | 2413401 | 91 05 | | | | | | |
| **1-C4=** | | 167684 | 151505 | 148436 | 156904 | 163469 | 157600 | 5 95 | | | | | | |
| **n-C4** | | 63699 | 57654 | 56566 | 59881 | 62204 | 60001 | 2 26 | | | | | | |
| **I/O Mass Ratio** | | 15 405 | 15 255 | 15 231 | 15 322 | 15 340 | 15 311 | | | | | | | |

Run F66EMT
(EMT; Tcalc=425degC; Trxn=53degC; P=382psig; I/O=14.9; butene WHSV=2.07h-1; t=1h; mcat=2.78g)

| Samp t [min] | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 21 | 24 | 29 | 39 | 69 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **T.O.S. [min.]** | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** | **9** | **10** | **12** | **15** | **20** | **30** | **60** |
| 1-C4= Disapp. [%] | 97 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 96 |
| t-2-C4= Prod. [%] | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 7 | 14 | 22 | 33 | 38 | 42 |
| c-2-C4= Prod. [%] | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 5 | 9 | 17 | 21 | 29 |
| **Butene Disapp. [%]** | **97** | **100** | **100** | **100** | **100** | **100** | **100** | **100** | **100** | **93** | **80** | **69** | **50** | **41** | **25** |
| n-Butane Change [%] | 6 | 5 | 7 | 7 | 8 | 22 | 8 | 8 | 3 | 6 | 3 | 3 | 3 | 2 | 2 |
| | | | | | | | | | | | | | | | |
| ***C5+ Product Analysis [mass %]*** | | | | | | | | | | | | | | | |
| C5-C7 | 34 | 22 | 21 | 21 | 22 | 21 | 20 | 20 | 16 | 16 | 8 | 6 | 4 | 0 | 0 |
| **C8** | **53** | **57** | **57** | **56** | **60** | **63** | **57** | **61** | **57** | **55** | **48** | **46** | **52** | **60** | **62** |
| C9+ | 13 | 21 | 22 | 23 | 18 | 17 | 23 | 19 | 28 | 29 | 45 | 47 | 44 | 40 | 38 |
| | | | | | | | | | | | | | | | |
| ***C8 Distribution [mass %]*** | | | | | | | | | | | | | | | |
| **TMP** | **79** | **73** | **72** | **72** | **73** | **70** | **70** | **70** | **68** | **66** | **59** | **50** | **29** | **7** | **0** |
| DMH | 16 | 20 | 21 | 21 | 20 | 25 | 24 | 25 | 27 | 29 | 32 | 33 | 30 | 28 | 23 |
| C8= | 5 | 7 | 7 | 7 | 6 | 6 | 5 | 5 | 5 | 5 | 8 | 17 | 41 | 65 | 77 |
| | | | | | | | | | | | | | | | |
| ***TMP Isomer Distribution [%]*** | | | | | | | | | | | | | | | |
| **2,2,4-TMP** | **46** | **40** | **37** | **37** | **36** | **34** | **30** | **28** | **27** | **28** | **27** | **24** | **22** | **26** | **0** |
| 2,2,3-TMP | 21 | 19 | 17 | 16 | 15 | 8 | 8 | 7 | 7 | 7 | 7 | 5 | 6 | 0 | 0 |
| 2,3,4-TMP | 12 | 16 | 18 | 19 | 21 | 26 | 29 | 31 | 31 | 30 | 31 | 35 | 36 | 35 | 0 |
| 2,3,3-TMP | 21 | 26 | 27 | 27 | 28 | 32 | 33 | 34 | 34 | 35 | 35 | 36 | 36 | 40 | 0 |
| | | | | | | | | | | | | | | | |
| ***Indicators [mass fraction]*** | | | | | | | | | | | | | | | |
| **TMP** | **4.98** | **3.61** | **3.44** | **3.46** | **3.58** | **2.83** | **2.87** | **2.81** | **2.51** | **2.26** | **1.86** | **1.52** | **0.96** | **0.25** | **0.00** |
| **DMH** | | | | | | | | | | | | | | | |
| TMP+DMH | 3.27 | 2.14 | 2.01 | 1.91 | 2.63 | 2.92 | 2.09 | 2.62 | 1.76 | 1.64 | 0.90 | 0.70 | 0.46 | 0.26 | 0.16 |
| C8= + C9+ | | | | | | | | | | | | | | | |
| (2,2,3-+2,2,4-TMP) | 2.03 | 1.41 | 1.20 | 1.15 | 1.03 | 0.73 | 0.60 | 0.54 | 0.53 | 0.55 | 0.51 | 0.41 | 0.40 | 0.35 | 0.00 |
| (2,3,4-+2,3,3-TMP) | | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | | |
| ***DMH Isomer Distribution [%]*** | | | | | | | | | | | | | | | |
| 2,5-DMH | 19 | 14 | 13 | 13 | 12 | 9 | 8 | 7 | 7 | 6 | 5 | 2 | 0 | 0 | 0 |
| 2,4-DMH | 12 | 9 | 9 | 8 | 9 | 24 | 21 | 20 | 19 | 18 | 15 | 9 | 7 | 11 | 13 |
| 2,3-DMH | 54 | 46 | 46 | 44 | 44 | 35 | 34 | 34 | 32 | 32 | 29 | 26 | 12 | 8 | 0 |
| 3,4-DMH | 15 | 30 | 32 | 35 | 36 | 32 | 36 | 39 | 42 | 44 | 51 | 64 | 81 | 82 | 87 |

Run F66EMT
(EMT, Tcalc=425degC, Trxn=53degC, P=382psig, I/O=14 9, butene WHSV=2 07h-1, t=1h, mcat=2 78g)

| TOS [min] | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 12 | 15 | 20 | 30 | 60 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Propane | 422260 | 353300 | 343280 | 315680 | 351840 | 196080 | 353320 | 355480 | 325860 | 358540 | 382900 | 374180 | 345000 | 361980 | 366660 |
| Isobutane | 57911020 | 43700060 | 40449000 | 36627040 | 40661900 | 23274940 | 40947140 | 41671740 | 35635700 | 41426480 | 44968080 | 44250240 | 40811880 | 43180480 | 44131760 |
| 1-butene | 110200 | | | | | | | | | | | | | | 108640 |
| n-butane | 1465280 | 1123080 | 1059740 | 964580 | 1070200 | 719280 | 1070220 | 1087340 | 893540 | 1063460 | 1124320 | 1101000 | 1006420 | 1059280 | 1077920 |
| t-2-butene | | | | | | | | | | 179960 | 414740 | 620600 | 841720 | 1037440 | 1176200 |
| c-2-butene | | | | | | | | | | | 152740 | 248080 | 446340 | 567120 | 821500 |
| **C5-C7** | **676541** | **559869** | **513990** | **459696** | **476008** | **444312** | **408251** | **385636** | **324963** | **310582** | **148107** | **87305** | **26560** | **0** | **0** |
| C5 | 268500 | 199840 | 185180 | 164260 | 167900 | 147940 | 148140 | 137460 | 107520 | 106700 | | | | | |
| 2,3-DMB | 107430 | 86634 | 79603 | 71694 | 75216 | 71600 | 63692 | 59953 | 50470 | 47194 | 33780 | 19769 | 6548 | | |
| 2,2-DMP | 40363 | 33389 | 29931 | 26746 | 27438 | 25002 | 21407 | 20057 | 17447 | 16692 | 12440 | 7463 | | | |
| 3-MP | 48581 | 40525 | 37451 | 33726 | 35254 | 34027 | 30760 | 29418 | 26564 | 26289 | 21205 | 14519 | 6462 | | |
| 2,4-DMP | 99720 | 88589 | 80075 | 72013 | 75016 | 73014 | 62760 | 58879 | 50437 | 45905 | 32504 | 18697 | 6041 | | |
| 2,2,3-TMB | 9735 | 8759 | 8204 | 7396 | 7999 | 8097 | 7543 | 7330 | 6433 | 5847 | | | | | |
| 2-MHx | 15752 | 15182 | 13572 | 12006 | 11946 | 11030 | 9090 | 8607 | 7899 | 7177 | 5461 | | | | |
| 2,3-DMP | 69275 | 69486 | 63809 | 57454 | 59614 | 59466 | 52795 | 51947 | 47131 | 43699 | 33510 | 20566 | 7509 | | |
| 3-MHx | 17185 | 17455 | 16165 | 14401 | 14625 | 14136 | 12064 | 11985 | 11062 | 11079 | 9207 | 6291 | | | |
| **C8** | **1066300** | **1474239** | **1421028** | **1233956** | **1288360** | **1326459** | **1186307** | **1199622** | **1174172** | **1071037** | **889019** | **643526** | **385332** | **314546** | **283714** |
| **2,2,4-TMP** | **390953** | **423609** | **378713** | **333106** | **335735** | **312382** | **248524** | **234138** | **217029** | **197030** | **140648** | **78297** | **22920** | **6686** | |
| 2,5-DMHx | 32963 | 42898 | 39178 | 32709 | 32248 | 29592 | 23608 | 22059 | 21450 | 19317 | 14003 | 5037 | | | |
| 2,2,3-TMP | 173616 | 202544 | 178352 | 144101 | 143208 | 76923 | 64152 | 61736 | 58534 | 51929 | 37309 | 16070 | 6197 | | |
| 2,4-DMHx | 19479 | 27488 | 25821 | 21809 | 22431 | 77065 | 61229 | 59950 | 60592 | 55893 | 42417 | 18083 | 7780 | 9203 | 8554 |
| 2,3,4-TMP | 99422 | 170183 | 184008 | 170221 | 197632 | 242180 | 243458 | 257680 | 246596 | 210173 | 165718 | 112713 | 36423 | 7627 | |
| 2,3,3-TMP | 178784 | 274821 | 278540 | 244174 | 266693 | 291399 | 276897 | 285841 | 274783 | 242531 | 185371 | 116444 | 36454 | 8702 | |
| 2,3-DMHx | 91672 | 137869 | 134895 | 113437 | 115023 | 113798 | 99830 | 100627 | 102483 | 97812 | 83690 | 54271 | 12823 | 6916 | |
| 3,4-DMHx | 25252 | 88542 | 96117 | 89501 | 94060 | 106039 | 105447 | 116448 | 132834 | 137468 | 144634 | 135000 | 85978 | 71084 | 56101 |
| 1 DMHx= | | | | | | | | | | | | | | | |
| 2 DMHx= | | 6580 | 6305 | 5363 | 5262 | 5272 | 5130 | 6932 | 5353 | 11882 | 35849 | 69619 | 100934 | 138478 | 153453 |
| 3 DMHx= | | | | | | | | | | | | | | | |
| 4 DMHx= | | | | | | | | | | | | | | | |
| 5 DMHx= | 54159 | 92923 | 91351 | 73364 | 70367 | 65523 | 52428 | 48614 | 49052 | 47002 | 39480 | 18326 | 5951 | 5803 | |
| 6 DMHx= | | 6782 | 7748 | 6171 | 5701 | 6286 | 5604 | 5497 | 5466 | | | 19666 | 39872 | 61046 | 65606 |
| **C9+** | 255644 | 533111 | 548120 | 515239 | 377648 | 351042 | 473834 | 373248 | 573264 | 560074 | 832237 | 654299 | 304497 | 210930 | 177409 |
| **C5+** | 1998485 | 2567209 | 2483138 | 2208891 | 2141016 | 2121813 | 2068392 | 1958406 | 2072399 | 1941693 | 1869363 | 1385130 | 686389 | 525475 | 461123 |
| Tot Peak Area | 61907245 | 47743649 | 44335158 | 40116191 | 44224956 | 26312113 | 44439072 | 45072966 | 38927499 | 44970133 | 48759403 | 47731150 | 43691409 | 46164655 | 47322303 |
| ***Feed Analysis*** | | Inj 1 | Inj 2 | Inj 3 | Inj 4 | Inj 5 | Avg | Mass % | | | | | | | |
| C3 | | 20175 | 18137 | 17972 | 16732 | 16589 | 17921 | 0 77 | | | | | | | |
| i-C4 | | 2406365 | 2150897 | 2131021 | 1979826 | 1976780 | 2128978 | 91 08 | | Avg Mass I/O Ratio | | 15 41 | | | |
| 1-C4= | | 154955 | 139665 | 138471 | 129070 | 128531 | 138138 | 5 91 | | Avg Molar I/O Ratio | | **14.873** | | | |
| n-C4 | | 58569 | 52885 | 52431 | 48919 | 48852 | 52331 | 2 24 | | | | | | | |
| **I/O Mass Ratio** | | 15 529 | 15 400 | 15 390 | 15 339 | 15 380 | 15 408 | | | | | | | | |

Run F67EMTr
(recalcined EMT; Tcalc=425degC; Trxn=52degC; P=382psig; I/O=15.0; butene WHSV=2.06h-1; t=1h, mcat=2.78g)

| Samp t [min] | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 21 | 24 | 29 | 39 | 69 | 70 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **T.O.S. [min.]** | **2** | **3** | **4** | **5** | **6** | **7** | **8** | **9** | **10** | **12** | **15** | **20** | **30** | **60** | **61** |
| 1-C4= Disapp. [%] | 95 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| t-2-C4= Prod. [%] | 0 | 0 | 0 | 0 | 6 | 10 | 16 | 20 | 20 | 23 | 33 | 37 | 42 | 47 | 48 |
| c-2-C4= Prod. [%] | 0 | 0 | 0 | 0 | 0 | 0 | 7 | 8 | 8 | 9 | 16 | 17 | 20 | 28 | 29 |
| **T.O.S. [min.]** | **2** | **3** | **4** | **5** | **6** | **7** | **8** | **9** | **10** | **12** | **15** | **20** | **30** | **60** | **61** |
| **Butene Disapp. [%]** | **95** | **100** | **100** | **100** | **94** | **90** | **77** | **73** | **72** | **67** | **51** | **46** | **38** | **25** | **23** |
| n-Butane Change [%] | 8 | 7 | 8 | 8 | 7 | 6 | 4 | 5 | 5 | 5 | 3 | 4 | 3 | 4 | 7 |
| | | | | | | | | | | | | | | | |
| ***C5+ Product Analysis [mass %]*** | | | | | | | | | | | | | | | |
| C5-C7 | 23 | 22 | 20 | 19 | 12 | 10 | 7 | 9 | 9 | 6 | 2 | 0 | 0 | 0 | 0 |
| **C8** | **62** | **58** | **61** | **61** | **64** | **55** | **48** | **57** | **59** | **49** | **45** | **51** | **63** | **72** | **70** |
| C9+ | 15 | 20 | 19 | 20 | 24 | 34 | 45 | 34 | 32 | 45 | 53 | 49 | 37 | 28 | 30 |
| | | | | | | | | | | | | | | | |
| ***C8 Distribution [mass %]*** | | | | | | | | | | | | | | | |
| **TMP** | **76** | **75** | **67** | **65** | **62** | **62** | **56** | **53** | **49** | **40** | **22** | **8** | **0** | **0** | **0** |
| DMH | 19 | 20 | 27 | 30 | 32 | 32 | 31 | 33 | 34 | 36 | 33 | 29 | 25 | 19 | 19 |
| C8= | 5 | 5 | 5 | 5 | 6 | 6 | 13 | 14 | 17 | 23 | 45 | 63 | 75 | 81 | 81 |
| | | | | | | | | | | | | | | | |
| ***TMP Isomer Distribution [%]*** | | | | | | | | | | | | | | | |
| **2,2,4-TMP** | **31** | **31** | **31** | **31** | **30** | **29** | **28** | **27** | **26** | **24** | **22** | **32** | **0** | **0** | **0** |
| 2,2,3-TMP | 13 | 13 | 8 | 7 | 7 | 6 | 5 | 5 | 4 | 5 | 0 | 0 | 0 | 0 | 0 |
| 2,3,4-TMP | 24 | 26 | 29 | 30 | 30 | 32 | 33 | 34 | 35 | 36 | 42 | 32 | 0 | 0 | 0 |
| 2,3,3-TMP | 31 | 31 | 33 | 32 | 33 | 33 | 34 | 35 | 35 | 36 | 36 | 36 | 0 | 0 | 0 |
| | | | | | | | | | | | | | | | |
| ***Indicators [mass fraction]*** | | | | | | | | | | | | | | | |
| **TMP** | **4.01** | **3.67** | **2.45** | **2.18** | **1.94** | **1.97** | **1.79** | **1.61** | **1.47** | **1.11** | **0.65** | **0.29** | **0.00** | **0.00** | **0.00** |
| **DMH** | | | | | | | | | | | | | | | |
| TMP+DMH | 3.23 | 2.40 | 2.61 | 2.50 | 2.16 | 1.39 | 0.82 | 1.17 | 1.15 | 0.66 | 0.34 | 0.23 | 0.18 | 0.16 | 0.15 |
| C8= + C9+ | | | | | | | | | | | | | | | |
| (2,2,3-+2,2,4-TMP) | 0.81 | 0.76 | 0.63 | 0.61 | 0.58 | 0.54 | 0.49 | 0.46 | 0.44 | 0.40 | 0.28 | 0.47 | 0.00 | 0.00 | 0.00 |
| (2,3,4-+2,3,3-TMP) | | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | | |
| ***DMH Isomer Distribution [%]*** | | | | | | | | | | | | | | | |
| 2,5-DMH | 11 | 10 | 7 | 6 | 6 | 4 | 3 | 3 | 6 | 5 | 5 | 6 | 0 | 0 | 0 |
| 2,4-DMH | 7 | 7 | 19 | 18 | 16 | 12 | 9 | 7 | 0 | 3 | 6 | 10 | 13 | 16 | 16 |
| 2,3-DMH | 44 | 42 | 33 | 33 | 31 | 34 | 32 | 29 | 28 | 24 | 15 | 9 | 0 | 0 | 0 |
| 3,4-DMH | 38 | 41 | 41 | 44 | 47 | 50 | 56 | 61 | 66 | 68 | 74 | 75 | 87 | 84 | 84 |

Run F67EMTr
(recalcined EMT, Tcalc=425degC, Trxn=52degC, P=382psig, I/O=15 0, butene WHSV=2 06h-1, t=1h, mcat=2 78g)

| TOS (min) | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 12 | 15 | 20 | 30 | 60 | 61 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Propane | 317540 | 379680 | 402980 | 328360 | 358860 | 352220 | 370760 | 356160 | 313360 | 356060 | 356080 | 372140 | 371780 | 345620 | 277560 |
| Isobutane | 40357080 | 45802120 | 47464180 | 38590600 | 41720960 | 41039540 | 43328960 | 42170040 | 37633180 | 42060020 | 42679920 | 44497200 | 44668100 | 41122540 | 32819540 |
| 1-butene | 115340 | | | | | | | | | | | | | | |
| n-butane | 1050160 | 1170680 | 1219740 | 995160 | 1068100 | 1043320 | 1088400 | 1060060 | 942520 | 1053080 | 1050560 | 1098020 | 1097400 | 1022660 | 840920 |
| t-2-butene | | | | | 155980 | 253440 | 445880 | 523420 | 475480 | 620980 | 901380 | 1033900 | 1174520 | 1211540 | 1004140 |
| c-2-butene | | | | | | | 179540 | 208300 | 185920 | 245280 | 428740 | 471440 | 576260 | 726480 | 594220 |
| **C5-C7** | **390671** | **410167** | **394977** | **291391** | **175246** | **144364** | **110191** | **89042** | **73129** | **61354** | **18177** | **0** | **0** | **0** | **0** |
| C5 | 135640 | 152940 | 141280 | 101320 | | | | | | | | | | | |
| 2,3-DMB | 62578 | 63549 | 60011 | 43920 | 39931 | 33232 | 25872 | 20566 | 16668 | 13091 | 5239 | | | | |
| 2,2-DMP | 20619 | 21660 | 21369 | 16142 | 14997 | 12862 | 9802 | 7997 | 6609 | 5531 | 6281 | | | | |
| 3-MP | 29993 | 31287 | 32332 | 24477 | 24186 | 20874 | 17249 | 14829 | 12749 | 11544 | | | | | |
| 2,4-DMP | 62702 | 59749 | 56053 | 40829 | 36320 | 30139 | 23644 | 18212 | 14231 | 11360 | | | | | |
| 2,2,3-TMB | 7515 | 7569 | 7601 | 5584 | 5080 | | | | | | | | | | |
| 2-MHx | 8854 | 8883 | 9190 | 7194 | 6493 | 5626 | | | | | | | | | |
| 2,3-DMP | 51430 | 52589 | 54004 | 41478 | 37991 | 32552 | 26281 | 21105 | 17357 | 14746 | 6657 | | | | |
| 3-MHx | 11340 | 11931 | 13137 | 10447 | 10248 | 9079 | 7343 | 6333 | 5515 | 5082 | | | | | |
| **C8** | **1075152** | **1107681** | **1210075** | **959022** | **935768** | **786096** | **714139** | **584269** | **496623** | **520752** | **393575** | **364741** | **324232** | **268778** | **263131** |
| **2,2,4-TMP** | **256086** | **264581** | **282824** | **191617** | **173388** | **143790** | **111028** | **82628** | **64329** | **60721** | **18774** | **9734** | | | |
| 2,5-DMHx | 21828 | 22201 | 23317 | 17923 | 16766 | 10719 | 7372 | 6321 | 10648 | 8541 | 5916 | 6009 | | | |
| 2,2,3-TMP | 110305 | 103513 | 61392 | 44890 | 40051 | 29055 | 20325 | 14082 | 10989 | 9579 | | | | | |
| 2,4-DMHx | 15206 | 16820 | 62294 | 50833 | 48573 | 30761 | 19566 | 12955 | | 6447 | 8465 | 10246 | 10106 | 7821 | 7766 |
| 2,3,4-TMP | 195378 | 211384 | 233869 | 185858 | 175331 | 156148 | 131688 | 105234 | 84765 | 74671 | 35893 | 9801 | | | |
| 2,3,3-TMP | 256975 | 258366 | 265177 | 201938 | 190670 | 162007 | 137264 | 106623 | 84907 | 74409 | 30739 | 10839 | | | |
| 2,3-DMHx | 89164 | 94776 | 109726 | 93281 | 93251 | 83528 | 71178 | 55180 | 46281 | 45272 | 19719 | 9721 | | | |
| 3,4-DMHx | 78043 | 91959 | 136099 | 124899 | 139714 | 124079 | 125726 | 117642 | 109590 | 129175 | 96425 | 78339 | 69474 | 41458 | 41254 |
| 1 DMHx= | | | | | | | | | | | | | | | |
| 2 DMHx= | | | 5558 | 5023 | 15102 | 11696 | 45408 | 50933 | 54400 | 78320 | 124195 | 152253 | 165890 | 149889 | 148134 |
| 3 DMHx= | | | | | | | | | | | | | | | |
| 4 DMHx= | | | | | | | | | | | | | | | |
| 5 DMHx= | 47001 | 48867 | 54006 | 42860 | 42922 | 34313 | 32973 | 17553 | 15299 | 13997 | 6188 | 6760 | 5414 | | |
| 6 DMHx= | 5166 | 5214 | 5813 | | | | 11611 | 15108 | 15415 | 29620 | 47261 | 71039 | 73348 | 59610 | 65977 |
| **C9+** | 264972 | 385665 | 372856 | 316442 | 347931 | 487177 | 671341 | 344535 | 273810 | 484829 | 464491 | 347066 | 189377 | 100001 | 114849 |
| **C5+** | 1730795 | 1903503 | 1977908 | 1566855 | 1458945 | 1417637 | 1495671 | 1017836 | 843562 | 1066935 | 876243 | 711807 | 513609 | 358779 | 377980 |
| Tot Peak Area | 43570915 | 49255983 | 51064808 | 41480975 | 44762845 | 44106157 | 46909211 | 45335816 | 40208102 | 45157075 | 45864183 | 47713067 | 47825409 | 44061139 | 35320140 |
| ***Feed Analysis*** | | Inj 1 | Inj 2 | Inj 3 | Inj 4 | Inj 5 | Avg | Mass % | | | | | | | |
| C3 | | 20515 | 18587 | 17803 | 18088 | 18124 | 18623 | 0 76 | | | | | | | |
| i-C4 | | 2487226 | 2217021 | 2107785 | 2141222 | 2166248 | 2223900 | 91 13 | | Avg Mass I/O Ratio | | 15 49 | | | |
| 1-C4= | | 159254 | 143282 | 136690 | 138674 | 139738 | 143528 | 5 88 | | Avg Molar I/O Ratio | | **14.954** | | | |
| n-C4 | | 60149 | 54007 | 51501 | 52540 | 52910 | 54221 | 2 22 | | | | | | | |
| **I/O Mass Ratio** | | 15 618 | 15 473 | 15 420 | 15 441 | 15 502 | 15 491 | | | | | | | | |

Run F68EMT
(EMT, Tcalc=425degC, Trxn=53degC, P=382psig, I/O=14 9, butene WHSV=2 06h-1, mcat=2 78g)

| Samp t [min] | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 21 | 24 | 29 | 39 | 69 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **T.O.S. [min.]** | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** | **9** | **10** | **12** | **15** | **20** | **30** | **60** |
| 1-C4= Disapp [%] | 86 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| t-2-C4= Prod [%] | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 10 | 20 | 28 | 33 | 37 | 42 |
| c-2-C4= Prod [%] | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 7 | 12 | 14 | 18 | 24 |
| **Butene Disapp. [%]** | **86** | **100** | **100** | **100** | **100** | **100** | **100** | **100** | **100** | **90** | **73** | **60** | **53** | **45** | **34** |
| n-Butane Change [%] | 7 | 7 | 27 | 6 | 8 | 7 | 7 | 6 | 5 | 4 | 4 | 2 | 2 | 2 | 4 |
| | | | | | | | | | | | | | | | |
| ***C5+ Product Analysis [mass %]*** | | | | | | | | | | | | | | | |
| C5-C7 | 36 | 24 | 22 | 23 | 23 | 20 | 21 | 18 | 12 | 8 | 6 | 3 | 1 | 0 | 0 |
| **C8** | **53** | **58** | **62** | **60** | **61** | **58** | **59** | **56** | **63** | **47** | **44** | **39** | **43** | **51** | **62** |
| C9+ | 11 | 17 | 15 | 16 | 16 | 25 | 21 | 26 | 35 | 45 | 50 | 58 | 56 | 49 | 38 |
| | | | | | | | | | | | | | | | |
| ***C8 Distribution [mass %]*** | | | | | | | | | | | | | | | |
| **TMP** | **84** | **79** | **75** | **74** | **72** | **68** | **69** | **68** | **64** | **59** | **42** | **27** | **10** | **7** | **0** |
| DMH | 13 | 15 | 18 | 20 | 21 | 26 | 25 | 27 | 31 | 36 | 41 | 40 | 38 | 28 | 24 |
| C8= | 2 | 5 | 6 | 6 | 6 | 6 | 6 | 5 | 5 | 5 | 17 | 33 | 52 | 65 | 76 |
| | | | | | | | | | | | | | | | |
| ***TMP Isomer Distribution*** | | | | | | | | | | | | | | | |
| **2,2,4-TMP** | **40** | **36** | **36** | **37** | **36** | **35** | **32** | **28** | **25** | **23** | **25** | **28** | **30** | **30** | **0** |
| 2,2,3-TMP | 18 | 18 | 17 | 16 | 15 | 8 | 6 | 6 | 6 | 4 | 5 | 6 | 0 | 0 | 0 |
| 2,3,4-TMP | 15 | 17 | 18 | 18 | 20 | 25 | 29 | 31 | 34 | 36 | 34 | 35 | 31 | 31 | 0 |
| 2,3,3-TMP | 26 | 29 | 29 | 29 | 29 | 32 | 34 | 35 | 36 | 36 | 36 | 31 | 38 | 38 | 0 |
| | | | | | | | | | | | | | | | |
| ***Indicators [mass fraction]*** | | | | | | | | | | | | | | | |
| **TMP** | **6.29** | **5.15** | **4.08** | **3.76** | **3.37** | **2.61** | **2.78** | **2.51** | **2.06** | **1.64** | **1.01** | **0.68** | **0.26** | **0.26** | **0.00** |
| **DMH** | | | | | | | | | | | | | | | |
| TMP+DMH | 4 42 | 2 66 | 3 07 | 2 84 | 2 86 | 1 86 | 2 30 | 1 85 | 1 33 | 0 96 | 0 64 | 0 37 | 0 26 | 0 22 | 0 17 |
| C8= + C9+ | | | | | | | | | | | | | | | |
| (2,2,3-+2,2,4-TMP) | 1 42 | 1 19 | 1 14 | 1 13 | 1 04 | 0 76 | 0 60 | 0 52 | 0 44 | 0 39 | 0 43 | 0 52 | 0 44 | 0 44 | 0 00 |
| (2,3,4-+2,3,3-TMP) | | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | | |
| ***DMH Isomer Distribution*** | | | | | | | | | | | | | | | |
| 2,5-DMH | 18 | 16 | 13 | 13 | 12 | 9 | 6 | 7 | 5 | 3 | 0 | 4 | 4 | 0 | 0 |
| 2,4-DMH | 12 | 10 | 8 | 9 | 8 | 22 | 18 | 19 | 14 | 6 | 5 | 5 | 7 | 11 | 14 |
| 2,3-DMH | 50 | 55 | 46 | 46 | 43 | 35 | 36 | 32 | 30 | 29 | 24 | 10 | 16 | 7 | 0 |
| 3,4-DMH | 21 | 19 | 33 | 33 | 38 | 34 | 39 | 41 | 51 | 62 | 71 | 81 | 72 | 82 | 86 |

Run F68EMT
(EMT, Tcalc=425degC, Trxn=53degC, P=382psig, I/O=14 9, butene WHSV=2 06h-1, mcat=2 78g)

| TOS [min] | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 12 | 15 | 20 | 30 | 60 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Propane | 332500 | 334940 | 156820 | 373980 | 333380 | 374100 | 364860 | 379940 | 378060 | 330260 | 371140 | 372680 | 383380 | 383620 | 366040 |
| Isobutane | 47510600 | 42407280 | 18748020 | 43932620 | 39162840 | 43458580 | 42227480 | 44392280 | 44607320 | 39407460 | 44220980 | 44836920 | 46209620 | 46297440 | 44225800 |
| 1-butene | 406440 | | | | | | | | | | | | | | |
| n-butane | 1214880 | 1104120 | 627260 | 1137520 | 1022260 | 1128580 | 1090580 | 1135360 | 1130840 | 990380 | 1097580 | 1094940 | 1127480 | 1137480 | 1097860 |
| t-2-butene | | | | | | | | | | 246260 | 557220 | 803700 | 948660 | 1084420 | 1179140 |
| c-2-butene | | | | | | | | | | | 192940 | 339480 | 410080 | 517900 | 659100 |
| | | | | | | | | | | | | | | | |
| **C6-C7** | **466914** | **512891** | **570654** | **530993** | **437806** | **439297** | **399626** | **364242** | **222496** | **110668** | **69884** | **33752** | **6511** | **0** | **0** |
| C5 | 190580 | 189440 | 178340 | 190280 | 157480 | 153680 | 140020 | 124020 | 35692 | | | | | | |
| 2,3-DMB | 76875 | 81903 | 96315 | 83210 | 68226 | 68974 | 62670 | 57009 | 41764 | 24941 | 14076 | 7992 | | | |
| 2,2-DMP | 25247 | 23883 | 33780 | 29608 | 24487 | 24018 | 21571 | 19369 | 14814 | 9493 | 6199 | | | | |
| 3-MP | 32556 | 36541 | 43794 | 39330 | 33187 | 33998 | 31563 | 30545 | 25978 | 18959 | 14042 | 9213 | 6511 | | |
| 2,4-DMP | 71614 | 85797 | 101362 | 84113 | 67336 | 67886 | 60226 | 53762 | 38679 | 21828 | 12245 | 6907 | | | |
| 2,2,3-TMB | 6880 | 7860 | 9961 | 9060 | 7323 | 7891 | 7429 | 7121 | 5651 | | | | | | |
| 2-MHx | 8722 | 12131 | 14813 | 13277 | 10916 | 10690 | 9267 | 8502 | 6680 | | | | | | |
| 2,3-DMP | 44704 | 61429 | 74923 | 66615 | 55229 | 58478 | 54221 | 51667 | 42626 | 27226 | 17036 | 9640 | | | |
| 3-MHx | 9736 | 13907 | 17366 | 15500 | 13621 | 13682 | 12858 | 12247 | 10611 | 8221 | 6286 | | | | |
| | | | | | | | | | | | | | | | |
| **C8** | **686281** | **1215069** | **1584391** | **1362646** | **1143647** | **1230323** | **1136349** | **1127112** | **970292** | **641666** | **474494** | **377666** | **313411** | **347969** | **298696** |
| **2,2,4-TMP** | **233276** | **349078** | **432767** | **370636** | **296917** | **293323** | **248808** | **214141** | **164368** | **89064** | **60025** | **28539** | **9444** | **7291** | |
| 2,5-DMHx | 16511 | 29638 | 38601 | 34449 | 28537 | 28866 | 17882 | 21593 | 16138 | 7735 | | 5415 | 5169 | | |
| 2,2,3-TMP | 106355 | 174770 | 203465 | 165670 | 125644 | 69272 | 46352 | 48232 | 36044 | 16893 | 9402 | 6269 | | | |
| 2,4-DMHx | 10777 | 19467 | 24463 | 22941 | 19271 | 70428 | 52010 | 58738 | 40831 | 14199 | 9851 | 7290 | 8543 | 10237 | 10205 |
| 2,3,4-TMP | 86764 | 161416 | 214309 | 181654 | 164540 | 206399 | 225707 | 239723 | 208432 | 136688 | 67411 | 35771 | 9718 | 7524 | |
| 2,3,3-TMP | 151914 | 277452 | 344892 | 293573 | 240677 | 269475 | 268540 | 264731 | 222986 | 137109 | 71725 | 31642 | 11875 | 9110 | |
| 2,3-DMHx | 45737 | 102823 | 134112 | 122521 | 105509 | 111956 | 102206 | 99155 | 90184 | 66616 | 47556 | 15257 | 19530 | 6860 | |
| 3,4-DMHx | 18957 | 35098 | 95420 | 89040 | 92329 | 110461 | 111782 | 126610 | 155198 | 143250 | 139361 | 122606 | 86852 | 79227 | 61610 |
| 1 DMHx= | | | | | | | | | | | | | | | |
| 2 DMHx= | | | 6024 | 5372 | | | | | 5197 | 7737 | 51393 | 96910 | 122516 | 153976 | 171661 |
| 3 DMHx= | | | | | | | | | | | | | | | |
| 4 DMHx= | | | | | | | | | | | 6484 | | | | |
| 5 DMHx= | 14990 | 59570 | 83549 | 70225 | 64172 | 64246 | 57308 | 48881 | 40914 | 22385 | 8052 | 6369 | 6513 | 6160 | |
| 6 DMHx= | | 5757 | 6599 | 6265 | 6051 | 5897 | 5754 | 5308 | | | 13214 | 21598 | 33251 | 67604 | 55119 |
| | | | | | | | | | | | | | | | |
| **C9+** | 136530 | 366281 | 387939 | 369363 | 305540 | 554670 | 404595 | 525203 | 646412 | 607306 | 534543 | 561003 | 413057 | 329339 | 183929 |
| | | | | | | | | | | | | | | | |
| **C5+** | 1288725 | 2094241 | 2542984 | 2262902 | 1886992 | 2224290 | 1940769 | 2016557 | 1839199 | 1359640 | 1078921 | 972421 | 732979 | 677328 | 482524 |
| | | | | | | | | | | | | | | | |
| Tot Peak Area | 50753145 | 45940581 | 22075084 | 47707022 | 42405472 | 47185550 | 45623689 | 47924137 | 47955419 | 42334000 | 47325841 | 48080661 | 49402119 | 49580288 | 47351364 |
| | | | | | | | | | | | | | | | |
| ***Feed Analysis*** | | Inj 1 | Inj 2 | Inj 3 | Inj 4 | Inj 5 | Avg | Mass % | | | | | | | |
| C3 | | 19091 | 17175 | 16540 | 16825 | 17392 | 17405 | 0 77 | | Avg Mass I/O Ratio | | 15 48 | | | |
| i-C4 | | 2267269 | 2035835 | 1959414 | 1999852 | 2084019 | 2069278 | 91 11 | | Avg Molar I/O Ratio | | 14 94 | | | |
| 1-C4= | | 145659 | 131935 | 127163 | 129456 | 134067 | 133656 | 5 88 | | | | | | | |
| n-C4 | | 55368 | 50187 | 48339 | 49319 | 51165 | 50876 | 2 24 | | | | | | | |
| **I/O Mass Ratio** | | 15 566 | 15 431 | 15 409 | 15 448 | 15 545 | 15 480 | | | | | | | | |

## A4.3 SENSITIVITY ANALYSIS

**Table A4.6:** Experimental Summary for Replicated Experiments

| Catalyst | Replicated Runs |
|---|---|
| Recalcined 0.5%Pt/EMT | F48Pt5EMTr<br>F50Pt5EMTr<br>F60Pt5EMTr |
| Recalcined 0.1%Pt/EMT | F63Pt1EMTr<br>F45Pt1EMTr |
| Fresh 0.5%Pt/Y | F44Pt5Y<br>F56Pt5Y |
| Fresh EMT | F66EMT<br>F68EMT |

Sensitivity Analysis - Useful Catalyst Lifetime, Yield*, Mass Liquid*, SA Spent Catalyst*
(where * denotes from 2 to 7 min TOS)

| | | SD | | | | |
|---|---|---|---|---|---|---|
| **Useful Catalyst Lifetime** | 11.8 | **0.9** | 12.8 | 11 5 | 11 | F48Pt5EMTr, F50Pt5EMTr, F60Pt5EMTr |
| **[min]** | 11.7 | **0.8** | 11.1 | 12 2 | | F63Pt1EMTr, F45Pt1EMTr |
| | 8.0 | **0.5** | 7.9 | 8 3 | | F44Pt5Y, F56Pt5Y |
| | 10.6 | **0.6** | 11.1 | 10.2 | | F66EMT, F68Pt5AEMT |
| | | **0.7** | | | | |
| **Yield** | 0.095128 | **0.01936** | 0.109488 | 0.080768 | 0.0726484 | F48Pt5EMTr, F50Pt5EMTr, F60Pt5EMTr |
| **[gC5+/gcat/gC4=fed]** | 0.064615 | **0.0193** | 0.064615 | 0.09197 | | F63Pt1EMTr, F45Pt1EMTr |
| | 0.062930 | **0.0179** | 0.0503001 | 0.0755603 | | F44Pt5Y, F56Pt5Y |
| | 0.082852 | **0.0057** | 0.0788383 | 0.086866 | | F66EMT, F68EMT |
| | | **0.01556** | | | | |
| **Mass Liquid** | 1.975000 | **0.39145** | 2.34 | 1.61 | 1.73 | F48Pt5EMTr, F50Pt5EMTr, F60Pt5EMTr |
| **[g]** | 1.710000 | **0.1838** | 1.58 | 1 84 | | F63Pt1EMTr, F45Pt1EMTr |
| | 1.375000 | **0.5020** | 1.02 | 1 73 | | F44Pt5Y, F56Pt5Y |
| | 1.725000 | **0.0919** | 1.79 | 1 66 | | F66EMT, F68Pt5AEMT |
| | | **0.29232** | | | | |
| **SA Spent Catalyst** | 246.0 | **67.9** | 294 | 198 | | F48Pt5EMTr, F60Pt5EMTr |
| **[m2/g]** | 242.5 | **16.3** | 231 | 254 | | F63Pt1EMTr, F45Pt1EMTr |
| | 279.5 | **0.7** | 280 | 279 | | F44Pt5Y, F58Pt5Y** samples lost due to malfunctioning multiposition valve |
| | | **28.3** | | | | |

Sensitivity Analysis - (C5-C7) in C5+ [%]
(2 to 7 min TOS)

| TOS [min] | SD | F50Pt5EMTr | F60Pt5EMTr | F48Pt5EMTr | SD | F63Pt1EMTr | F45Pt1EMTr | SD | F44Pt5Y | F56Pt5Y | SD | F66EMT | F68EMT |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 9.3 | 29 | 24 | 42 | 7.1 | 29 | 39 | 5.7 | 25 | 33 | 1.4 | 34 | 36 |
| 2 | 4.2 | 27 | 21 | 29 | 0.0 | 26 | 26 | 2.1 | 30 | 27 | 1.4 | 22 | 24 |
| 3 | 4.0 | 24 | 20 | 28 | 1.4 | 25 | 27 | 0.0 | 27 | 27 | 0.7 | 21 | 22 |
| 4 | 2.0 | 25 | 23 | 27 | 1.4 | 24 | 26 | 0.0 | 27 | 27 | 1.4 | 21 | 23 |
| 5 | 3.1 | 26 | 22 | 28 | 2.8 | 22 | 26 | 0.0 | 26 | 26 | 0.7 | 22 | 23 |
| 6 | 4.6 | 25 | 22 | 16 | 3.5 | 21 | 26 | 6.4 | 27 | 18 | 0.7 | 21 | 20 |
| 7 | 4.9 | 29 | 21 | 20 | 4.9 | 19 | 26 | 4.9 | 16 | 23 | 0.7 | 20 | 21 |
| 8 | 6.1 | 25 | 21 | 13 | 7.8 | 16 | 27 | 5.7 | 14 | 22 | 1.4 | 20 | 18 |
| 9 | 3.6 | 16 | 18 | 11 | 4.9 | 10 | 17 | 0.7 | 11 | 12 | 2.8 | 16 | 12 |
| 10 | 1.0 | 12 | 10 | 11 | 9.9 | 7 | 21 | 0.0 | 6 | 6 | 5.7 | 16 | 8 |
| 12 | 3.1 | 10 | 8 | 4 | 5.7 | 6 | 14 | 0.7 | 0 | 1 | 1.4 | 8 | 6 |
| 15 | 3.6 | 7 | 2 | 0 | 5.7 | 19 | 11 | 1.4 | 0 | 2 | 2.1 | 6 | 3 |
| 20 | 1.2 | 2 | 0 | 0 | 0.7 | 1 | 2 | 0.0 | 0 | 0 | 2.1 | 4 | 1 |
| 30 | 0.0 | 0 | 0 | 0 | 0.0 | 0 | 0 | 0.0 | 0 | 0 | 0.0 | 0 | 0 |
| 60 | 0.0 | 0 | 0 | 0 | 0.0 | 0 | 0 | 0.0 | 0 | 0 | 0.0 | 0 | 0 |
| SD | 3.8 | | | | 2.4 | | | | 2.2 | | | 0.9 | |
| Average SD | | 2.3 | | | | | | | | | | | |

Sensitivity Analysis - C8 in C5+ [%]
(2 to 7 min TOS)

| TOS [min] | SD | F50Pt5EMTr | F60Pt5EMTr | F48Pt5EMTr | SD | F63Pt1EMTr | F45Pt1EMTr | SD | F44Pt5Y | F56Pt5Y | SD | F66EMT | F68EMT |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.6 | 57 | 57 | 58 | 2.8 | 64 | 60 | 5.7 | 68 | 60 | 0.0 | 53 | 53 |
| 2 | 4.6 | 57 | 54 | 63 | 1.4 | 59 | 57 | 0.7 | 57 | 56 | 0.7 | 57 | 58 |
| 3 | 9.5 | 55 | 44 | 63 | 0.0 | 62 | 62 | 1.4 | 54 | 56 | 3.5 | 57 | 62 |
| 4 | 4.2 | 57 | 55 | 63 | 0.0 | 63 | 63 | 0.0 | 56 | 56 | 2.8 | 56 | 60 |
| 5 | 3.2 | 59 | 53 | 58 | 0.7 | 63 | 62 | 1.4 | 54 | 56 | 0.7 | 60 | 61 |
| 6 | 5.5 | 60 | 55 | 66 | 0.7 | 63 | 62 | 4.9 | 51 | 58 | 5.7 | 63 | 55 |
| 7 | 1.2 | 58 | 56 | 56 | 0.7 | 61 | 62 | 4.9 | 62 | 55 | 1.4 | 57 | 59 |
| 8 | 3.2 | 62 | 56 | 57 | 2.1 | 55 | 58 | 2.1 | 58 | 55 | 3.5 | 61 | 56 |
| 9 | 7.6 | 67 | 52 | 57 | 11.3 | 52 | 68 | 7.8 | 46 | 57 | 2.8 | 57 | 53 |
| 10 | 3.8 | 55 | 49 | 56 | 7.8 | 47 | 58 | 4.9 | 46 | 53 | 5.7 | 55 | 47 |
| 12 | 7.5 | 53 | 59 | 44 | 12.0 | 48 | 65 | 2.1 | 52 | 49 | 2.8 | 48 | 44 |
| 15 | 2.3 | 51 | 55 | 55 | 17.0 | 39 | 63 | 4.2 | 62 | 56 | 4.9 | 46 | 39 |
| 20 | 12.3 | 62 | 38 | 55 | 4.2 | 56 | 50 | 11.3 | 74 | 58 | 6.4 | 52 | 43 |
| 30 | 6.1 | 50 | 46 | 58 | 5.7 | 62 | 54 | 0.7 | 63 | 62 | 6.4 | 60 | 51 |
| 60 | 4.7 | 62 | 60 | 69 | 1.4 | 80 | 82 | 1.4 | 69 | 71 | 0.0 | 62 | 62 |
| SD | 4.7 | | | | 0.6 | | | 2.2 | | | 2.5 | | |
| Average SD | | 2.5 | | | | | | | | | | | |

Sensitivity Analysis - C9+ in C5+ [%]
(2 to 7 min TOS)

| TOS [min] | SD | F50Pt5EMTr | F60Pt5EMTr | F48Pt5EMTr | SD | F63Pt1EMTr | F45Pt1EMTr | SD | F44Pt5Y | F56Pt5Y | SD | F66EMT | F68EMT |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 9.8 | 14 | 19 | 0 | 3.5 | 7 | 2 | 0.7 | 7 | 8 | 1.4 | 13 | 11 |
| 2 | 8.5 | 16 | 25 | 8 | 1.4 | 15 | 17 | 2.8 | 13 | 17 | 2.8 | 21 | 17 |
| 3 | 13.5 | 21 | 36 | 9 | 2.1 | 13 | 10 | 2.1 | 19 | 16 | 4.9 | 22 | 15 |
| 4 | 6.1 | 18 | 22 | 10 | 1.4 | 13 | 11 | 0.7 | 18 | 17 | 4.9 | 23 | 16 |
| 5 | 6.1 | 15 | 25 | 14 | 0.7 | 14 | 13 | 1.4 | 20 | 18 | 1.4 | 18 | 16 |
| 6 | 4.0 | 15 | 23 | 18 | 3.5 | 17 | 12 | 2.1 | 22 | 25 | 5.7 | 17 | 25 |
| 7 | 6.1 | 13 | 23 | 24 | 5.7 | 20 | 12 | 0.0 | 22 | 22 | 1.4 | 23 | 21 |
| 8 | 8.5 | 13 | 21 | 30 | 9.9 | 29 | 15 | 3.5 | 28 | 23 | 4.9 | 19 | 26 |
| 9 | 8.4 | 17 | 31 | 32 | 17.0 | 39 | 15 | 8.5 | 43 | 31 | 4.9 | 28 | 35 |
| 10 | 4.6 | 33 | 41 | 33 | 17.0 | 45 | 21 | 4.2 | 48 | 42 | 11.3 | 29 | 45 |
| 12 | 10.7 | 34 | 33 | 52 | 17.7 | 46 | 21 | 1.4 | 48 | 50 | 3.5 | 45 | 50 |
| 15 | 1.5 | 42 | 43 | 45 | 11.3 | 42 | 26 | 2.8 | 38 | 42 | 7.8 | 47 | 58 |
| 20 | 13.2 | 36 | 62 | 45 | 3.5 | 43 | 48 | 11.3 | 26 | 42 | 8.5 | 44 | 56 |
| 30 | 6.1 | 50 | 54 | 42 | 5.7 | 38 | 46 | 0.7 | 37 | 38 | 6.4 | 40 | 49 |
| 60 | 4.7 | 38 | 40 | 31 | | | 18 | 1.4 | 31 | 29 | 0.0 | 38 | 38 |
| SD | 7.4 | | | | 2.5 | | | 1.5 | | | 3.5 | | |
| Average SD | | 3.7 | | | | | | | | | | | |

Sensitivity Analyisis - TMP in C8 [%]
(2 to 7 min TOS)

| TOS [min] | SD | F50Pt5EMTr | F60Pt5EMTr | F48Pt5EMTr | SD | F63Pt1EMTr | F45Pt1EMTr | SD | F44Pt5Y | F56Pt5Y | SD | F66EMT | F68EMT |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 10.4 | 86 | 71 | 91 | 1.4 | 82 | 84 | 6.4 | 80 | 71 | 3.5 | 79 | 84 |
| 2 | 2.1 | 80 | 77 | 81 | 0.0 | 80 | 80 | 4.9 | 76 | 69 | 4.2 | 73 | 79 |
| 3 | 1.2 | 77 | 77 | 79 | 0.7 | 80 | 79 | 5.7 | 76 | 68 | 2.1 | 72 | 75 |
| 4 | 2.5 | 77 | 74 | 79 | 0.7 | 77 | 78 | 7.1 | 76 | 66 | 1.4 | 72 | 74 |
| 5 | 1.5 | 77 | 74 | 76 | 1.4 | 75 | 77 | 7.8 | 75 | 64 | 0.7 | 73 | 72 |
| 6 | 5.6 | 78 | 67 | 71 | 4.9 | 69 | 76 | 8.5 | 73 | 61 | 1.4 | 70 | 68 |
| 7 | 6.1 | 78 | 66 | 70 | 5.7 | 68 | 76 | 2.8 | 66 | 62 | 0.7 | 70 | 69 |
| 8 | 4.0 | 74 | 66 | 70 | 8.5 | 64 | 76 | 1.4 | 59 | 61 | 1.4 | 70 | 68 |
| 9 | 3.8 | 72 | 65 | 66 | 4.9 | 62 | 69 | 2.1 | 56 | 53 | 2.8 | 68 | 64 |
| 10 | 4.9 | 70 | 62 | 61 | 10.6 | 52 | 67 | 6.4 | 22 | 31 | 4.9 | 66 | 59 |
| 12 | 18.1 | 65 | 44 | 29 | 23.3 | 37 | 70 | 4.9 | 0 | 7 | 12.0 | 59 | 42 |
| 15 | 26.1 | 50 | 7 | 3 | 29.7 | 19 | 61 | 0.0 | 0 | 0 | 16.3 | 50 | 27 |
| 20 | 13.9 | 24 | 0 | 0 | 5.7 | 8 | 16 | 0.0 | 0 | 0 | 13.4 | 29 | 10 |
| 30 | 1.7 | 3 | 0 | 0 | 3.5 | 5 | 0 | 0.0 | 0 | 0 | 0.0 | 7 | 7 |
| 60 | 0.0 | 0 | 0 | 0 | | 0 | 0 | 0.0 | 0 | 0 | 0.0 | 0 | 0 |
| SD | 3.2 | | | | 2.2 | | | 6.1 | | | 1.8 | | |

Sensitivity Analysis - DMH in C8 [%]
(2 to 7 min TOS)

| TOS [min] | SD | F50Pt5EMTr | F60Pt5EMTr | F48Pt5EMTr | SD | F63Pt1EMTr | F45Pt1EMTr | SD | F44Pt5Y | F56Pt5Y | SD | F66EMT | F68EMT |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 6.2 | 10 | 19 | 7 | 1.4 | 14 | 12 | 4.2 | 18 | 24 | 2.1 | 16 | 13 |
| 2 | 1.2 | 14 | 16 | 14 | 0.7 | 15 | 14 | 4.2 | 20 | 26 | 3.5 | 20 | 15 |
| 3 | 1.0 | 17 | 16 | 15 | 0.0 | 15 | 15 | 4.2 | 21 | 27 | 2.1 | 21 | 18 |
| 4 | 1.5 | 17 | 19 | 16 | 0.7 | 18 | 17 | 4.9 | 22 | 29 | 0.7 | 21 | 20 |
| 5 | 1.0 | 17 | 19 | 18 | 1.4 | 20 | 18 | 7.1 | 20 | 30 | 0.7 | 20 | 21 |
| 6 | 4.7 | 17 | 26 | 24 | 4.2 | 25 | 19 | 7.1 | 23 | 33 | 0.7 | 25 | 26 |
| 7 | 5.3 | 17 | 27 | 25 | 6.4 | 27 | 18 | 1.4 | 31 | 33 | 0.7 | 24 | 25 |
| 8 | 3.1 | 22 | 28 | 26 | 9.2 | 31 | 18 | 2.1 | 37 | 34 | 1.4 | 25 | 27 |
| 9 | 4.4 | 22 | 29 | 30 | 4.9 | 33 | 26 | 4.2 | 36 | 42 | 2.8 | 27 | 31 |
| 10 | 5.5 | 24 | 33 | 34 | 5.7 | 35 | 27 | 1.4 | 46 | 48 | 4.9 | 29 | 36 |
| 12 | 13.0 | 29 | 42 | 55 | 9.2 | 38 | 25 | 7.8 | 28 | 39 | 6.4 | 32 | 41 |
| 15 | 4.2 | 33 | 41 | 35 | 10.6 | 39 | 24 | 2.1 | 29 | 32 | 4.9 | 33 | 40 |
| 20 | 3.5 | 29 | 33 | 26 | 4.9 | 29 | 36 | 2.8 | 23 | 27 | 5.7 | 30 | 38 |
| 30 | 6.1 | 37 | 25 | 29 | 2.1 | 26 | 29 | 2.1 | 21 | 24 | 0.0 | 28 | 28 |
| 60 | 3.1 | 24 | 22 | 18 | | 0 | 17 | 4.2 | 15 | 21 | 0.7 | 23 | 24 |
| SD | 2.4 | | | | 2.2 | | | 4.8 | | | 1.4 | | |

Sensitivity Analysis - C8= in C8 [%]
(2 to 7 min TOS)

| TOS [min] | SD | F50Pt5EMTr | F60Pt5EMTr | F48Pt5EMTr | SD | F63Pt1EMTr | F45Pt1EMTr | SD | F44Pt5Y | F56Pt5Y | SD | F66EMT | F68EMT |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 4.6 | 3 | 11 | 3 | 0.7 | 4 | 3 | 0.7 | 3 | 4 | 2.1 | 5 | 2 |
| 2 | 1.0 | 6 | 7 | 5 | 0.7 | 5 | 6 | 0.7 | 4 | 5 | 1.4 | 7 | 5 |
| 3 | 0.6 | 6 | 7 | 6 | 0.0 | 5 | 5 | 1.4 | 3 | 5 | 0.7 | 7 | 6 |
| 4 | 1.0 | 6 | 7 | 5 | 0.0 | 6 | 6 | 2.1 | 2 | 5 | 0.7 | 7 | 6 |
| 5 | 0.6 | 6 | 7 | 6 | 0.7 | 6 | 5 | 0.0 | 5 | 5 | 0.0 | 6 | 6 |
| 6 | 1.2 | 5 | 7 | 5 | 0.0 | 6 | 6 | 1.4 | 4 | 6 | 0.0 | 6 | 6 |
| 7 | 1.5 | 4 | 7 | 5 | 0.7 | 5 | 6 | 1.4 | 3 | 5 | 0.7 | 5 | 6 |
| 8 | 1.2 | 4 | 6 | 4 | 0.0 | 6 | 6 | 0.7 | 4 | 5 | 0.0 | 5 | 5 |
| 9 | 1.0 | 5 | 6 | 4 | 0.0 | 5 | 5 | 2.1 | 8 | 5 | 0.0 | 5 | 5 |
| 10 | 1.0 | 6 | 5 | 4 | 4.9 | 13 | 6 | 7.1 | 31 | 21 | 0.0 | 5 | 5 |
| 12 | 5.5 | 6 | 15 | 16 | 14.1 | 25 | 5 | 12.7 | 72 | 54 | 6.4 | 8 | 17 |
| 15 | 23.8 | 17 | 53 | 62 | 19.1 | 42 | 15 | 2.1 | 71 | 68 | 11.3 | 17 | 33 |
| 20 | 14.0 | 47 | 67 | 74 | 10.6 | 63 | 48 | 2.8 | 77 | 73 | 7.8 | 41 | 52 |
| 30 | 7.8 | 60 | 75 | 71 | 0.7 | 70 | 71 | 2.1 | 79 | 76 | 0.0 | 65 | 65 |
| 60 | 3.1 | 76 | 78 | 82 | 0.0 | 0 | 83 | 4.2 | 85 | 79 | 0.7 | 77 | 76 |
| SD | 1.0 | | | | 0.4 | | | 1.2 | | | 0.6 | | |
| Average SD | | 0.8 | | | | | | | | | | | |

Sensitivity Analysis - 2,2,4-TMP in TMP [%]

| TOS [min] | SD | F50Pt5EMTr | F60Pt5EMTr | F48Pt5EMTr | SD | F63Pt11EMTr | F45Pt11EMTr | SD | F44Pt5Y | F56Pt5Y | SD | F66EMT | F68EMT |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 11.7 | 54 | 31 | 46 | 7.8 | 38 | 49 | 0.0 | 33 | 33 | 4.2 | 46 | 40 |
| 2 | 1.5 | 43 | 41 | 40 | 4.9 | 36 | 43 | 0.7 | 32 | 33 | 2.8 | 40 | 36 |
| 3 | 0.6 | 42 | 41 | 41 | 4.9 | 35 | 42 | 2.8 | 32 | 36 | 0.7 | 37 | 36 |
| 4 | 1.5 | 41 | 42 | 39 | 4.2 | 35 | 41 | 6.4 | 31 | 40 | 0.0 | 37 | 37 |
| 5 | 1.5 | 40 | 42 | 39 | 4.2 | 34 | 40 | 5.7 | 31 | 39 | 0.0 | 36 | 36 |
| 6 | 2.6 | 38 | 43 | 39 | 4.9 | 34 | 41 | 0.0 | 32 | 32 | 0.7 | 34 | 35 |
| 7 | 2.5 | 38 | 40 | 35 | 5.7 | 32 | 40 | 0.0 | 33 | 33 | 1.4 | 30 | 32 |
| 8 | 3.5 | 38 | 38 | 32 | 7.1 | 29 | 39 | 0.7 | 33 | 32 | 0.0 | 28 | 28 |
| 9 | 4.7 | 36 | 34 | 27 | 8.5 | 28 | 40 | 1.4 | 30 | 28 | 1.4 | 27 | 25 |
| 10 | 4.5 | 34 | 30 | 25 | 6.4 | 28 | 37 | 7.1 | 35 | 25 | 3.5 | 28 | 23 |
| 12 | 4.2 | 29 | 23 | 31 | 4.9 | 27 | 34 | 23.3 | 0 | 33 | 1.4 | 27 | 25 |
| 15 | 15.9 | 30 | 24 | 0 | 15.6 | 52 | 30 | 0.0 | 0 | 0 | 2.8 | 24 | 28 |
| 20 | 24.8 | 43 | 0 | 0 | 0.7 | 29 | 28 | 0.0 | 0 | 0 | 5.7 | 22 | 30 |
| 30 | 0.0 | 0 | 0 | 0 | 25.5 | 36 | 0 | 0.0 | 0 | 0 | 2.8 | 26 | 30 |
| 60 | 0.0 | 0 | 0 | 0 | 0.0 | 0 | 0 | 0.0 | 0 | 0 | 0.0 | 0 | 0 |
| SD | 1.7 | | | | 4.8 | | | 2.6 | | | 0.9 | | |
| Average SD | | 2.5 | | | | | | | | | | | |

Sensitivity Analysis - 2,2,3-TMP in TMP [%]

| TOS [min] | SD | F50Pt5EMTr | F60Pt5EMTr | F48Pt5EMTr | SD | F63Pt1EMTr | F45Pt1EMTr | SD | F44Pt5Y | F56Pt5Y | SD | F66EMT | F68EMT |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 3.8 | 20 | 26 | 19 | 0.7 | 20 | 19 | 1.4 | 3 | 5 | 2.1 | 21 | 18 |
| 2 | 0.6 | 23 | 23 | 22 | 3.5 | 19 | 24 | 1.4 | 3 | 5 | 0.7 | 19 | 18 |
| 3 | 4.4 | 22 | 21 | 14 | 3.5 | 17 | 22 | 0.7 | 4 | 5 | 0.0 | 17 | 17 |
| 4 | 1.0 | 19 | 20 | 18 | 4.2 | 15 | 21 | 1.4 | 3 | 5 | 0.0 | 16 | 16 |
| 5 | 1.5 | 18 | 19 | 16 | 2.8 | 14 | 18 | 1.4 | 3 | 5 | 0.0 | 15 | 15 |
| 6 | 3.6 | 16 | 11 | 9 | 7.1 | 8 | 18 | 0.7 | 4 | 5 | 0.0 | 8 | 8 |
| 7 | 2.6 | 13 | 9 | 8 | 7.8 | 7 | 18 | 0.7 | 3 | 4 | 1.4 | 8 | 6 |
| 8 | 2.1 | 9 | 8 | 5 | 6.4 | 7 | 16 | 0.0 | 3 | 3 | 0.7 | 7 | 6 |
| 9 | 1.5 | 8 | 7 | 5 | 2.8 | 6 | 10 | 2.1 | 0 | 3 | 0.7 | 7 | 6 |
| 10 | 1.5 | 7 | 5 | 4 | 2.8 | 5 | 9 | 4.9 | 0 | 7 | 2.1 | 7 | 4 |
| 12 | 3.5 | 7 | 4 | 0 | 1.4 | 5 | 7 | 0.0 | 0 | 0 | 1.4 | 7 | 5 |
| 15 | 3.5 | 6 | 0 | 0 | 0.7 | 6 | 5 | 0.0 | 0 | 0 | 0.7 | 5 | 6 |
| 20 | 0.0 | 0 | 0 | 0 | 0.0 | 0 | 0 | 0.0 | 0 | 0 | 4.2 | 6 | 0 |
| 30 | 0.0 | 0 | 0 | 0 | 0.0 | 0 | 0 | 0.0 | 0 | 0 | 0.0 | 0 | 0 |
| 60 | 0.0 | 0 | 0 | 0 | 0.0 | 0 | 0 | 0.0 | 0 | 0 | 0.0 | 0 | 0 |
| SD | 2.3 | | | | 4.8 | | | 1.1 | | | 0.4 | | |
| Average SD | | 2.1 | | | | | | | | | | | |

Sensitivity Analysis - 2,3,4-TMP in TMP [%]
(2 to 7 min TOS)

| TOS [min] | SD | F50Pt5EMTr | F60Pt5EMTr | F48Pt5EMTr | SD | F63Pt1EMTr | F45Pt1EMTr | SD | F44Pt5Y | F56Pt5Y | SD | F66EMT | F68EMT |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 4.5 | 6 | 15 | 10 | 2.8 | 15 | 11 | 0.7 | 29 | 30 | 2.1 | 12 | 15 |
| 2 | 0.6 | 12 | 12 | 13 | 2.8 | 16 | 12 | 1.4 | 32 | 30 | 0.7 | 16 | 17 |
| 3 | 2.1 | 12 | 13 | 16 | 3.5 | 18 | 13 | 2.1 | 30 | 27 | 0.0 | 18 | 18 |
| 4 | 1.2 | 14 | 14 | 16 | 4.2 | 20 | 14 | 5.7 | 32 | 24 | 0.7 | 19 | 18 |
| 5 | 1.5 | 15 | 14 | 17 | 4.2 | 22 | 16 | 4.9 | 32 | 25 | 0.7 | 21 | 20 |
| 6 | 2.3 | 18 | 18 | 22 | 6.4 | 25 | 16 | 1.4 | 31 | 29 | 0.7 | 26 | 25 |
| 7 | 2.6 | 20 | 21 | 25 | 8.5 | 28 | 16 | 0.0 | 30 | 30 | 0.0 | 29 | 29 |
| 8 | 4.0 | 23 | 23 | 30 | 9.9 | 31 | 17 | 0.0 | 32 | 32 | 0.0 | 31 | 31 |
| 9 | 4.2 | 25 | 27 | 33 | 8.5 | 33 | 21 | 1.4 | 35 | 37 | 2.1 | 31 | 34 |
| 10 | 3.5 | 27 | 31 | 34 | 7.1 | 33 | 23 | 0.7 | 39 | 38 | 4.2 | 30 | 36 |
| 12 | 3.1 | 31 | 37 | 35 | 4.9 | 33 | 26 | 23.3 | 0 | 33 | 2.1 | 31 | 34 |
| 15 | 19.2 | 31 | 35 | 0 | 9.9 | 16 | 30 | 0.0 | 0 | 0 | 0.0 | 35 | 35 |
| 20 | 15.6 | 27 | 0 | 0 | 0.0 | 34 | 34 | 0.0 | 0 | 0 | 3.5 | 36 | 31 |
| 30 | 0.0 | 0 | 0 | 0 | 21.2 | 30 | 0 | 0.0 | 0 | 0 | 2.8 | 35 | 31 |
| 60 | 0.0 | 0 | 0 | 0 | 0.0 | 0 | 0 | 0.0 | 0 | 0 | 0.0 | 0 | 0 |
| SD | 1.7 | | | | 4.9 | | | 2.6 | | | 0.5 | | |
| Average SD | | 2.4 | | | | | | | | | | | |

Sensitivity Analysis - 2,3,3-TMP in TMP [%]
(2 to 7 min)

| TOS [min] | SD | F50Pt5EMTr | F60Pt5EMTr | F48Pt5EMTr | SD | F63Pt1EMTr | F45Pt1EMTr | SD | F44Pt5Y | F56Pt5Y | SD | F66EMT | F68EMT |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 3.5 | 21 | 28 | 25 | 3.5 | 26 | 21 | 2.1 | 35 | 32 | 3.5 | 21 | 26 |
| 2 | 1.5 | 22 | 23 | 25 | 4.2 | 28 | 22 | 0.7 | 33 | 32 | 2.1 | 26 | 29 |
| 3 | 2.9 | 24 | 24 | 29 | 4.2 | 29 | 23 | 1.4 | 34 | 32 | 1.4 | 27 | 29 |
| 4 | 1.0 | 26 | 25 | 27 | 4.2 | 30 | 24 | 1.4 | 34 | 32 | 1.4 | 27 | 29 |
| 5 | 2.1 | 26 | 25 | 29 | 2.8 | 30 | 26 | 2.1 | 34 | 31 | 0.7 | 28 | 29 |
| 6 | 1.7 | 28 | 28 | 31 | 4.2 | 32 | 26 | 0.7 | 33 | 34 | 0.0 | 32 | 32 |
| 7 | 2.1 | 29 | 30 | 33 | 4.9 | 33 | 26 | 0.7 | 34 | 33 | 0.7 | 33 | 34 |
| 8 | 2.1 | 30 | 31 | 34 | 4.2 | 33 | 27 | 0.7 | 32 | 33 | 0.7 | 34 | 35 |
| 9 | 2.0 | 31 | 33 | 35 | 4.2 | 34 | 28 | 2.1 | 35 | 32 | 1.4 | 34 | 36 |
| 10 | 2.5 | 32 | 34 | 37 | 2.1 | 34 | 31 | 2.8 | 26 | 30 | 0.7 | 35 | 36 |
| 12 | 1.2 | 34 | 36 | 34 | 1.4 | 35 | 33 | 24.0 | 0 | 34 | 0.7 | 35 | 36 |
| 15 | 36.5 | 34 | 40 | 100 | 6.4 | 26 | 35 | 0.0 | 0 | 0 | 3.5 | 35 | 31 |
| 20 | 17.3 | 30 | 0 | 0 | 0.7 | 37 | 38 | 0.0 | 0 | 0 | 1.4 | 36 | 38 |
| 30 | 57.7 | 100 | 0 | 0 | 24.0 | 34 | 0 | 0.0 | 0 | 0 | 1.4 | 40 | 38 |
| 60 | 0.0 | 0 | 0 | 0 | 0.0 | 0 | 0 | 0.0 | 0 | 0 | 0.0 | 0 | 0 |
| SD | 1.9 | | | | 4.1 | | | 1.2 | | | 1.1 | | |
| Average SD | | 2.1 | | | | | | | | | | | |

Sensitivity Analysis - TMP/DMH [mass fraction]
(2 to 7 min)

| TOS [min] | SD | F50Pt5EMTr | F60Pt5EMTr | F48Pt5EMTr | SD | F63Pt1EMTr | F45Pt1EMTr | SD | F44Pt5Y | F56Pt5Y | SD | F66EMT | F68EMT |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 4.90 | 8.51 | 2.83 | 13.59 | 0.64 | 5.88 | 6.79 | 1.10 | 4.47 | 2.91 | 0.93 | 4.98 | 6.29 |
| 2 | 0.55 | 5.74 | 4.89 | 5.92 | 0.08 | 5.52 | 5.63 | 0.85 | 3.88 | 2.68 | 1.09 | 3.61 | 5.15 |
| 3 | 0.35 | 4.59 | 4.88 | 5.28 | 0.17 | 5.43 | 5.19 | 0.74 | 3.59 | 2.55 | 0.45 | 3.44 | 4.08 |
| 4 | 0.49 | 4.39 | 3.97 | 4.95 | 0.25 | 4.30 | 4.66 | 0.78 | 3.42 | 2.32 | 0.21 | 3.46 | 3.76 |
| 5 | 0.33 | 4.49 | 3.84 | 4.12 | 0.30 | 3.82 | 4.24 | 1.14 | 3.73 | 2.12 | 0.15 | 3.58 | 3.37 |
| 6 | 1.00 | 4.48 | 2.58 | 2.99 | 0.97 | 2.72 | 4.09 | 0.99 | 3.23 | 1.83 | 0.16 | 2.83 | 2.61 |
| 7 | 1.12 | 4.56 | 2.45 | 2.85 | 1.17 | 2.46 | 4.11 | 0.19 | 2.14 | 1.87 | 0.06 | 2.87 | 2.78 |
| 8 | 0.47 | 3.30 | 2.36 | 2.73 | 1.48 | 2.08 | 4.17 | 0.12 | 1.62 | 1.79 | 0.21 | 2.81 | 2.51 |
| 9 | 0.62 | 3.28 | 2.19 | 2.24 | 0.56 | 1.85 | 2.64 | 0.23 | 1.58 | 1.26 | 0.32 | 2.51 | 2.06 |
| 10 | 0.62 | 2.90 | 1.86 | 1.80 | 0.71 | 1.49 | 2.50 | 0.11 | 0.48 | 0.64 | 0.44 | 2.26 | 1.64 |
| 12 | 0.94 | 2.34 | 1.04 | 0.52 | 1.30 | 0.95 | 2.79 | 0.13 | 0.00 | 0.19 | 0.60 | 1.86 | 1.01 |
| 15 | 0.81 | 1.52 | 0.16 | 0.09 | 1.48 | 0.48 | 2.57 | 0.00 | 0.00 | 0.00 | 0.83 | 1.52 | 0.35 |
| 20 | 0.48 | 0.84 | 0.00 | 0.00 | 0.13 | 0.26 | 0.44 | 0.00 | 0.00 | 0.00 | 0.49 | 0.96 | 0.26 |
| 30 | 0.05 | 0.09 | 0.00 | 0.00 | 0.13 | 0.18 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.25 | 0.25 |
| 60 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| SD | 0.64 | | | | 0.49 | | | 0.78 | | | 0.35 | | |
| Average SD | | 0.57 | | | | | | | | | | | |

Sensitivity Analysis - (TMP + DMH)/(C8= + C9+)
(2 to 7 min TOS)

| TOS [min] | SD | F50Pt5EM | F60Pt5EM | F48Pt5EMTr | SD | F63Pt1EM | F45Pt1EMTr | SD | F44Pt5Y | F56Pt5Y | SD | F66EMT | F68EMT |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 20.89 | 0.46 | 0.07 | 36.44 | 7.31 | 6.17 | 16.51 | 1.27 | 7.36 | 5.57 | 0.81 | 3.27 | 4.42 |
| 2 | 2.67 | 2.74 | 0.02 | 5.35 | 0.28 | 3.00 | 2.61 | 0.72 | 3.73 | 2.71 | 0.34 | 2.17 | 2.66 |
| 3 | 1.74 | 2.17 | 1.06 | 4.48 | 0.51 | 3.63 | 4.35 | 0.16 | 2.50 | 2.73 | 0.75 | 2.01 | 3.07 |
| 4 | 1.24 | 2.57 | 1.93 | 4.32 | 0.27 | 3.73 | 4.11 | 0.11 | 2.86 | 2.70 | 0.66 | 1.91 | 2.84 |
| 5 | 0.81 | 3.00 | 1.71 | 3.19 | 0.24 | 3.33 | 3.67 | 0.21 | 2.28 | 2.58 | 0.16 | 2.63 | 2.86 |
| 6 | 0.67 | 3.14 | 1.86 | 2.84 | 0.61 | 2.92 | 3.78 | 0.07 | 2.05 | 1.95 | 0.75 | 2.92 | 1.86 |
| 7 | 0.89 | 3.52 | 1.96 | 2.00 | 0.86 | 2.50 | 3.71 | 0.25 | 2.53 | 2.18 | 0.15 | 2.09 | 2.30 |
| 8 | 1.12 | 3.81 | 2.21 | 1.65 | 0.92 | 1.62 | 2.92 | 0.11 | 1.83 | 1.99 | 0.54 | 2.62 | 1.85 |
| 9 | 0.93 | 3.12 | 1.44 | 1.58 | 1.67 | 1.19 | 3.55 | 0.49 | 0.93 | 1.63 | 0.30 | 1.76 | 1.33 |
| 10 | 0.23 | 1.42 | 1.07 | 1.51 | 1.04 | 0.80 | 2.27 | 0.19 | 0.51 | 0.78 | 0.48 | 1.64 | 0.96 |
| 12 | 0.40 | 1.39 | 1.20 | 0.62 | 1.41 | 0.62 | 2.62 | 0.08 | 0.17 | 0.29 | 0.18 | 0.90 | 0.64 |
| 15 | 0.30 | 0.82 | 0.36 | 0.26 | 0.79 | 0.39 | 1.51 | 0.01 | 0.21 | 0.22 | 0.23 | 0.70 | 0.37 |
| 20 | 0.21 | 0.51 | 0.14 | 0.17 | 0.07 | 0.26 | 0.36 | 0.01 | 0.20 | 0.19 | 0.14 | 0.46 | 0.26 |
| 30 | 0.06 | 0.25 | 0.13 | 0.20 | 0.03 | 0.23 | 0.19 | 0.02 | 0.15 | 0.18 | 0.03 | 0.26 | 0.22 |
| 60 | 0.02 | 0.18 | 0.15 | 0.14 | 0.00 | 0.00 | 0.17 | 0.04 | 0.11 | 0.17 | 0.01 | 0.16 | 0.17 |
| SD | 1.34 | | | | 0.46 | | | 0.25 | | | 0.01 | | |
| Average SD | | 0.63 | | | | | | | | | | | |

Sensitivity Analysis - (2,2,3-TMP + 2,2,4-TMP)/(2,3,3-TMP + 2,3,4-TMP) [mass fraction]
(2 to 7 min)

| TOS [min] | SD | F50Pt5EMTr | F60Pt5EMTr | F48Pt5EMTr | SD | F63Pt1EMTr | F45Pt1EMTr | SD | F44Pt5Y | F56Pt5Y | SD | F66EMT | F68EMT |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.76 | 2.83 | 1.34 | 1.86 | 0.50 | 1.41 | 2.12 | 0.04 | 0.56 | 0.61 | 0.43 | 2.03 | 1.42 |
| 2 | 0.15 | 1.93 | 1.82 | 1.64 | 0.53 | 1.24 | 1.99 | 0.06 | 0.54 | 0.62 | 0.16 | 1.41 | 1.19 |
| 3 | 0.30 | 1.77 | 1.69 | 1.22 | 0.49 | 1.12 | 1.82 | 0.09 | 0.56 | 0.69 | 0.04 | 1.20 | 1.14 |
| 4 | 0.14 | 1.53 | 1.60 | 1.33 | 0.45 | 1.01 | 1.65 | 0.20 | 0.52 | 0.80 | 0.01 | 1.15 | 1.13 |
| 5 | 0.17 | 1.41 | 1.53 | 1.20 | 0.32 | 0.94 | 1.39 | 0.18 | 0.52 | 0.78 | 0.01 | 1.03 | 1.04 |
| 6 | 0.16 | 1.18 | 1.17 | 0.90 | 0.48 | 0.75 | 1.43 | 0.01 | 0.56 | 0.57 | 0.02 | 0.73 | 0.76 |
| 7 | 0.16 | 1.05 | 0.96 | 0.74 | 0.51 | 0.65 | 1.37 | 0.02 | 0.56 | 0.59 | 0.22 | 0.30 | 0.61 |
| 8 | 0.18 | 0.90 | 0.84 | 0.57 | 0.47 | 0.56 | 1.23 | 0.01 | 0.56 | 0.54 | 0.01 | 0.54 | 0.52 |
| 9 | 0.17 | 0.81 | 0.68 | 0.48 | 0.36 | 0.50 | 1.01 | 0.01 | 0.44 | 0.45 | 0.06 | 0.53 | 0.44 |
| 10 | 0.14 | 0.68 | 0.54 | 0.40 | 0.27 | 0.48 | 0.86 | 0.06 | 0.54 | 0.46 | 0.11 | 0.55 | 0.39 |
| 12 | 0.10 | 0.55 | 0.36 | 0.45 | 0.16 | 0.47 | 0.70 | 0.35 | 0.00 | 0.50 | 0.06 | 0.51 | 0.43 |
| 15 | 0.28 | 0.55 | 0.32 | 0.00 | 0.59 | 1.38 | 0.54 | 0.00 | 0.00 | 0.00 | 0.08 | 0.41 | 0.52 |
| 20 | 0.44 | 0.77 | 0.00 | 0.00 | 0.02 | 0.42 | 0.39 | 0.00 | 0.00 | 0.00 | 0.03 | 0.40 | 0.44 |
| 30 | 0.00 | 0.00 | 0.00 | 0.00 | 0.40 | 0.57 | 0.00 | 0.00 | 0.00 | 0.00 | 0.06 | 0.35 | 0.44 |
| 60 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| SD | 0.18 | | | | 0.46 | | | 0.09 | | | 0.08 | | |