

Optimal and Sustainable Design of Integrated Biorefineries for Microalgae and Municipal Solid Waste Processing

by

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A thesis

presented to the University of Waterloo

in fulfillment of the

thesis requirement for the degree of

Master of Applied Science

in

Chemical Engineering

Waterloo, Ontario, Canada, 2022

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Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Abstract

With drastic advances occurred in society over decades, there have been growing concerns towards global energy demand and sustainable feedstock supply. Particularly, biomass emerged as one of the potential energy sources due to its renewability and sustainability. Biomass is characterized to contain a variety of compositions, which could be used to produce numerous products that ranges from energy, chemicals, and other value-added materials. However, economic uncertainties exist due to possibilities in processing multiple biomass sources. With a concept of biorefinery, a systematic framework is developed for the superstructure-based optimization of combined microalgae and municipal solid waste (MSW) processing pathways.

Microalgae and municipal solid waste (MSW) have great potential as feedstocks to produce a wide range of valuable end-products. The proposed superstructure includes all the potential technological alternatives for producing valuable products from microalgae and MSW. A mixed integer linear programming (MILP) model is developed and solved in GAMS to determine the optimal biorefinery configurations. With multiple feedstocks for multiple products, more complex decisions have to be made to determine the best combinations of feedstocks, technologies and products out of available options.

In order to draft a superstructure of a potential biorefinery process for optimization, all the available methods of microscopic and macroscopic process operations for a biorefinery are to be collected and investigated. Some challenges include: 1) diverse amounts of possible biorefinery feedstocks and their processing pathways for the production due to many technological alternatives available, and 2) inconsistent and preliminary nature of technological and economic data. Especially, research in the field of biorefineries based on the second- and third-generation feedstocks such as municipal solid waste (MSW) and microalgae are at an early phase of study. Therefore, there is still many possibilities in complete optimization of operation selection and sequence of processing.

For this report, a case study was selected to assess economic feasibility of an integrated biorefinery in Seoul metropolitan area, South Korea. Being a highly industrialized city, solid waste management and energy supply issues have led social and environmental concerns. Given the superstructure-based model and case study parameters, a MILP problem was solved in

GAMS for optimization. As a result, the optimal solution included a selection of technological pathways to yield \$253,857,000 USD in and \$1433,859,000 USD in annual profit and revenue, respectively. Top products included 403,520 tonnes of biodiesel, 742,370 tonnes of bioethanol, and 3,490,500 MWh of electricity production annually. The optimal solution omitted landfill of waste, and increase the waste directed to electricity, which were ideal suggestion for the case study scenario. Moreover, recycling of water and methanol within the process cycle could potentially save \$116,171,320 USD per year.

Sensitivity analysis was done with three adjustable parameters: biodiesel market price, MSW composition, and microalgae cultivation efficiency. Biodiesel price was linearly correlated to total profit as it is one of the main products anticipated in this biorefinery. MSW composition caused a noticeable, exponential increase in profit as the proportion of recyclable components increased. Lastly, microalgae cultivation efficiency was selected to observe effects of potential weather variation on microalgal growth rate, and final profit. Profit value was linearly dependent on negative variation region of cultivation rate. This suggested extreme climate which hinders microalgae growth, could significantly affect the economic feasibility of this biorefinery.

For future study, suggestions were made to investigate the modeling and optimization of an integrated biorefinery in a more comprehensive manner. It was recommended to investigate possibilities to partially sell intermediate products directly to the market while the rest could be sent to further processing. Quantification of CO₂ emission was also recommended to assess environmental feasibility of the model. Lastly, the superstructure model could be applied to a different case study with different feed types and compositions to see the effect of feed condition on optimal route selection.

Acknowledgements

First and foremost, I would like to express my sincere gratitude and appreciation to my supervisors, Professor Ali Elkamel and Professor Michael Fowler, for their knowledge and guidance to my research. Over the past year, they have been providing me both academic and emotional support which taught me so much even apart from research works. This thesis would have been impossible without their encouragement, trust, and patience. These acknowledgements are also for Department of Chemical Engineering, University of Waterloo for allowing me to continue my study as a master's student, which I gained a lot of knowledge and sense of determination. I also would like to thank my research committee members, Professor Xianshe Feng and Associate Professor Tiz Mekonnen, for reviewing my thesis and providing their insightful suggestions.

My appreciation to Dr. Muhammad Rizwan for great support on my research and providing the material and information to execute this research. Special thanks to Dr. Abdul Halim Abdul Razik for technical help and continuous advice for this research. The suggestions I received help me better my work.

Finally, I would like to express my most sincere gratitude to my parents for their endless encouragement and support throughout this journey. Without them, I could never have come this far. I also thank my family and friends who made me all I am today.

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List of Abbreviations

Abbreviation	Full Name
AD	Anaerobic digestion
CBGTL	Coal, biomass, and natural gas to liquid
CH ₄	Methane
CHP	Combined heat and power
CO ₂	Carbon dioxide
DAF	Dissolved air floatation
DiAF	Dispersed air floatation
FA	Fatty acids
FAME	Fatty acid alkyl esters
FFA	Free fatty acids
GAMS	General Algebraic Modelling System
GDP	Gross domestic product
GHG	Greenhouse gas
HPLC	High-performance liquid chromatography
ICE	Internal combusting engine
IEA	International energy agency
IL	Ionic liquid
IPCC	The Intergovernmental Panel on Climate Change
kWh	Kilowatts per hour
MILP	Mixed integer linear programming
MINLP	Mixed integer nonlinear programming
MRF	Material recycling facility
MSW	Municipal solid waste
MTIE	The Ministry of Trade, Industry, and Energy of Korea
MWh	Megawatts per hour
ODF	Ozonation dispersed floatation
PAYT	Pay as you throw
PBR	Packed bed reactor
SFE	Supercritical fluid extraction
VBGD	Volume-based garbage disposal

Chapter 1 Introduction

1.1 Research Motivation

In the 21st century, the world's economic growth requires a continuous supply for energy. Energy is an essential component of an everyday life, and comes in various forms: chemical, thermal, electrical, and many more. With a vast technology in science and technology, the current human population consume substantial amount of energy in their daily lives and the energy demand has been exponentially increasing. According to International Energy Agency (IEA), the world's final energy consumption was 9,717 Mtoe and the total energy supply reached 162,494 Mtoe in 2017. Fossil fuels is acting as the world's primary energy source, accounting for up to 66.3% of total energy supply (i.e., Oil: 40.4%, Natural Gas: 16.4% and Coal: 9.5%) (IEA, 2021).

However, as the global trend of energy use is moving towards sustainable development, the environmental consequences including global warming, climate change, formation of smog and acid ran, and pollution, from using fossil fuels have become the most crucial issue to be solved in the next decades. When fossil fuels are burned, they release a large amount of carbon dioxide into the air, causing it to trap heat in our atmosphere and cause global warming and climate change. They also emit nitrogen oxide or ammonia when burned, causing excess nitrogen in the air and water, ultimately contributing to pollution (De et al., 2018). Issues with utilizing fossil fuels necessitated alternative energy production technologies. Therefore, the role of renewable energy resources such as biomass energy, solar, wind, geothermal power, and hydropower has become much more important recently.

As one of possible solutions, biomass resources have emerged as promising feedstocks for the next-generation energy production because of their attractive properties. It is widely acknowledged that combustion of biofuels, energy-producing materials derived from biomass, do not contribute to the greenhouse effect due to the carbon-neutral property of biomass and CO₂-neutral conversion processes. Hence, the overall biomass processes from the beginning feedstocks to the end products are considered renewable. To add on, biomass resources are abundant almost everywhere in the world in different forms and could be acquired very easily. Different types of biomass come in a variety of compositions, thus have potential to yield various forms of bioproducts and biofuels. Typical biomass resources include agricultural crops, wood

products, energy crops, animal manure, microalgae, residues from crops and trees, and municipal solid waste (MSW). Biofuels produced from biomass are highly attractive in transportation sector due to its high energy density and similarity to conventional transportation fuels such as gasoline and diesel. Furthermore, biomass not only acts as a renewable energy supplier, but also as a growing provider of renewable raw materials or additives used in various industries including food, pharmaceutical, cosmetics, and packing industries.

Despite the fact that biomass has become a promising option for energy production, there still remains numbers of significant barriers to commercial application and success of this feedstock. The main drawback is high operating cost associated with bioenergy production process, starting from production of feedstock to pre-treatment to conversion into bioproducts. A techno-economic assessment by Davis et al. (2011), has shown that it would require the cost of 2.25 USD per L to produce microalgal oil via hydrotreating, with an assumption of 10% internal rate of return, which is significantly greater than current costs of conventional fuel production. The high cost could also be due to the complexity of biofuel production. A typical biomass processing route is composed of multiple stages including cultivating, harvesting, transporting, concentrating, pre-treatment and conversion, which systematic design and organization of material flow are the most important factor determining the efficiency of the overall process.

Biorefinery is a term used for a multifunctional system that produces a wide range of chemicals, energy resources and power through the optimal usage of various biomass feedstocks (Takkellapati, 2018). Over the last couple decades, biorefinery has received much interest as the most strategically important and prospective industry as it could associate with many aspects of social development and sustainable future as opposed to fossil fuels. Potential development could focus on optimizing unit operations and plants, or apply process, energy, water and waste integration. Still, some technologies of utilizing and recycling alternative renewable energy resources are not fully developed. Especially, there are more types of raw resources recently identified as substitutive biomass feedstock sources that are sufficient for producing meaningful products. With more options in selection of feedstocks and processing methods, the current focus of process engineering research is about integrating multiple process routes and optimize the pathways to improve economic feasibility, transformation efficiency and final product yield (Srirangan et al., 2012).

In addition, the complete biorefinery concept includes the entire processing stages covering cultivation, collection, pre-treatment, product conversion via chemical reaction, separation of products, post-treatment and even distribution of products. Realistically, it is unfeasible to operate the complete biorefinery processes using a single feedstock to produce a single main product due to its complexity and high capital and operational costs of most operational stages like drying, separation and chemical conversion. Therefore, many researchers are currently focusing on combination of more than one biomass feedstock to produce various major products and by-products simultaneously to raise the production capacity and minimum feed supply, similar to a supply chain network. Most multi-feedstock biorefinery studies focused on integrating various first-generation feedstocks such as agricultural crops, wood products and their residues to accommodate greater feedstock supply even with irregular harvesting period of these crops. As a result, studies have shown that processing multiple biomass resources resulted in higher yield, lower processing cost, and/or higher processing efficiency.

On the other hand, second- and third-generation feedstocks such as municipal solid waste and microalgae are not yet examined deeply in multi-feedstock biorefinery concept. This could be due to their relatively early stage of real-life implementation, high process complexity and low product yield. However, as other studies have shown, there could be environmental and economic advantages if the two feedstock resources are combined and processed together. By only considering the agricultural and woody products and residues as main biomass sources, the impact on the local environment and economics would be much less than examining all the other possible feedstock sources. Systematic process network design of the next generation biomass feedstocks would be crucial to maximize the potential of biomass energy production. The research presented in this thesis focuses on a systematic modelling of a combined biomass energy production utilizing microalgae and municipal solid waste, and introduces an optimization model which utilizes a mixed integer linear programming (MILP) method to select the most economically optimized multi-feedstock-multi-product biorefinery processing routes. The results from this research are crucial in microalgae and MSW derived energy system design practices.

1.2 Research Objectives

The goal of this thesis is to develop and optimize an integrated multi-feedstock-multi-product biorefinery, specifically for a simultaneous microalgae and municipal solid waste utilization. The specific objectives of this research are outlined as below:

- Identify all potential technological processing alternatives available for converting MSW and microalgae into various energy and other valuable products as well as handling and/or recycling of waste materials. It will include the identification of potential value-added products that could be generated other than biofuels to exhaust the remaining solid wastes, thus increase the conversion rate and contribute towards primary energy supply.
- Develop a superstructure for a biorefinery optimization model. The superstructure should contain all possible processing routes for the production of biofuels and valued-added chemicals from microalgae along with the treatment/processing of MSW into energy and useful products.
- Formulate a mathematical model based on the developed superstructure to find the optimal choice of feedstocks, products, technologies, and processing pathways with annual profitability as the objective function. The model along with the objective function will search for optimal results including selection of technologies and processing routes, total annual yield of each product, and annual profit. The developed model will lead to formulation of mixed integer linear programming (MILP) model.
- Solve the optimization formulation by using a suitable solver from General Algebraic Modelling System (GAMS) and obtain the optimal results. Relevant analysis will be carried out to show the significance of the results.

1.3 Scope of the Thesis

The thesis is organized in five chapters as follows:

- Chapter 1. Introduction

This chapter introduces the motivation of this study. It outlines current environmental issues in energy industry, as well as potential solution to it by utilizing renewable energy such as biomass

energy. It overviews introductory information regarding biomass feedstock, energy and utilizations and its advantages and challenges.

- Chapter 2. Background Information and Literature Review

This chapter provides a detailed explanation on biomass feedstocks, biomass-derived products, and up-to-date technologies developed for processing microalgae and MSW into useful products, as well as reviews systematic design procedures.

- Chapter 3. Methodology and Problem Definition

This chapter outlines the superstructure-based methodology and mixed integer linear programming (MILP) being applied in this research. In addition, a problem scenario of Seoul metropolitan area, South Korea, will be clearly defined including geographical characteristics, feedstock characteristics, possible technologies, and products, which will be incorporated in the final model design.

- Chapter 4. Case Study Results Analysis

This chapter presents the results taken from the modelling and optimization about the optimal processing route network model of a multi-feedstock-multi-product biorefinery. The model is formulated using MILP via GAMS software.

- Chapter 5. Conclusions and Future Work

This chapter outlines the conclusions of this research and suggests directions for future research in integrated biorefinery systems design.

Chapter 2 Background Information and Literature Review

A systematic design and optimization of a biomass-based energy production process requires basic understanding of background information including: 1) biomass feedstocks and their characteristics; 2) bioenergy products and conversion technologies; 3) issues related to bioenergy conversion; and 4) current biomass energy systems design approaches and challenges. This chapter will mainly focus on discussing the background and review contents as listed above. From the summary at the end of this chapter, this research has identified its distinctiveness and expected contributions.

2.1 Biomass Feedstocks and Their Characteristics

As briefly mentioned in Chapter 1, the vast consumption of fossil fuels has resulted in global warming and subsequent environmental issues. Therefore, alternative renewable energy resources have become a priority to researchers. Biomass is referred to biological material derived from all living or organic matter. This section will discuss currently available types of biomass being studied and utilized, as well as their major characteristics to be considered when designing a biorefinery.

By definition, biomass is “the total mass of living organisms in a given area or of a given species usually expressed as dry weight. Biomass also includes organic matter products, by-products and waste derived from living organisms (especially regarded as fuel) excluding peat from such material.” (IPCC, 2007) Historically, it is the oldest energy source for mankind and is still contributing up to 14% of the world’s total energy supply nowadays. Energy existing in various forms of carbonaceous compounds inside biomass is solar energy in nature. For example, plants absorb the sun's energy in a process called photosynthesis. Biomass can be burned directly or converted to biofuels or biogas that can be burned as fuels (Mussatto, 2015).

Biomass covers a wide range of energy forms. Forestry and agricultural products including wood from trees, grass, crops, and oilseeds are the common forms of biomass in the past. Biomass also includes plant residues, biomass processing residues, animal manure, and even municipal solid wastes (MSW). The following are brief explanations of common biomass resources, excerpt from the U.S. Department of Energy (2018).

- Energy crops are non-consumable crops that can be harvested even on malnutritional land, which most traditional crops cannot grow. These crops can be classified into two categories: herbaceous and woody. Herbaceous energy crops are grasses that live for more than 2 years and are harvested after reaching full productivity. Examples of this type includes switchgrass, bamboo, tall fescue and wheatgrass. Woody crops are fast-growing, short-rotation hardwood trees that are fully harvested after 5 to 8 years since they are planted. Some examples include hybrid poplar, hybrid willow, silver maple, black walnut, and sycamore. Cultivating these types of crops could restimulate wildlife habitat and circulate water and soil quality, thus improving the overall crop land productivity.
- Residues from forest and agricultural crops also have potential to be used to produce biofuels, instead of being left on existing lands. Agricultural crop residues including stalks, leaves, husks and cobs are abundant worldwide. Forest residues can be either the leftover tree parts after logging timber, or dead, diseased trees left in the woods. The use of this type of biomass for energy production does not negatively alter or impact the ecosystem. Removal of these excess residues could rather clear up acres of land available for other purposes such as crop cultivation and animal habitat. In addition, periodic removal of organic residues in forests and fields also aid in ecosystem restoration, functional vitality and structural resilience.
- Other organic wastes produced by mankind could be utilized as biomass feedstocks. These include wood processing residues, wet wastes and municipal solid waste (MSW). Wet waste is a broad term used to describe any of the commercial, institutional and residential organic wastes: food wastes, organic-rich sludges, biogas, and manure slurries are the examples. MSW is mixed commercial and residential solid waste composed of yard trimming, paper, cardboard, plastics, rubber, leather and textiles. MSW requires sorting in order to separate different parts from the mix prior to generate bioenergy. Utilizing organic wastes is an emerging opportunity to produce bioenergy and reduce significant volume of landfills.
- Algae is defined as a group of photosynthetic phytoplankton typically found in freshwater and marine systems. Recent studies have discovered potential to harvest bioenergy from algal biomass due to its lipid-rich compositions. It also contains proteins, carbohydrates

and other useful contents that can be converted into a variety of biofuels and products. Depending on the strain, some algae can grow in second-use wastewater which offers opportunity for wastewater recycling and utilization in a biorefinery concept.

From the presented sources of biomass, it could be concluded that biomass is widely available all over the world and is easy to be acquired. Thus, one of the main considerations when systems planning would be location of the processing plants for optimized resource acquisition and bioenergy distribution. Furthermore, biomass derived energy comes in various forms due to a variety of feedstock options, thus offering different bulk density, volume, chemical compositions, and properties. Therefore, biofuels are often classified by “generations,” based on their main properties and processing methods, as listed below (Nanda et al., 2018).

- First generation biofuels: They are mainly derived from agricultural products such as crops, sugarcane and oilseed. These types of feedstocks are naturally abundant and known to be very high in carbohydrate or energy content to generate bioethanol and biodiesel. Fermentation or chemical processes are commonly utilized to convert sugars, starches, and oils into liquid fuels. Also, conversion and treatment technologies for these biofuels are relatively well-established. Thus, bioethanol and biodiesel are the only two type of biofuels that are produced on an industrial scale. Currently, corn ethanol is blended into most domestic gasoline products in the U.S. However, there has been drastically increased demand of energy recently that the first-generation feedstock is no longer considered ideal. Crop cultivation results in nitrogen oxides (NO_x), which are gaseous chemicals that accelerate greenhouse effect (Davis et al., 2011). Any displacement of food crops to biofuel crop production could decrease food supply and food prices. Furthermore, the competition for crops supply between food and fuel production increased the crop purchasing price up to US \$338/ton in 2012 (IEA, 2021), ultimately decreasing cost efficiency of these processes.
- Second generation biofuels: As opposed to the first-generation biofuels, second generation biofuels are derived from non-food biomass, which eliminates the concern regarding global food production. Feedstocks such as switchgrass, willow and hybrid poplar are perennial, fast-growing woods and are well-suited to being cultivated on desolated land. In addition, agricultural, municipal, and institutional by-products and

waste also fall under second-generation biofuel feedstocks (Hirani, 2018). The price value for lignocellulosic biomass ranges between US \$60-100/ton and municipal solid wastes cost between US \$0 and US \$60/ton (IEA, 2021). These feedstocks could be categorized based on their homogeneity: homogenous, quasi-homogeneous, or non-homogeneous. Despite their advantages, the processes to convert into useful bioproducts is more complex and less developed at this time. Biomass contains lignin and cellulose, which increases the complexity of conversion processes. Also, non-homogenous feedstocks contain a variety of materials which require an additional series of separation stages and multiple conversion techniques . With more thorough research, this could turn into a benefit to construct a “biorefinery” since it allows the opportunity to generate a variety of products out of the same feedstock. Thus, more research and development are required for efficient bioenergy production. Still, underlying environmental concerns for land use and potential ecosystem interference is crucial if fertilizer is used for farming.

- Third generation biofuels: Third generation biofuels are derived from algae, which has a very distinctive and rapid growth pattern compared to other traditional feedstocks. It has a diverse biochemical composition including carbohydrates, lipids, and proteins, which allows production of a wide range of commercially valuable bioproducts. Especially, the lipid content in algae is the main material for producing biofuels. Therefore, certain algae strains like *Chlorella* are getting more attention due to their high lipid content up to 70% (Mofijur, 2019). However, cultivating algae requires a specific range of growth conditions including warm temperature and large volumes of water, which could be a major problem in areas with water shortage or low temperature climate. In technical aspects, its high-water content requires significant dewatering process, as well as complex stages of filtration and transesterification for lipids to be further processed for biodiesel production (Nagler & Gerace, n.d.).

As mentioned above, first-generation biofuels are currently well-studied and produced on an industrial scale worldwide. However, issues such as high energy consumption, arable land use, competition with food resource and high feedstock cost, have accelerated recent attention toward the next-generation biofuels (Abdullah, 2019). As many other types of resources have been proposed as future generation of biorefinery feedstock, the future of biorefinery may not only be

a production of multiple bioproducts from one feedstock but also a combination of multiple generations of feedstocks to maximize the yield and sustainability.

2.2 Bioenergy Products and Conversion Methods

With a wide range of biomass feedstock options and processing methods, a variety of possible biomass-derived products could be produced. One of the most important factors in assessing the possibility to commercialize biorefinery would be the quality of final bioenergy products. If bioenergy products, also known as biofuels, have similar or advantageous energy properties compared to the conventional fossil fuels, it can be said that biorefinery process is worth being studied and commercialized. Table 1 below summarizes a list of common biomass derived products and conventional fossil fuels.

Table 1 Bulk Density and Volumetric Energy of Biomass and Conventional Fuels (retrieved from Brown, 2003).

Product	Bulk Density (kg/m³)	Volumetric Energy (GJ/m³)
Agricultural Residues	50-200	0.8-3.6
Softwood	200-340	1.0-6.8
Hardwood	280-480	5.3-9.1
Straw	160-300	2.6-4.9
Bagasse	160	2.8
Rice Hulls	130	2.1
Ethanol	790	23.5
Methanol	790	17.6
Biodiesel	900	35.6
Pyrolysis Oil	1280	10.6
Coal	600-900	11-33
Gasoline	740	35.7
Diesel	850	39.1

As summarized above, the first section of product list is raw biomass commonly found in agricultural and forestry landscape. In the past, this type of biomass was directly burned, heated or cooked to generate energy, which led low energy efficiency. However, if the raw biomass materials are converted into biofuels (listed in second section of the table) like ethanol, methanol, biodiesel and pyrolysis oil, the values show that both bulk density and volumetric energy increases, becoming comparable or even better than those of conventional fossil fuels (listed in the third section of the table). When the bulk density and volumetric energy increases,

transportation and distribution cost could be saved compared to raw biomass. Thus, transforming biomass feedstocks into higher energy applications in the most economic, energy efficient and eco-friendly method would be the main objective for a biorefinery concept.

Biomass conversion methods can be classified into three main process technologies: i) chemical, ii) thermo-chemical, and iii) bio-chemical conversions (Ghedini et al., 2021). The following figure is the overview of common bioenergy conversion methods and their expected bioproducts, classified into three categories.

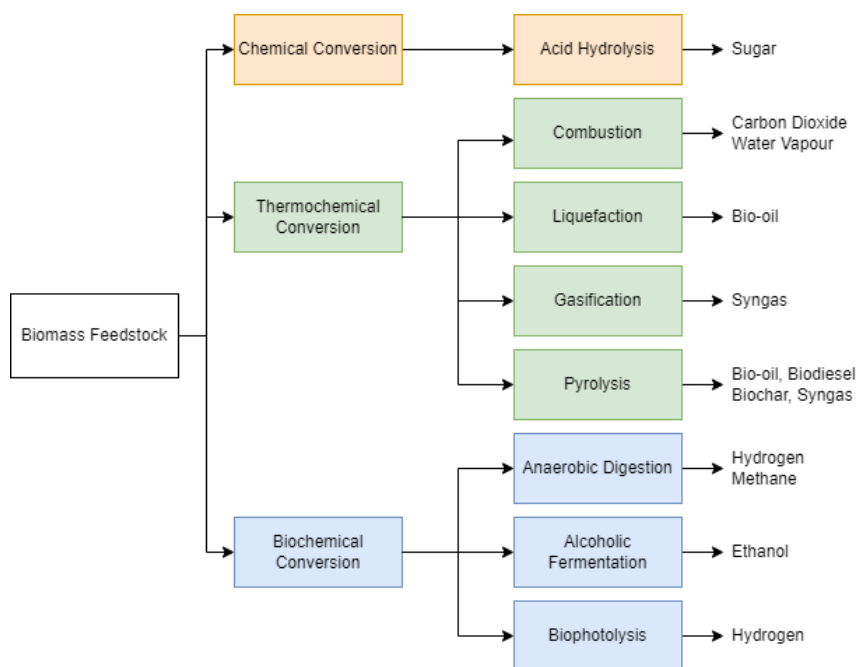


Figure 1 Biomass Conversion Methods Pathway (adapted from Ghedini et al., 2021)

2.2.1 Chemical Conversion Methods

Chemical conversion in a biorefinery is particularly crucial if the major feedstock resources are from agricultural and forestry products as most of their composition comes from polymeric structures such as cellulose, hemicellulose and lignin. First of all, if a feedstock comes in a polymeric nature, depolymerization should be the initial step to be taken (Wang et al., 2019). Hydrolysis is a term to describe a conversion process that breaks down a compound due to reaction with water. Especially, acid catalyzed hydrolysis is the most studied and well-established process to chemically split cellulose and hemicellulose into glucose and xylose, respectively. Lignin, on the other hand, is a complex polymer with random aromatic structures

which will likely remain as a polymer by-product after extraction. Numbers of studies are currently focusing on developing ways to obtain valuable chemicals to be used in other purposes. (Wang et al., 2019)

Depending on the acid concentration, different process settings are required. With a strong acid, low temperature around 40°C is ideal to result in high sugar yield up to 90%. However, equipment corrosion and high energy consumption from acid recovery process are disadvantageous. Therefore, dilute acid or mild acid reaction conditions are more favoured in the industrial processes. With mild acidity, the reaction must be carried out at a relatively high temperature around 200°C. Another concern is that glucose, xylose and other sugar monomers could be reacted again via dehydration reaction to produce unwanted by-products. (Gallo and Trapp, 2017) For example, glucose is dehydrated into 5-hydroxymethylfurfural (HMF), which can be then hydrolyzed into levulinic acid and formic acid. Xylose is dehydrated into furfural, which is subsequently reduced into sorbitol and xylitol or oxidized into saccharic acid.

However, in the context of biorefinery, these side reactions are new opportunities to produce a wider range of valuable products. They can be intermediates for production of important chemicals, known as platform molecules. As an example, a selective hydrogenation of HMF with a Ru/CeO_x catalyst can yield dihydroxymethyltetrahydrofuran, which is a precursor for solvents and monomers. With CuRu/C catalyst, HMF can also provide the fuel additive 2,5-dimethylfuran (DMF). Another platform molecule furfural can be converted into tetrahydrofuran via decarbonylation with Pd/SiO₂. (Alamillo et al., 2012) Therefore, different catalysts and reaction condition settings could be determined depending on the desired products. Utilizing reaction simulation software could aid in calculating the expected product and by-product yield to plan the sequential processes.

2.2.2 Thermochemical Conversion Methods

Thermochemical conversion is defined as a degradation process of biomass structure involving high temperature under aerobic or anaerobic condition (Wang, 2018). Depending on the conversion mechanism and reaction condition, there are 4 main processes, which are explained below.

1. Combustion

Combustion is defined as a process where a substance is rapidly burned in the presence of oxygen, releasing a significant amount of heat energy (Adams et al., 2018). Biomass resources composed of carbon, hydrogen and oxygen, produce carbon dioxide and water vapour as the main oxidation products. Advantages of combusting biomass over coal include higher fuel reactivity and lower greenhouse gas emission. With this conversion method, production of unwanted intermediates and by-products could be prevented. For combustion to take place, moisture content of biomass feedstock must be less than 50%. If not, additional dewatering and drying step before combustion is required to remove excess moisture. (McKendry, 2002)

The ultimate goal of a combustion process is to convert chemical energy stored in biomass into electrical energy. Thus, a combustion power plant is composed of three key steps: i) chemical energy to heat, ii) heat into mechanical energy, and iii) mechanical energy into electrical energy. By applying a number of equipment including combustor, boiler, steam turbine and turbo-generators, all three sequences of energy conversion could be achieved. Studies have shown that the net energy conversion efficiency for biomass combustion power plants range between 25% to 40%, and the higher efficiency is achieved with systems over 100 MWe. (McKendry, 2002) Co-combustion is another strategy to increase the conversion efficiency. A study by Vanek and Albright (2008) showed improved thermal efficiency when the biomass is co-combusted in a coal-fired power plant.

2. Liquefaction

Liquefaction refers to a conversion of biomass feedstock into liquid hydrocarbons, also known as bio-oil, at a lower temperature (280-370°C) and high pressure. Compared to other thermochemical processes, there are fewer applications of liquefaction since the reactor system requires is much more complex and expensive. During this process, biomass is decomposed and depolymerized into highly reactive molecules, then they get repolymerized and condensed into different compounds. Due to a complex nature of biomass compositions, various reactions occur at once to transform biomass feedstocks into bio-oil. During the reaction, phase separation takes place spontaneously, resulting in phases: carbon dioxide gas, solid bio-char trace, bio-oil, and traces of aqueous phase (Cristino, 2021). Most importantly, the great majority of the product is bio-oil and only a small amount is other unwanted by-products. Therefore, only a simple

treatment and separation process is required for the products' commercial utilization. Another advantage of liquefaction process is that its efficiency could reach up to 85-90% since it does not require too much additional energy taken from feedstock (Adams, 2018).

3. Gasification

Gasification involves partial oxidation of biomass feedstock under high pressure and temperature to produce gaseous product mixture, also known as synthesis gas or syngas. Syngas is mostly composed of hydrogen gas and carbon monoxide, with smaller quantities of methane, nitrogen, carbon dioxide and other hydrocarbons (Ciferno and Marano, 2002). Gasification process is also considered highly efficient since it allows biomass sources to produce both chemical products as well as energy. This provides a possibility for biomass product to take over the role of natural gas and fossil fuels in energy sector. It is also gaining attention to process solid wastes into useful energy forms (Puig-Arnabat et al., 2010). The overall efficiency of a gasification system has been improved over decades, recently reaching 40-55%, from the study by BIOCAP Canada (2006). However, optimization in pre- and post-treatment stages are still incomplete, which has been causing slow development and implementation of biomass gasification.

Syngas can be further processed in various ways for different final desired products. To produce heat and power, a combined heat and power (CHP) system is selected to further process syngas. Other processing options like methanol production system and Fischer-Tropsch system could produce chemicals and liquid fuels, respectively.

4. Pyrolysis

Pyrolysis is a thermal decomposition process at a relatively lower temperature (~500°C) without oxygen in the atmosphere. Solid or liquid biomass thermally degrades into smaller volatile molecules (Basu, 2010). Depending on the biomass type, catalyst, rate of temperature increase, and maximum temperature reached, different pyrolysis products could be produced. Especially, the rate of temperature change is an important variable for producing desired products. In the case of fast pyrolysis, time required for heating biomass feedstock is short. The residence time is also short, so that rapid quenching of condensable products results in production of bio-oil. On the other hand, slow pyrolysis with lower heating rate and longer residence time will offer more condensation and predominantly produce bio-chars (Dong et al., 2019).

2.2.3 Biochemical Conversion Methods

There are three commonly utilized biochemical conversion methods: anaerobic digestion, fermentation, and biophotolysis. These three methods each produce different types of products.

1. Anaerobic Digestion (AD)

Anaerobic digestion is a biological decomposition of an organic material including polysaccharides, proteins and lipids into gaseous materials by microbes under oxygen-free conditions. The resulting product is called biogas, as it is a mixture of up to 60% of methane (CH_4), 35% of carbon dioxide (CO_2), and trace gases. The conversion from biomass feedstock to biogas product via AD has shown a relatively low efficiency of around 15-20%.

Although the process seems to have a low efficiency, AD of biomass has been evaluated as a highly advantageous process to produce biofuel due to many reasons. First of all, AD is a universal process. Almost all types of organic biomass source either showed good digestion characteristics or can be pre-treated to promote digestion. Studies by Gonzales et al. (2011), Park and Li (2012), and many more researchers discovered that co-digestion of various types of biomass with waste streams to increase C/N ratio of a feedstock and accelerate bacterial activity. These studies showed higher methane production and increased organic loading rate due to less reaction inhibition. This suggests that utilizing AD could be a suitable process to convert multiple feedstocks simultaneously for a greater yield of bioenergy products. Lastly, AD is considered as an alternative for a conventional landfill process of organic wastes. Released methane gas from landfill contributes to a build up of greenhouse gases (GHGs) in the atmosphere. By replacing landfill process with AD, it can mitigate GHG issues by directly capturing biogas and utilize it as a fuel for a turbine to produce power (electricity).

2. Fermentation

Fermentation is a biological decomposition of sugar-containing organic substrates by enzymes produced by microorganisms under anaerobic conditions (Garcia et al., 2011). Production of ethanol is the major application of fermentation process. Starch and cellulose, which are rigid polysaccharide structures could also be fermented after they are first converted into sugar by hydrolysis reaction. After post-treatment processes, which are distillation and dehydration process, a 99% purity ethanol could be acquired (McKendry, 2002).

There are several factors to consider for a large-scale commercial biomass fermentation process. Aseptic condition is required for most fermentation process, which could be difficult and costly to achieve in an industrial scale operation. After a separation and post-treatment of ethanol product, there will be a body of dilute wastewater remaining to be treated before discharge. However, studies show that the wastewater could be recirculated into fermentation process or reused in other biological process without noticeable disadvantages over fresh water (Garcia et al., 2011). Therefore, extensive studies on wastewater recycling system within a biorefinery design is highly suggested.

3. Biophotolysis

Biophotolysis is a biological process to produce hydrogen gas using a photosynthetic apparatus (Nagarajan et al., 2017). The biomass feedstock for hydrogen production with this technique is only limited to eukaryotic microalgae and prokaryotic cyanobacterial, which possess light harvesting pigments. Photosynthesis takes place in chloroplasts or thylakoid membranes and initiates the electron transfer across membranes involving both photosystems and generation of ATP. This condition leads to water splitting activity associated with hydrogen generation. The reaction is catalyzed by hydrogenase enzyme (Eroglu and Melis, 2011). A simplified chemical reaction equation is as below:



There are several factors affecting photo-biological hydrogen production. First of all, the light intensity is considered the most important factor affecting the efficiency of microbial hydrogen production (Nagarajan et al., 2017). Under strong artificial light illumination, cells could show altered metabolic capacity and reduce efficiency. On the other hand, if the light is too dark, cells could experience light inhibition, also resulting in reduced process efficiency. Second, basic essential macro and micronutrients such as vitamins, nitrogen source, carbon source, iron, copper and other trace elements are needed for microalgal growth. In addition, as photolysis occurs simultaneously with microalgae growth, maintaining the growth condition is essential for maximizing product yield. To improve efficiency, a closed reactor system could be commercially implemented for this process, although it is much more expensive than conventional open systems with natural light (Nagarajan et al., 2017).

2.3 Microalgae-Based Biorefinery Conversion Techniques

Microalgae are microorganisms growing through photosynthesis, which requires light, carbon dioxide, water and nutrients (Sen et al., 2012). The major chemical constituents of microalgae are lipids, proteins and carbohydrates with different compositions stored in the cell depending on their strains. Minor contents include pigments, vitamins and polyunsaturated fatty acids, which are value-added chemicals used in pharmaceuticals, food and cosmetics industries. [6]

Microalgae-based biorefinery process can be divided into eight major processing stages: 1) cultivation of microalgae, 2) harvesting of microalgal biomass, 3) pre-treatment (drying and cell disruption), 4) lipid extraction, 5) transesterification, 6) post-transesterification purification, 7) pre-treatment of residue, and 8) conversion of the residue into other value-added products (Rizwan et al., 2013). At each processing stage, various technological alternatives are available to be considered. As the technology evolves, more options will be generated that can be later incorporated into the superstructure.

2.3.1 Cultivation of Microalgae

Microalgae-based biorefinery begins with the growth of microalgae. Cultivation conditions such as light, carbon dioxide, temperature, pH, and nutrients affect the characteristics of microalgae. The growth rate of biomass can be predicted as a function of light. As temperature alters the biochemical processes in the cells, cultivation of microalgae at non-optimal temperature will hinder biomass production (Khan et al., 2018). Depending on the species, the pH of the culture media is preferred to be kept between 6 and 8.76. Phosphorus and nitrogen are the main nutrients required for microalgae growth. Applying wastewater in microalgae cultivation could be considered as it usually contains phosphorus and nitrogen nutrients, and it can also reduce contaminants in wastewater (Suparmaniam et al., 2019). Systematic analysis of wastewater is needed if it is being considered as an alternative nutrient source (Zullaikah et al., 2019).

Employing photoautotrophic method, microalgae biomass can be cultivated commercially in largely two different types of setting, either in open ponds or enclosed photobioreactor (PBR).

1. Open Pond System

Cultivation of microalgae in open ponds can be carried out either open or covered surface, and in natural waters or artificial sinks. Open pond system has a great economic advantage and ease of

scalability since it utilizes natural sunlight and atmosphere. Also, sewage or wastewater treatment plants can incorporate the cultivation system to use wastewater for water and nutrient supply to microalgae, thus minimizing upstream processing cost (Tan et al., 2017). However, system could be contaminated easily and is difficult to control the environment. Difficulty to control the culture temperature results in loss of water due to evaporation. Guieysse et al. (2013) conducted a case study of water evaporation prediction in five typical climatic zones to quantify the variable water demand in each region. In addition, efficiency of an open pond system is highly climate dependent. For example, at high latitudes, light levels vary a lot during the day and between seasons, resulting in lower annual cultivation efficiency compared to it of moderate climate zones. Therefore, careful study of land selection is essential before the construction of biorefinery system.

Open ponds are typically built in circular or raceway configurations. In raceway ponds, microalgae biomass is recirculated around a track loop, as shown in the Figure 2a (Tan et al., 2017). The depth of the pond is approximately 0.3 m to increase exposure to sunlight thus increasing growth yield. A paddlewheel assists in agitation and recirculation of the culture, while the baffle is constructed at the center of the pond system to guide the mixing flow. The system is continuous with constant addition of carbon dioxide and nutrients from the feed ports. Circular pond system, as shown in Figure 2b, utilizes a central pivot rotating agitator for mixing the culture. However, the scalability cannot be over 10,000 m² due to the limitation of effective mixing offered by the rotating arm (Tan et al., 2017).

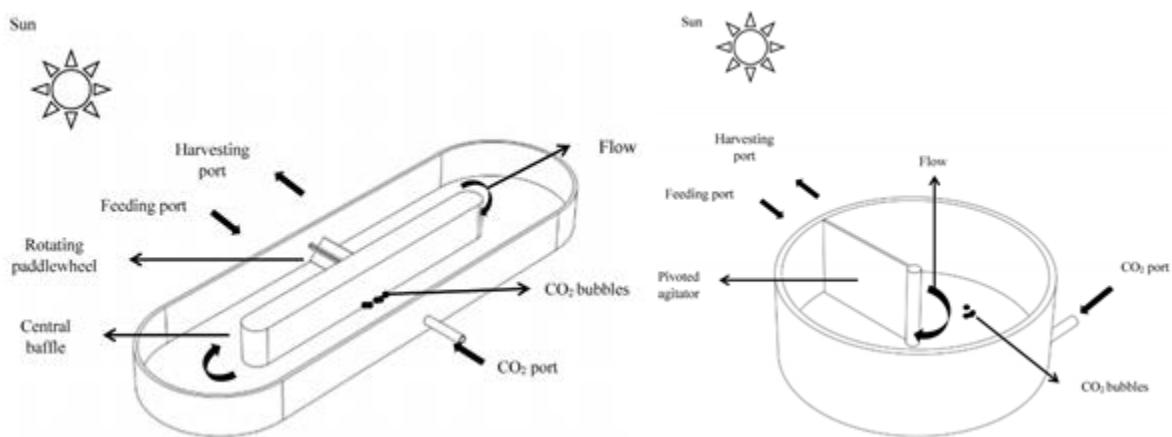


Figure 2 a) Open raceway pond cultivation system, and b) circular pond (retrieved from Tan et al., 2017)

Closed pond system is a new alternative proposed for more control over the cultivation environment. To address the contamination issue, the pond is covered with greenhouse. This method could minimize water and carbon dioxide loss and enhance cell growth rate. The building material is often plexiglass which is more expensive than open pond's concrete material but cheaper than constructing a photobioreactor system.

2. Photobioreactor (PBR)

Photobioreactor is an enclosed vessel with supply of artificial and/or solar light as energy source. The most prominent advantage of PBRs is that they require less or no agricultural land. In addition, biomass cultivation is possible with higher efficiency yearlong, regardless of outdoor climate conditions (Suparmaniam et al., 2019). Due to limitations with artificial lighting system, PBR often incorporates the utilization of natural sunlight. To enhance the microalgae production rate, various photobioreactor configurations have been developed (Ma and Hanna, 1999). Currently, tubular PRB is the most common industrial configuration. A tubular BPR consists of a parallel array of horizontal, vertical or inclined tubes made of glass or plastic, such that they are exposed to maximum amount of sunlight depending on the outdoor condition (Wang et al., 2012). Despite its large surface area and suitability for scaling up, this configuration has poor mass transfer. A greater mechanical pump load is required to continuously facilitate mass transfer of carbon dioxide, nutrients and culture within the system. In addition, temperature control may be difficult in such configuration. An automated temperature control system is available to be implemented, however, it is very costly and complex. Improving the mixing system in the tubes can significantly enhance the light distribution efficiency and thus cell productivity (Tan et al., 2018).

Flat panel PBR is another common configuration, commonly used for lab-scale studies of algae cultivation. The most prominent advantage of this type is a high surface to volume ratio. The configuration also makes the light path to be very short and evenly distributed across the reactor, resulting in high light efficiency. It is relatively easy to alter light capture angle and agitation rate by changing the light source location and agitation method, respectively. Currently, sparging and stirring are the most popular agitation methods used in this system. Disadvantages of flat panel configuration are related to agitation methods. Sparging method involves dilution or recirculation of the produced gas, resulting in higher risk of gas leak. Stirring method is very energy intensive,

requiring much higher energy input. (Skjanes et al., 2016) Therefore, agitation method selection should focus on the main objective of microalgae cultivation.

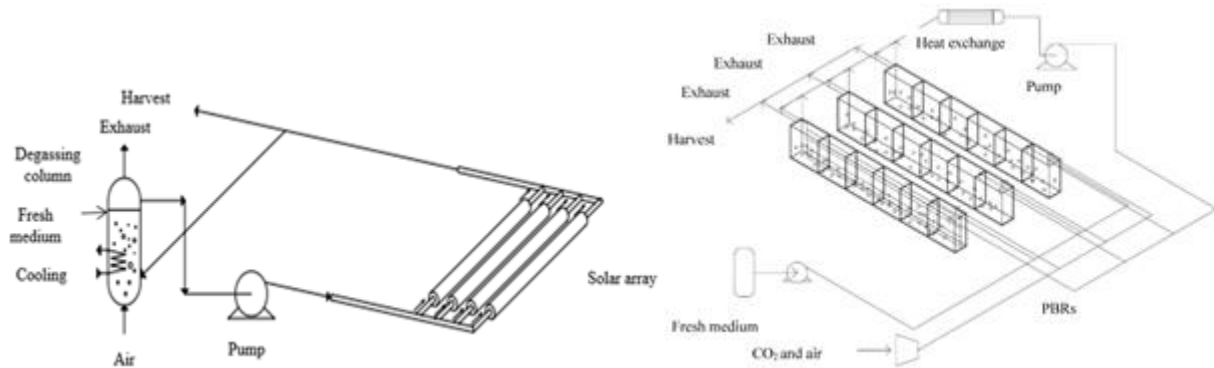


Figure 3 a) Tubular PBR, and b) flat panel PBR (retrieved from Tan et al., 2018, and Dasan et al., 2019)

For commercial process, both open pond and PBR are feasible alternatives for microalgae cultivation. Open pond is more cost effective and less energy-intensive, only requiring 4 W/m^3 compared to $2000\text{-}3000 \text{ W/m}^3$ for a PBR. A PBR has a higher production cost, but its controlled conditions make the system less contaminable and more process efficient (Dasan et al., 2019).

2.3.2 Harvesting of Microalgae Biomass

The goal of harvesting step is to separate cultivated microalgae cells from culture media. Here, a large volume of water must be removed to isolate concentrated microalgae, which is a costly process (Mallick et al., 2016). Factors including biomass recovery rate, operating and maintenance cost, and energy consumption must all be considered in alternatives selection. The process must also be non-toxic as the residual biomass after lipid extraction has potential to produce value-added chemical products. Also, the separated water-based medium could be reused in the previous cultivation step, providing approximately 84% of water and 55% of nitrate required (Zullaikah et al., 2019). Harvesting step of microalgae is more complex than that of macroalgae since it involves concentration of microalgae culture followed by dewatering. The mass and concentration of microalgae culture can be estimated in terms of dry weight. The harvesting techniques can be largely categorized into mechanical and chemical methods, and often combination of two technologies could be applied for higher separation efficiency (Mathimani & Mallick, 2018).

1. Gravitational Sedimentation

Gravitational sedimentation method is the oldest method that has been used to separate culture from media (Mallick et al., 2016). It uses natural gravitational force to settle down microalgae based on density and radial size of cells. Although it is the most inexpensive and simple method, sedimentation process is highly time-consuming and inefficient. Prolonged duration of harvesting can significantly affect the biological and chemical activity of cells that biomass could start deteriorating and alter its composition which is not favourable for biofuel production (Shuba & Kifle, 2018). Therefore, it is currently not the favourable method to be considered in most biorefineries.

2. Centrifugation

Centrifugation is similar to gravitational sedimentation, where centrifugal force replaces gravity for separation force (Milledge and Heaven, 2011). Harvesting efficiency of centrifugation depends on the cell size and density difference of microalgae cell to culture medium. Also, there are various types of centrifuges, including disk stack centrifuges, basket centrifuges, decanters and hydrocyclones, where disk stack centrifuges are currently the most used in industrial settings. It is capable of concentrating microalgae between 3 and 30 μm in sizes. It was also suggested that hydrocyclone centrifuge could be primarily used to pre-concentrate microalgae to remove majority of medium then utilize other high-energy requiring centrifuge to remove remaining moisture, as hydrocyclone can be operated in a continuous fashion with low maintenance (Milledge and Heaven, 2011).

Centrifugation is widely known for its high separation efficiency greater than 90% under low flow rates and high energy intake. With high energy utilization, the process is relatively fast and effective, regardless of microalgae cell types (Pahl et al., 2013). However, it is highly energy-demanding and requires high operation and maintenance costs. For a large-scale operation, the maintenance, capital and operation cost are especially very high in order to reach high efficiency.

3. Floatation

Floatation is a gravity separation process which utilizes gas bubbles passing through liquid-solid suspension (Sim et al., 1988). Microalgae cells are then absorbed on to bubbles and floated to the top of a liquid surface. This method is especially fast and effective for separation of microalgal

species with low density and self-float characteristics. Factors that affect floatation efficiency include type of surfactant or flocculant used, pH, ionic strength of the medium, air tank pressure, hydraulic retention time and particle floating rate (Phoochinda and White, 2003). The size of the bubbles and particles significantly affects the process efficiency (preferably less than 500 microns) as lighter particles will be more easily float to the top of the medium (Wang et al., 2015). A study by Hantou et al. (2012) showed that micro-sized bubbles were ideal for separating microalgal cells from growth medium due to their high surface area per volume and low-rise velocity resulting in faster attachment of the cells onto them. It is noted that only hydrophobic cells with high molecular weight are ideal for this separation method. To overcome this limitation, addition of surfactants or flocculants could be a solution.

Floatation method could be classified according to the method of bubble production. Dissolved air floatation (DAF), dispersed air floatation (DiAF), and ozonation-dispersed floatation (ODF) are the most popular floatation methods. DAF generates bubbles with air dissolved in water under very high pressure. With the aid of coagulants to increase surface adsorption energy, this method could reach up to 95% removal efficiency (Park et al., 2011).

4. Filtration

In a filtration method, microalgae culture is passed through filters with the aid of gravity, pressure or vacuum force (Tan et al., 2017). The resulting microalgae culture remains as a thick past form on the membrane. Depending on the hydrodynamic conditions and solvent/solute properties, correct selection of membrane including membrane pore size, material, and filter design is crucial. Membrane filtration can recover smaller microalgae cells such as *Scenedesmus*, *Dunaliella* and *Chlorella* species. Conventional filtration with strainers with 70 mm pore size could be used in conjunction with flocculation by flocculating smaller cells into bigger flocs (Tan et al., 2017). Advanced from the conventional method, microfiltration and ultrafiltration with much smaller pore sizes are widely used to recover more particles, even shear-sensitive species (Kotasthane, 2017).

Advantages of filtration method are low energy consumption, high-cost efficiency and high recovery efficiency. Also, the quality of the harvested microalgae cells is relatively in good condition, without significant cell disruption, compared to other methods. Also, it is environmentally friendly as it does not require additional chemicals. Thus, the recycling of spent

media is much easier (Singh & Patidar, 2018). On the other hand, membrane fouling and clogging are major issues of filtration method. Regular cleaning and replacement of membranes could be costly and must be included in cost estimation.

5. Flocculation

Flocculation utilizes chemicals called flocculants to neutralize the negative surface charge of microalgae cells and allow aggregation of the cells to form bigger flocs (Singh & Patidar, 2018). Microalgae cells are negatively charged due to the ionized functional groups on their surface, which causes repulsive force between cells. Therefore, flocculants must be able to overcome such forces to enable cell aggregation (Dubanowitz, 2000). Inorganic flocculants such as $\text{Fe}_2(\text{SO}_4)_3$, FeCl_3 and trivalent metal sulfates are widely used but must be cautious due to its toxicity and sludge generation which further require dewatering steps. They can also be hazardous to environment and even cause contamination of microalgal biomass. Therefore, careful selection of chemicals would be crucial in a biorefinery study (Singh & Patidar, 2018). Farooq et al. (2015) studied cultivation efficiency of *C. vulgaris* using chemical flocculation with FeCl_3 and alum, compared to reference centrifugation method in terms of cost and energy factor. The study showed that centrifugation and flocculation with ferric chloride were suitable for microalgae harvesting due to their high harvesting efficiencies up to 90%. Table 2 shows the comparison of major chemical flocculants in terms of their unit price (Li et al., 2017)

Table 2 Price comparison of common chemical flocculants (retrieved from Li et al., 2017)

Type of chemical flocculant	Flocculant name	Price/kg (in US\$)	Cost involved in flocculation for 1000 L (in US\$)
Inorganic	FeCl_3	14.1	0.7
	$\text{Al}_2(\text{SO}_4)_3$	5.6	0.3
	CaCl_2	60.7	3.7
Organic	Chitosan	207.2	31.1
	Carboxymethyl cellulose	18.3	2.2
	Rice starch	5.9 (1 kg of each, total 8 kg) US\$ 0.7	0.1
	Maize starch		
	Oxidized starch	approximately per kg	
	Tapioca starch		
	Yellow dextrin		
	Potato starch		
	Pregelatinized starch		
Cationic starch			

Other than utilizing flocculants for cell flocculation, different methods have been developed over years. Electro-flocculation method uses a set of a nonreactive anode and a sacrificial cathode to draw negatively charged microalgae cells towards the charged anode via electrophoretic motion (Mathmani & Mallick, 2018). As a result, cells undergo charge neutralization and aggregate into flocs. Mathimani et al. (2018) used aluminum electrodes to supply 2 kWh/kg of energy to freshwater *C. vulgaris*, which showed 93.6% flocculation efficiency in 30 min settling time. When it was combined with dispersed-air floatation (DAF) method, the recovery rate increased up to 99% (Vandamme et al., 2011). The efficiency of the process largely depends on electrode material, processing time, density and pH, resulting in biomass recovery efficiency ranging between 80-95% (Chen et al., 2011).

Autoflocculation does not require any addition of flocculants, as certain microalgae strains can naturally coagulate in response to environmental stresses. The mechanism is derived from changes in pH, dissolved oxygen concentration and nitrogen concentration (Vandamme et al., 2011). Especially, pH alteration is commonly selected as pH change could be easily induced by adding inexpensive hydroxides. At higher pH, calcium and magnesium precipitates are formed from microalgae cells, which subsequently induces flocculation. This is considered as a cheap, safe and low energy method. Vandamme et al. (2011) demonstrated autoflocculation of *C. vulgaris* using various techniques and showed that addition of calcium hydroxide increased the biomass concentration by 50 times. This method reached up to 98% biomass recovery within 30 minutes of flocculation. It should be noted that the effects of base and acid used in adjusting pH must be considered in economic feasibility analysis and environmental issues.

Bioflocculation is induced by co-cultivation of microalgae along with other microorganisms, such as bacteria or fungus. This method may be cost-effective as it does not require alternation of culture condition or use of expensive and/or toxic flocculants (Barros et al., 2015). However, the reaction mechanism must be thoroughly understood to establish this method in a commercial scale with high efficiency. The harvesting efficiency was shown to be above 90% at the optimal condition tested. Furthermore, studies have been drawing attention to the use of waste biomass-derived bioflocculant, including animal protein waste, plants, fruits, shell waste and more. The process efficiency varied between 50-94% depending on the system environment as well as the compatibility of the co-cultivated microorganism types.

2.3.3 Drying

After harvesting of microalgal biomass through separation from culture media, the resulting product is dewatered slurry. The algae biomass must be fully dried prior to lipid extraction to produce biodiesel. Drying step is the largest economic constraint in the microalgae biorefinery as it can take up to 75% of the overall cost requirement due to its high energy consumption (Gulto & Hu, 2013). Therefore, the most feasible drying technique must be selected to not only prevent deteriorating of cells and lowering cell quality but also produce bioproducts with reasonable cost. The main consideration in method selection would be cost, simplicity and energy requirement.

1. Rotary Drying

Rotary drying involves the use of an inclined rotational cylinder to continuously move algae from one end to the other by gravity. This method is possible to achieve both drying the samples and breaking the cell wall (cell disruption). Soeder and Pabst (1980) assessed the energy requirement for drying algae with 4% water content to be 15.7 Mcal for evaporating 18.2 kg water/kg dry algae product. Electrically heated drum dryer is preferred over a steam heated dryer due to its energy conservation by 6.8 times. The energy input was 1.4 kW h for such system. Drying algae in a drum dryer is advantageous as it can simultaneously sterilize samples and break cell wall, reducing additional disruption stage. To minimize energy cost, it should be aimed to maintain relatively higher water content for the final product.

2. Air and Vacuum Drying

Air drying utilizes cross-flow air to dry out moisture in biomass slurry kept in an oven or a shelf. Similarly in vacuum drying, biomass is kept in a vacuum oven. In the study by Becker and Venkataraman (1982) process effectiveness of air and vacuum drying were compared. Wet slurry of microalgae culture with 55-66% water content was dried using cross-flow air drying for 14 h at 62 °C. The resulting dried algae product had 4-8% moisture. Another set of algae sample was dried to 4% water content in a vacuum-shelf dryer at 50-65 °C and 0.06 atm. Unlike rotary drying method, the cell wall was found to be undisrupted after drying.

2.3.4 Cell Disruption

Disruption of microalgae cells comes after the drying process. This step is required to break the tough cell wall and extract valuable cell components such as lipid, protein, and pigment.

Selection of an appropriate disruption method is important as the contents of extracted lipids could vary depending on the technique selected. Classification of methods is often divided into mechanical and non-mechanical technologies. Scalability, input cost and process effectiveness will be assessed to select the optimal option (Lee et al., 2012). Recently, studies have been focusing on cell disruption methods directly on wet biomass to reduce economic concerns on additional drying step.

1. Mechanical Disruption

Common mechanical disruption techniques include bead-milling, ultrasound and homogenization. These methods are energy intensive and optimally operated at high cell density. Bead milling is one of the most prospective methods for commercialization due to its high disruption efficiency and simplicity. Compression of cells is caused by solid beads agitated at high velocities in a rotating chamber unit. Taleb et al. (2016) assessed disruption efficiency of the cell wall of *N. oculata* in a bead-milling-based high-pressure disrupter. This unit achieved up to 98% disruption efficiency at 1750 bar for 1 L volume of biomass.

Freeze drying can damage cell walls as intracellular content expands upon freezing. A study conducted by Fernandez-Sevilla et al. (2010) reported 45% of extraction efficiency for lutein extraction from microalgal biomass. Also, it required high energy input when the cells were dried first. Despite its relatively low yield, freeze drying may be preferred over other drying methods as it does not interfere with lipid quality (Guldhe et al., 2014).

2. Non-Mechanical Disruption

Non-mechanical methods involve chemical or biological additives that directly act on cell wall. Therefore, the required dosage and type of materials would be crucial for economic feasibility analysis. First, various chemical materials are utilized for cell wall disruption. Sulfuric acid is a common option as it is very effective with low cost (\$185/ton) (Lee & Han, 2015). Park et al. (2014) treated *C. vulgaris* with sulfuric acid-catalyzed hot-water. Less than 1% sulfuric acid

concentration was maintained at 120 °C for 60 min, which resulted in 337 mg/g cell and 935 mg/g lipid extraction yield.

Ionic liquids are salts composed of relatively large asymmetric organic cations interlocked with smaller anions in liquid form (Praveenkuman et al, 2014). They are known for non-flammability, thermal stability, high heat capacity, reusability and short reaction time. Kim et al (2012) extracted lipid from *C. vulgaris* using [Bmim] CF₃SO₃ with methanol as a co-solvent, resulting in 19.0% of total lipid content extracted. Compared to traditional chloroform/methanol (1:1 v/v) extraction method, the total lipid content was improved.

Cationic surfactants can be used to adhere onto negatively charged biomass cell surface and cause disruption. Park et al. (2014) tested the effects of sodium dodecyl benzene sulfonate (SDBS) in conjunction with 1% sulfuric acid catalyzed hot-water bath for lipid extraction of *Chlorella vulgaris*. The results showed that the lipid recovery efficiency was increased to 96.7%, relative to only using sulfuric acid. In addition, the amount of required sulfuric acid to result in the same yield also decreased. Practical application is possible if minimization of dosage and efficient recovery processes are designed.

Microwave treatment heats the overall biomass via conduction and damages cellulose structures in the cell walls by cavitation mechanism. Solvent is required for extraction of lipids, including hexane, chloroform, dichloromethane and sodium sulfate. Balasubramanian et al. (2011) developed a continuous microwave technology for hexane solvent at 1.2 kW, 2450 MHz. In this system, *Scenedesmus obliquus* was suspended in water and was heated to 80–95 °C for 30 min. The extraction efficiency was up to 77%. Despite certain benefits, microwave treatment has relatively high energy consumption.

High-power ultrasound extraction generates intensive microbubbles in liquid medium. Similar to microwave disruption method, it uses cavitation mechanism to break cell wall as microbubbles gradually grow in size and eventually collapse violently (Lee & Han, 2015). When these bubbles collapse on the cell wall, the temperature and pressure could rise up to 5000K and several hundred atmospheres, effectively disrupting cell and releasing intracellular materials into the bulk liquid. Therefore, the sample temperature should be constantly monitored to prevent any

chemical changes due to high temperature rise. In addition, high energy requirement is necessary for effective performance.

Biological disruption method involves enzyme treatments (lysis). This method is operated at non-extreme conditions with low energy requirements. Chen et al. (2016) used cellulose, lipase and protease and thermal bath for lipid extraction from *Nannochloropsis oceanica*. The recovery efficiencies for lipid and protein were reported to be 88.3% and 62.4%, respectively. Challenges still exist as this method is relatively slow and the cost of enzymes can be high.

2.3.5 Lipid Extraction

After biomass is dried, lipid content is extracted from concentrated algae or directly from wet slurry phase. The efficiency of lipid extraction is highly dependent on the polarity of the organic solvent used. Solvent mixtures of polar and non-polar solvent have shown greater efficiency in lipid extraction (Ryckebosch et al., 2012). However, lipid extraction is still a challenge towards the commercial production of microalgal oil production as part of a downstream biorefinery, even though there are multiple extraction methods studied in many literatures. Biosafety of extraction solvents could be a concern in selecting biocompatible and non-toxic processes. In addition, lack of a standard extraction method for fatty acids analysis raises the importance to browse all possible oil extraction methods and determine the yield and suitability.

1. Bligh and Dyer Method

First published in 1959, Bligh and Dyer extraction is one of the most common and oldest lipid extraction method that is still used in many processes. It uses a solvent mixture of chloroform/methanol/water in a ratio of 1:1:0.9 v/v/v. The biological sample is mixed with the solvent mixture of exact ratio, then sufficient amount of water is added. This causes formation of biphasic system, leading to the partitioning into water-methanol rich upper layer containing protein and carbohydrates, and chloroform-rich lower containing lipids. A clear separation into two phases is then easy to be separated. Among all the lipid extraction methods available, Bligh and Dyer method is known to have one of the highest separation efficiencies. However, this method has a serious disadvantage in terms of safety, especially with the use of chloroform which is highly toxic and carcinogenic. In addition, since a phase separation is based on gravimetric force, a long settling time could be required in a large-scale application.

2. Modified Bligh and Dyer Method

In order to improve the above method, modifications were proposed to replace these toxic solvents. Especially, environmentally safer solvents are alternatively selected. A modified Bligh and Dyer method introduced by Hara and Radin (1978) used n-hexane/isopropanol in a ratio of 3:2 v/v to extract lipids from biological samples. Smedes (1999) later proposed the use of isopropanol/cyclohexane/water solvent mixture in a ratio of 8:10:11 v/v/v. Comparing the original Bligh and Dyer method with the modified versions, the results showed that the modified method had a slightly lower yield of lipids, potentially due to the high proportions of polar solvents.

3. Supercritical Fluid Extraction (SFE)

Supercritical extraction separates lipids from biological sample utilizing the supercritical carbon dioxide (CO₂) as the extracting solvent. In the SFE process, carbon dioxide diffuses into biological sample matrices and dissolves valuable chemicals using its solvent density properties. It is operated at moderate temperature and pressure for the separation stage. Then, a depressurizing setup releases final product to be solvent-free. Depending on the pressure and temperature, properties of carbon dioxide can be altered, thus this method could offer a wide range of extraction selectivity. In addition, a study by Solana et al. (2014) showed an enhanced extraction yield by adding ethanol as a co-solvent. Reaching the optimal operation temperature depending on the sample could also result in higher lipid yield up to 90%.

4. Ionic Liquid Extraction (IL)

Ionic liquids are organic salts that melt below 100°C. Similar to SFE, ionic liquids are considered to be less toxic to successfully substitute toxic and volatile organic solvents. ILs with chloride as the anion are known to be hydrogen bonding competitors. As a result, their hydrogen bonding interaction leads to interfacial formation when biomass sample with hydrogen bonding at cell boundaries are mixed. With ILs, direct lipid extraction from wet and undisrupted biomass is also possible. A study by Pan et al. (2017) extracted lipid from unbroken wet *Chlorella* sp. using choline chloride-acetic acid with reaction time of 60 min at 110°C.

[Bmim][MeSO₄] is another popular selection for lipid extraction from biomass. It dissolves biomass, leaving the lipids insoluble. The undissolved lipids then form a separated lipid phase

due to the lower density, making it easy to be isolated. Furthermore, ultrasound irradiation could highly enhance the extraction rate and yield with ILs by strengthening mass transfer of liquid-liquid systems. A study by Kim et al. (2013) compared the lipid extraction efficiency by [Bmim][MeSO₄] and with ultrasound assistance. It showed that with ultrasound, the extraction rate was 2.7 times greater.

Non-volatility, thermal stability and operation simplicity are benefits of ILs. The main concerns would be their relatively high cost, which could require the study of recycling efficiency. Their high viscosity and moisture sensitivity could limit their usage in various fields.

2.3.6 Transesterification

After lipid extraction, the resulting mixture consists of lipids, extraction solvent, residual water, and cell debris. Various separation methods including filtration, distillation, vacuum evaporation and solvent adsorption are used to isolate and purify extracted lipids. After large and branched fatty acids (FA) are converted into smaller, straight-chained fatty acid alkyl esters (FAME) (i.e. biodiesel) and glycerol via reaction with alcohol in the presence of a catalyst (Tan et al., 2009). Among possible alcohols, methanol is the most frequently used. For transesterification process, catalysis and in-situ methods are widely studied and commercialized. There are three most known types of catalysts: alkalis, acids and enzymes.

1. Catalytic Transesterification

Most of the commercial biodiesel production requires the use of a catalyst to accelerate the reaction, which later requires a separation step to recover pure biodiesel from catalyst and other residual chemicals. Several transesterification processes using acidic catalysts, alkali catalysts, enzymatic catalysts and nano catalysts have been reported.

The most common acidic catalyst is concentrated sulphuric acid. By using solid acid catalyst, additional separation step is unnecessary, and the solid catalyst could be reused again. Study by Li et al. (2008), a mixture of methanol and sulphuric acid is added into lipids in a ratio of 3:1 and reacted for about 2 hours at 80°C. Disadvantages of this method include equipment corrosion, high reaction temperature, long reaction times and weak catalytic activity.

Alkaline catalyst transesterification involves a base catalyst ($\text{pH} > 7$) such as sodium hydroxide, potassium hydroxide and sodium methoxide. It can be performed at low temperature ranges close to alcohol boiling point, and results in high conversion rate within a short time. Vladimir et al. demonstrated homogeneous transesterification of lipids extracted from *Chlorella vulgaris* using 0.42 wt% sodium hydroxide in methanol at 43°C for 90 min. After distillation, the final free fatty acid yield was 98% (Plata et al., 2010).

Enzymatic transesterification commonly refers to the addition of lipase, which catalyzes methanolysis reactions. They do not form emulsions, which requires additional washing and purification steps to isolate biodiesel. On the other hand, these reactions are often slow, and can go inactive depending on the amount of methanol added to the system. Kose et al. (2002) demonstrated a lipase-catalyzed transesterification with methanol in the presence of Novozym 435. The reaction was proceeded at 50 °C, with 1:4 lipid to alcohol ration and 30 wt% enzyme concentration. The final product conversion rate was 92% after 24 h. Similarly, a study by Royon et al. (2007) used Novozym 435 at the same condition, but with tert-butanol as a solvent, which resulted in 97% conversion rate after 24 h. Long reaction time and higher catalyst cost hinder this method to be selected for industrial processes.

Nanocatalysts have emerged as a novel material as it converts crude lipids into FFA through a cheaper and simpler process with lower water consumption (Akubude et al., 2019). CaO is one of the most common nanocatalysts explored for algae biodiesel production. Siva and Marimuthu (2015) used CaO extracted from eggshell to catalyze methanol transesterification. The reaction was set up to be at 9:1 methanol to oil ratio, 1.25 wt% catalyst loading at 55 °C, which resulted in 96.3% conversion rate. The fact that CaO is produced from eggshell suggests a potential to incorporate the use of residual biomass from MSW.

2. In-Situ Transesterification

In-situ transesterification reacts biomass directly with alcohol without lipid extraction step. The oil-bearing biomass is ground and reacted directly with the alcohol and catalyst to produce biodiesel. Simultaneous transesterification is shown to generate higher FFA yield (Nelson et al., 1996) Based on research by Vicente et al. (2004), in situ technology is used to extract and produce biodiesel from microalgae biomass with acid catalysts, BF_3 , H_2SO_4 and HCl , and methanol. After 8 h of reaction at 65 °C, the product conversion rate was 99%. For in-situ

transesterification, acidic, alkali and enzymatic catalysts can be all used similar to the conventional transesterification methods.

2.3.7 Post-Treatment Stages of Lipid Products

Following transesterification of microalgal lipid content, a mixture of biodiesel, glycerol, methane, and other residual chemicals must be separated into each content. The product will then undergo post-transesterification purification to isolate pure biodiesel product. The purification step is already highly standardized.

The first step of purification is separation of crude glycerol and alcohol (Huang et al., 2008). Although biodiesel is the main desired product, glycerol is another important product that could be utilized in different industrial products including moisturizers, soaps, cosmetics, medicine, etc. In a crude mixture, the produced glycerol has a purity of 50% or less and contains water, salts, unreacted alcohol and catalysts. Hydrochloric or sulphuric acids are added to the glycerol phase for re-neutralization and produce salts. Vacuum flash process is then operated to vaporize unreacted alcohol. It is then condensed back into liquid and reused in the process. Additional distillation stage could recover 99% or higher purity glycerol.

After separation from the glycerol phase, crude biodiesel is composed of residual catalyst, water, unreacted alcohol, residual glycerol and biodiesel. The mixture enters a neutralization step for catalyst, and alcohol stripping process (Dhar & Kirtania, 2009). Distillation process is then operated to remove all the residuals. With the separated crude biodiesel, warm and slightly acidic water is used to wash down contamination and remaining catalysts. After washing multiple times, biodiesel and water phases are separated.

2.3.8 Production of Other By-Products

Residual microalgae biomass after lipid extraction are still highly valuable as it is rich in proteins and other compounds of commercial interest. Instead of disposing, this residual biomass can be further processed to produce valuable materials including bioethanol, bio-oil, biogas, bioplastic, pigments, and many more through biorefinery schemes. *Chlorella vulgaris* was selected as a main model of microalgae. Additional sub-sections may provide other production pathways using different types of microalgae as feedstock, opening up the possibilities to incorporate various biomass options in a biorefinery design.

1. Bioethanol

Carbohydrates can be upgraded into bioethanol through enzymatic hydrolysis followed by fermentation with yeast. Microalgae can contain 40-60% of structural and storage carbohydrates (Doan et al., 2012). Hydrolysis of *Chlorella* carbohydrates by dilute sulfuric acid pretreatment was shown as an efficient strategy to increase total biomass utilization, based on study by Laurens et al. (2015). This approach produces fermentable sugars while making the lipid and protein fractions more extractible. The sugar solution can be separated from the residual biomass via solid-liquid extraction with hexane solution. The remaining slurry after pretreatment was filtered and fermented with *Zymomonas mobilis* at pH of 5.8 at 33 °C for 29 hours. The final ethanol yield of 78 wt% relative to theoretical number of fermentable sugar content.

2. Protein

Microalgae biomass originally has up to 60% of protein content. Protein extracted from microalgae has a lot of potential applications, including food additives, enzymes, nutraceuticals and probiotics. Protein purification can be performed by precipitation, concentration using ultrafiltration, HPLC and foam fractionation. A study conducted by Ursu et al. (2014) tested protein extraction efficiency via precipitation at pI and concentration using tangential ultrafiltration (300 kDa MWCO). With the first method, cell residue after lipid extraction was solubilized into an alkaline solution then progressively reduced pH from 12 to 4 using 1 M HCl to precipitate proteins. The second method used tangential ultrafiltration at room temperature and 1.5 bar for five times. The result showed isoelectric precipitation by pH shifting yielded 76 wt% of protein extraction.

3. Pigments

Natural pigments exist in microalgae cells, including carotenoids, chlorophylls and phycobiliproteins. These pigments can also be used as precursors of vitamins in food and pharmaceutical applications. Carotenoids are fat-soluble pigments which give visible colour to plants. Chlorophylls are hydrophobic pigments present in photosynthetic organisms. Lastly, phycobiliproteins are the major photosynthetic pigments in microalgae with antioxidants, antiviral, anti-inflammatory properties (Taher et al., 2011). Various separation and purification methods are currently available and are combined with lipid extraction step. Pasquet et al. (2011)

extracted chlorophyll via suspension with acetone under argon atmosphere to inhibit photo-oxidation. The extract was filtered onto PVDF membrane filters and purified by HPLC.

4. Biopolymers/Bioplastics

Biopolymers are organic-driven material from renewable biomass sources such as vegetable oil, starch, and microalgae. Microalgae biopolymers can be produced from two pathways: 1) carbohydrate-based and 2) protein-based bioplastics. After lipid extraction, about 30% of biomass is composed of cellulose, which is an excellent feedstock for carbohydrate-based bioplastics (Taher et al., 2011). Also, biomass is originally composed of about 55-58% protein. The most common production pathway is through compression molding where a mixture of biomass, polymers and additives are placed in a mold and compressed at elevated temperature and pressure to form a composite material. Zeller et al. (2013) successfully protein-based bioplastics from *S. platensis* and *C. vulgaris* using compression molding at 150 °C for 20 min.

2.4 Municipal Solid Waste (MSW)-Based Biorefinery

Municipal solid waste (MSW) is defined as solid waste generated from residential and commercial institutions. Studies have suggested that MSW generation may exceed 2 billion tons annually worldwide, which is a serious concern for health and environmental issues if handled and disposed inappropriately (Qdais et al., 1997). Since MSW is composed of a large variety of materials, hierarchy in processing order is proposed in order: 1) reduce waste, 2) reuse, 3) recycle of recyclable components, 4) treatment and heat recovery, and 5) landfill disposal. [78] The study will focus on the alternatives for: 1) separation, 2) recycling and 3) treatment and conversion into valuable products.

Currently, the majority of MSW is landfilled in most countries. However, rapid accumulation of MSW, increasing cost of landfills, and subsequent environmental issues emphasize the need to find alternative methods to handle MSW and potentially produce value-added products. Being aware of its nutrient and energy content, effective waste treatment could generate renewable energy and products. Therefore, waste-to-energy analysis of MSW biorefinery could help manage increasing demand of energy.

2.4.1 MSW Segregation

About 1/3 of MSW consists of various solid components including food waste, paper, plastic, wood waste, glass, metal, textile, etc. (Qdais, 1997). Segregation step is to primarily recover recyclable components. Such valuable component will be collected based on final purpose then sent to treatment stage.

Segregation or sorting is the process of separating MSW into groups of organic, inorganic, recyclables and hazardous wastes. Sorting can be carried out manually through mechanized systems, which includes unloading of waste, manual spreading, hand picking visibly identifiable waste for reuse, collecting and stockpiling of the remains (Alamgir & Ahsan, 2007). Size reduction of waste through shredders and crushers and separation based on size, density, magnetic forces using screening devices can be carried out using fully mechanized sorting process (Ohri & Singh, 2011). Depending on the region, climate and population density, MSW component varies drastically. Therefore, most studies had solid assumptions on MSW composition, landfill area and other parameters to design the optimal segregation facilities (Khan et al., 2016).

2.4.2 Recycling of MSW

After sorting and collecting, valuable solid materials such as paper, plastic, glass, metal and textile that can be directly recycled are sent to material recycling facility (MRF). MRF is where all solid wastes are further separated, processed and stored for later use as raw materials for manufacturing and reprocessing (Dubanowitz, 2000). In addition, the classification of MSW and availability for recycling could vary depending on legislation. The study by Dubanowitz (2000) estimated MRF in New York City to be 16 acres of land and cost \$127 per ton of solid wastes, based on an assumption of 150 tons per hour processing rate. This would correspond to about \$46 million savings annually in waste management.

2.4.3 Treatment and Conversion of MSW

The recovery of value-added chemicals from MSW is crucial for reducing the amount and cost of landfill disposal. Major constituents of MSW are organics. Various potential alternatives exist to produce multiple recovered products including biofuel, syngas, bioethanol, biogas and electricity. Only the part of MSW that cannot be further process will be sent compost or landfill.

The following section will explain various processing alternatives and their resulting yields for energy production.

1. Gasification (Syngas)

Gasification is a thermo-chemical partial oxidation reaction that converts carbonaceous materials into carbon monoxide, hydrogen and methane by reacting the material at above 700 °C with a controlled amount of oxygen and/or steam (Khan et al., 2016). Gasification process is used to produce syngas through methyl carbonylation and hydrogenolysis reactions (Consultancy, 2013). Most biomass gasification use air instead of oxygen, which significantly reduces processing cost for large plants. Syngas is produced through three consecutive processes: 1) synthesis gas generation, 2) waste heat recovery and 3) gas processing. Depending on the chemical reaction route it takes, a wide variety of syngas can be produced ranging from hydrogen to carbon monoxide.

Gasification of MSW has been applied to generate other valuable products, including electricity, heat, and ethanol. Especially, a concept of trigeneration refers to the simultaneous generation of electricity, heat and cooling as an extension of cogeneration. Rentizelas et al. (2009) conducted a study on trigeneration biomass gasification plant with a gasifier in a rotating fluidized bed producing around 2.0 MW of electrical energy and 4.5 MW of thermal energy. In addition, Combined Heat and Power (CHP) process combines biomass gasification and a gas engine for heat and power production, which has high biomass to power efficiency potential of 35-40%. Damartzis et al. (2012) utilizes CHP biomass bubbling fluidized bed gasification unit in conjunction with an internal combusting engine (ICE) based on Aspen Plus simulation.

2. Anaerobic Digestion (Biogas)

The organic fraction of MSW could be processed via anaerobic digestion to degrade the organic matter into biogas. With the absence of oxygen, various microorganisms break down carbohydrate, protein, and lipid polymers into soluble molecules and produce methane gas, which is also known as biogas (Wang, 2018). AD process is considered as a reliable process as it has less impact on air quality than combustion dependent processes and minimizes GHG emissions. Also, the by-product of AD could be an alternative to chemical fertilizers. The construction cost of AD processes is also relatively low. Factors such as pH and temperature

could highly affect gas production efficiency as there are multiple pathways the reaction could take place.

3. Plasma Arc Gasification (Syngas)

Plasma arc gasification is a thermal process at a very elevated temperature, between 2000 to 14,000°C by plasma. In the presence of oxygen, MSW is exposed to plasma heat and converted into syngas, which is mostly composed of carbon monoxide and hydrogen (Paulino et al., 2020). Especially, plasma gasification converts nitrogen and sulphur content in the feedstock to nitrogen gas and hydrogen sulphide, without forming GHGs like nitrogen oxide and sulphur dioxide. Also, it is considerably environmentally friendly as it only produces inert slag and minimal air pollutants. With this method, there is a possibility of recovering high purity hydrogen as a product as well.

4. Pyrolysis (Bio-oil)

With the absence of air, MSW is heated to produce gases, bio-oil and char. Pyrolysis has a relatively high energy recovery efficiency compared to other thermochemical processes. In addition, it showed high bio-oil product yield after only a very short reaction residence time of less than 3 seconds at the maximum reaction temperature (Dong et al., 2019). Other by-products can also be utilized for other purposes, which increases the overall efficiency of the process while reducing GHG emissions. Studies have shown that the compositions of MSW can vary the product yield and composition. Different temperature and residence time must also be applied for different sample to reach the optimal processing pathway.

5. Incineration

With the drastic increase of waste due to continued population growth and industrial revolution, incineration is one of the oldest MSW management systems applied commercially (Dong et al., 2019). Some advantages of incineration process include easy recovery of heat and remaining materials (ash), and high volumetric reduction efficiency. Despite the process and economic advantages, pollution from incinerators was the major concern. Therefore, government regulations are currently strictly controlling the emission limits. There are various combustion technologies including movable grates, fluidized grates and rotary kilns.

To combat the emission issues regarding incineration processes, air pollution control technologies have been developed. One example is re-circulation of flue gases which increases thermal capacity and reduces GHG generation during combustion (Shi et al., 2018). The use of catalysts have also aided in suppressing the formation of NO_x and SO_x gases (Yufei et al., 2008).

6. Composting

The remaining organic materials are decomposed under controlled aerobic conditions with temperature of 55 °C or higher (Sabki et al., 2018). The final product of this process is called compost. Composting is considered as a sustainable management of organic wastes since the organic compost matter reduces in volume and the process avoids the risk of pathogen infections if it is directly wasted to landfill. Some industries such as farming, sugar and wine industries use the compost as a fertilizer or organic amendment, which saves cost for commercial chemical fertilizers. Multiple factors must be considered for composting environment such as initial water content between 45-75%, air humidity below 75%, turning frequency, and carbon to nitrogen ratio of 50:1 (Ruggieri et al., 2009). Currently, windrow technique is the simplest and the most accomplished method with standard equipment. Specialized windrow aeration equipment is developed and used for processes with large amounts of waste. Studies by Ruggieri et al. (2009) and Emery et al. (2007) demonstrated the environmental and economic modelling of composting process. The cost data include site development, pre-development, operation, gas capturing cost and post-closure.

7. Landfill

For the materials that could not be further processed to produce value-added products, or any remaining waste could be landfilled (Cudjoe & Han, 2020). Landfill still remain as an attractive disposal route for MSW due to its economic benefit. However, over time the organic materials will begin biodegradation, which results in voids between landfill settlement and deformation will lower structural strength of the land. Also, gas and leachate generation could be a significant environmental issue (Cudjoe & Han, 2020). Therefore, careful selection of landfill location as well as prediction of settlement are key issues in designing and constructing landfill sites.

2.5 Biorefinery Optimization Approaches and Challenges

Lockhart and Johnson (1996) defined optimization as “the process of finding the most effective or favorable value or condition.” In the engineering field, a systematic process using design constraints and criteria is applied for a systematic decision-making process with various uncertainties. With an assistance of quantitative tool, model could provide the optimal selection results. Especially for a biorefinery study, optimization techniques could be utilized to estimate the optimal supply chain, size, operational stages selection, energy requirement, and many more valuable information. By considering feedstock costs, chemical costs, operational costs, capital costs for the facilities, the final profit of a biorefinery system could be estimated as well.

Published studies established the combined optimization approach in techno-economic analysis for production of biodiesel, bioethanol, biogas, electricity and other value-added products. Many studies identify the most optimal pathways from the superstructure flowsheets, solving it with a mixed-integer programming. For instance, Slegers et al. (2014) proposed a model-based combinatorial approach for energy-efficient processing of microalgae into biodiesel. Elia et al. (2011) proposed a mixed-integer linear programming (MILP) model to analyze the US energy supply network for hybrid coal, biomass, and natural gas to liquid (CBGTL) plants. Martin and Grossman (2012) formulated a mixed-integer non-linear programming (MINLP) model to evaluate a superstructure for biodiesel production from cooking oil and algae, considering heat and water integration. Rizwan et al. (2013) proposed a superstructure-based modeling framework for the production of biodiesel from microalgae, solving the network system with MILP and MINLP for model comparison. In their follow-up study, (2015) the optimization was extended by adding microalgae residue processing and water recycling for wider aspects of process economics. Hytoenen and Stuart assessed the feasibility of integrated biofuel production from several feedstocks and conversion technologies under uncertainty. The study emphasized the inclusion of technical and market-based uncertainties in the assessment model so that the results consider wider range of potential risks.

Recent studies in bioenergy production technologies showed meaningful results in combining multiple feedstock conversion processes to reduce the need for separate processing. Advanced from multi-product biorefinery, which is a process network that produces multiple bioproducts from one feedstock, a multi-feedstock multi-product biorefinery is a network which begins with

multiple feedstock supply to product multiple valuable products. In addition, multi-feedstock nature helps secure feedstock availability under continuous operation throughout the year. Due to its complexity of network, an optimization study could be an effective method to optimize such process design. Recent studies that focused on integration of multiple feedstock sources to produce multiple products are organized in the table below.

Table 3 Multi-feedstock multi-product biorefinery studies

Feedstocks	Combined Processes	Major Products	References
Lignocellulosic biomass (black liquor, sawdust, straw, etc.)	Hydrothermal conversion	Lignin, syngas, bio-oil	Özdenkçi et al. (2017).
Cassava (agricultural crop)	Microalgae cultivation	Biogas	de Carvalho et al. (2018).
Microalgae			
Sewage sludge	-	Biodiesel	Hackl and Harvey (2010).
Edible waste oil			
Microalgae			
heat (barley, oat, ryegrass)	Hydrothermal pretreatment	Bioethanol	Zhang et al. (2018).
Poultry litter	Gasification	Biodiesel, gasoline, natural gas, electricity	
Forest residue	Dilute-acid pretreatment,	Bioethanol	Zhang et al. (2018)
Corn stover			
Winter Wheat Straw	Chemical conversions	Omega-3 acids, chlorophylls, lutein, etc.	Psycha et al. (2018).
Microalgae strains (<i>Dunaliella</i> , <i>Nannochloropsis</i> and			
Lignocellulosic residues (Bermuda grass, Jasmine hedges, date palm fronds)	Hydrothermal pretreatment, enzymatic hydrolysis	Glucose	Ashraf and Schmidt (2018).
Lignocellulosic biomass (switchgrass, crop residue)	Bioethanol processing stages	Bioethanol	Osmani and Zhang (2013).
Switchgrass	Bioethanol processing stages	Bioethanol	Osmani and Zhang (2017).
Crop residue			
Woody materials			

Although there have already been various studies on multi-feedstock multi-product biorefinery, most studies only focused on the integration of agricultural and forestry feedstocks. These feedstocks mostly share similar chemical characteristics and produce similar range of products. Thus, pre- and post-treatments as well as conversion techniques should be similar. However, as there has been growing interest in not only agricultural feedstocks but also various next-generation feedstock options, there is a need to browse possibilities in combined conversion methods and biorefinery network formation of other types of feedstocks including microalgae and MSW. Differences in feedstocks' chemical compositions and conversion technologies may

also have opportunities to recycle and reuse waste from one process to another. Therefore, this report will also suggest possible recycling routes within the integrated biorefinery.

2.6 Summary

This chapter introduced the biomass resources, bioenergy products, conversion technologies and common biorefinery stages of microalgae and MSW. The research motivation regarding the world energy supply and environmental issues are also discussed. A brief review on previous biorefinery studies showed that superstructure-based MILP and MINLP methods are commonly used for optimizing biorefinery network supply chain. However, studies in multi-feedstock multi-product biorefinery only limited to combination of agricultural and forestry products strongly suggested the need to integrate other types of biomass feedstocks. The next chapter introduces the main methodologies and tools utilized in this study.

3. Methodology and Problem Definition

A goal of this chapter is to introduce the systems design methodology utilized for this study, as well as outline the selected case study. In the first section of this chapter, process synthesis approaches including superstructure development and MILP optimization are introduced. Reasons for selecting a certain methodology is also outlined. In the second section, a case study problem for this study is outlined in a detail. Then in the following third and fourth section, the superstructure and the mathematical mixed integer linear programming model for developing the proposed multi-feedstock multi-product biorefinery network are outlined.

3.1 Process Synthesis Methodology

Conceptual process design in chemical engineering deals with defining, simulating, optimizing and controlling of chemical processes. The process network is depicted by numbers of simpler unit blocks, which are characterized by distinct physical and chemical properties. Each unit block could represent a single operation stage, storage location, or chemicals. Design task then involves the integration of the unit blocks to represent a complex chemical process. During the past decades, the Process Systems Engineering (PSE) community has achieved meaningful developments in methodological process synthesis research, which has developed several powerful mathematical optimization and simulation tools for chemical process design (Grossmann and Harjunkoski, 2019). Especially, Generalized Disjunctive Programming (GDP) and Mixed-Integer Nonlinear Programming (MINLP) methods are known to be ideal for solving problems with discrete numbers of process alternatives (Mencarelli et al., 2020).

In process synthesis, there are two main approaches to carry out a conceptual process design, identifying the optimal process flow and its operating conditions: hierarchical decomposition (Douglas, 1985) and superstructure synthesis (Umeda et al., 1972; Grossmann, 1996). First, hierarchical decomposition requires a sequential procedure of progressively defining a process at each stage or level. At each level, heuristic rules and engineering judgement are involved to determine changes in the flowsheet that may lead to an improved solution. Studies conducted by Douglas (1988), Dimian (2003) and Goh and Ng (2015) show thorough reviews on hierarchical decomposition method. Although this approach provides simplicity in implantation, it is difficult to interactions between different levels and can lead to sub-optimal designs.

On the other hand, superstructure synthesis method involves solving a simultaneous optimization problem using mathematical programming (Grossmann, 1996). This approach is composed of three main sequential steps: i) postulation of a superstructure; ii) translation of the superstructure into a mathematical programming model; and iii) computation of an optimal solution by solving the mathematical model. A successful superstructure must include all possible alternatives that can be potentially selected in the final flowsheet, as well as correct interconnection between the alternatives. As it involves solving of a mathematical model, a poorly constructed superstructure may lead to omission of several feasible and/or optimal solutions. Therefore, it is important to depict the problem as accurate as possible in the superstructure. All the alternatives, interconnections, and constraints for the operation within the network are then represented as a series of equations. These equations are incorporated in an optimization problem where an objective function is specified as, for example, cost minimization or profit maximization. Lastly, computation of an optimization problem is solved with a mixed integer linear (MILP) or non-linear program (MINLP) since the problem generally deals with the choice of discrete variables such as equipment and feedstock options. As a result, superstructure synthesis is more preferred for its possibility to systematically evaluate many structural alternatives. The following figure depicts the sequential steps taken to find the optimal solution in this study using superstructure synthesis methodology.

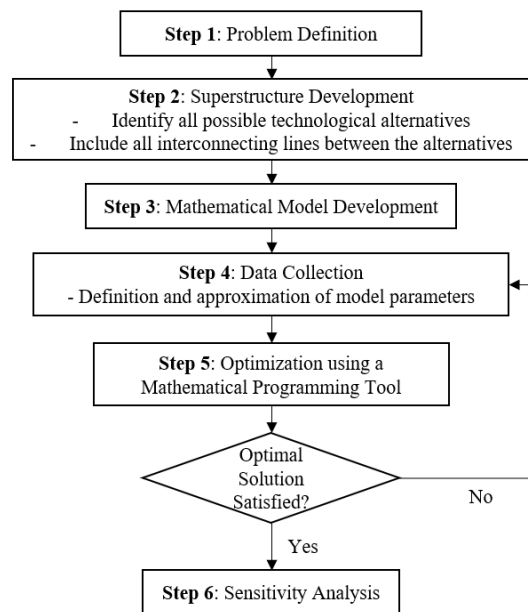


Figure 4 Sequential steps for superstructure synthesis methodology

In this study, superstructure synthesis is selected as a problem solving methodology. A biorefinery network is composed of diverse amounts of possible feedstocks and their processing pathways for the production of various products. Especially, with multiple feedstocks there are a larger number of possible process alternatives interconnected with each other in a more complex nature. A simplified superstructure network of a multi-feedstock multi-product biorefinery is depicted in Figure 5. A mathematical model solved by a programming tool is expected to simultaneously solve the complex nature of this network flow.

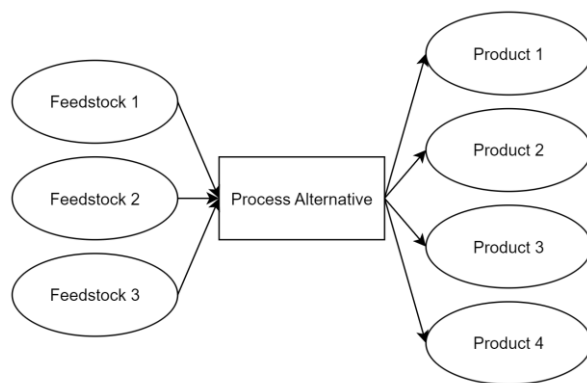


Figure 5 A simplified network of a multi-feedstock multi-product biorefinery

3.2 Problem Definition: A Case Study of Seoul Metropolitan Area, South Korea

The proposed methodology for superstructure process synthesis optimization is applied to the case of Seoul metropolitan area, South Korea. South Korea is a country in East Asia, with a population of 51.75 million. Seoul is a capital city of South Korea, and its metropolitan area is a geographical region of 12,685 km², containing a large population nucleus. The metropolitan area is about 12% of the country's area, however, roughly half of the total population of South Korea live in the Seoul metropolitan area. With population of 26 million as of 2020, it is the world's fourth largest metropolitan area (Korean Statistical Information Service, 2022). Rapid urbanization and drastic increase in population and economic growth have required government to deal with a substantial amount of municipal waste.

In Seoul's growth process, apartments, shopping malls, hospitals, and parks are located in the center of the city, while waste treatment facilities, sewage treatment facilities, and public garages

that support the city's functions are pushed into urban borders. Various wastes are generated every day in Seoul, and 15 material recovery facilities (MRFs), 4 large incineration facilities, 5 food treatment facilities, and a metropolitan landfill used by Seoul, Incheon, and Gyeonggi-do are being used for their treatment. Although the facilities were built after spending more than 20 years, they are far from sufficient to deal with the actual amount generated. The Seoul Metropolitan Government's current method of overcoming the insufficient processing base is active recycling. In 1995 and 2005, Seoul has implemented the Volume-Based Garbage Disposal (VBGD) and Pay-As-You-Throw (PAYT) systems, which charge cost per garbage bag for non-recyclable waste and food waste, respectively. As a result, Seoul metropolitan city's recycling rate has reached 68% in 2018, which is much higher than 26% recycling rate of New York City, as an example (NYDS, 2019).

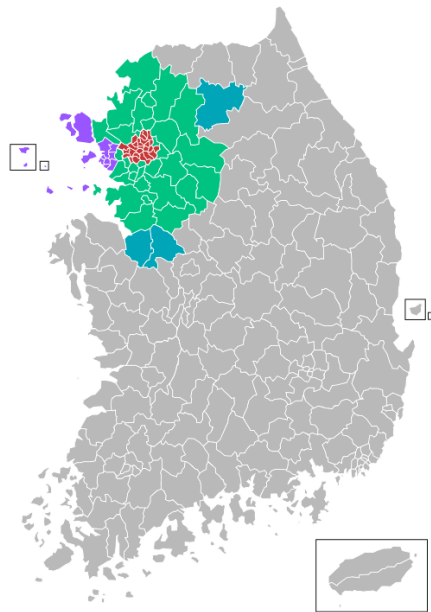


Figure 6 Map of South Korea, with coloured area being Seoul metropolitan area.

Currently, waste generated are processed in three ways: recycling 64%, incineration 27%, and landfill 9% (Ministry of Environment, 2014). The most urgent task in the field of waste management in Seoul is to curb landfill. This is because Seoul does not have its own landfills due to limitations in geographical space, and social rejection of landfills is greater than any other waste facility. Therefore, additional solid waste management and utilization alternatives must be developed and incorporated into current waste treatment plan.

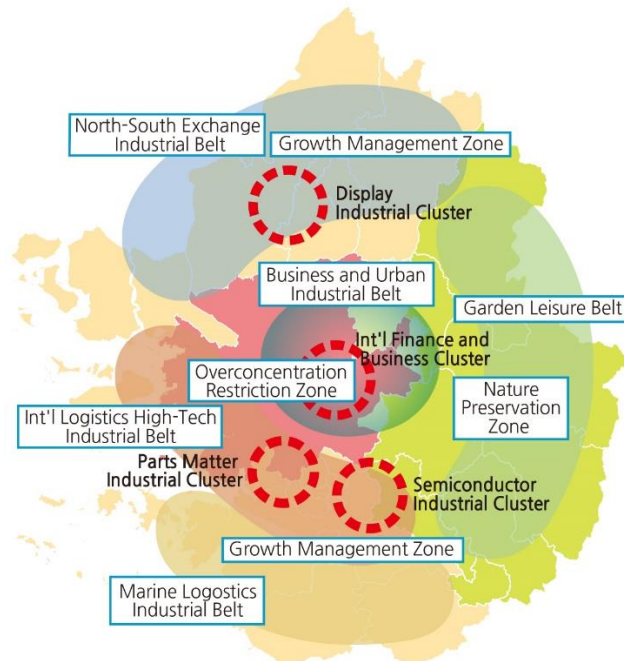


Figure 7 Seoul metropolitan area territorial planning (MOCT, 2006)

In addition, Korea has minimal fossil fuel resources and relies 99% of coal, oil and natural gas supply on imports. The country relies heavily on fossil energy, with oil taking up to 38% of primary energy supply, coal 29% and gas 15%. Nuclear power accounts for 16% and renewables for the rest (OECD, 2022). They were also ranked as one of the world’s biggest greenhouse gas emitters, with over 600 million tons of carbon dioxide emitted every year (MITE, 2013). The government has aimed to increase biofuel market share up to 5-7% by 2020. Although the country’s infrastructure is capable of reaching the goal, biodiesel in Korea is mainly derived from palm oil imported from Indonesia and Malaysia, and vegetable oil imported from Argentina and Brazil (KETEP, 2011). To lessen the dependence of foreign biofuel sources, the Korean government released “Green Energy Strategic Roadmap 2011” stating that algal biomass could be the main fuel feedstock that sufficiently meets the biofuel demands of South Korea without causing food shortages or environment issues.

One of the largest microalgae cultivation establishments in Korea is a 4,000 m² raceway facility at Chilgok-gun Agricultural Technology Center, conducted by the research group ABRC at Kyungpook National University. Freshwater microalgae strains were mass-produced for 3 consecutive years since 2013, and the raceways covered in a semi-transparent film cover was compared with the ones without to compare the yield of biomass under monsoon and winter

seasons in Korea (Hong et al., 2015). More recently, The Ministry of Trade, Industry, and Energy (MTIE) and the local government of Gyeongsangbuk-do are planned to construct a 73,000 m² pilot plant for microalgae biofuel production, with a customized microalgae cultivation system.



Figure 8 a) Experimental raceway pond in a glass greenhouse at Chilgok-gun Agricultural Technology Center (Yoon, 2012), **b)** Design drawing of the algae biofuel pilot plant (Gyeongsangbuk-do, 2010)

To conclude, Seoul metropolitan area is determined to be a suitable location of study, that could cultivate microalgae as well as gather enough amount of MSW. Studying opportunities to utilize MSW and microalgae, as well as integrate the two feedstocks into one integrated biorefinery is expected to bring meaningful economic and environmental effects to energy supply and management of Seoul metropolitan area.

3.2.1 Problem Parameters and Assumptions

MSW in Seoul is largely divided into residential waste and commercial waste. In Seoul, 3332 thousand tons of residential waste and 745 thousand tons of commercial waste are generated per year. The estimated composition of MSW is 35% papers, 7% glasses, 10.5% metals, 5.5% plastics, 33.5% food waste, 6% wood waste, and 2.5% rubber. About 38.95% of total MSW are recyclables, in which 91.88% are successfully recycled (Yi et al., 2011).

For microalgae strain, *Chlorella vulgaris* (31.5% lipids, 54.5% proteins and 14% carbohydrates) is selected for this study. It is assumed that 4,000 m² raceway ponds and photobioreactors are available for cultivation. Seasonal variations in microalgal growth rate are ignored.

3.3 Superstructure Formation

Following the sequential problem solving steps outlined in Figure 4, superstructure was initially constructed after problem identification. The final superstructure included all possible technological microscopic and macroscopic process options up to date that could convert microalgae and/or MSW. Figure 6 is the constructed biorefinery superstructure that encompasses both microalgae and MSW processes.

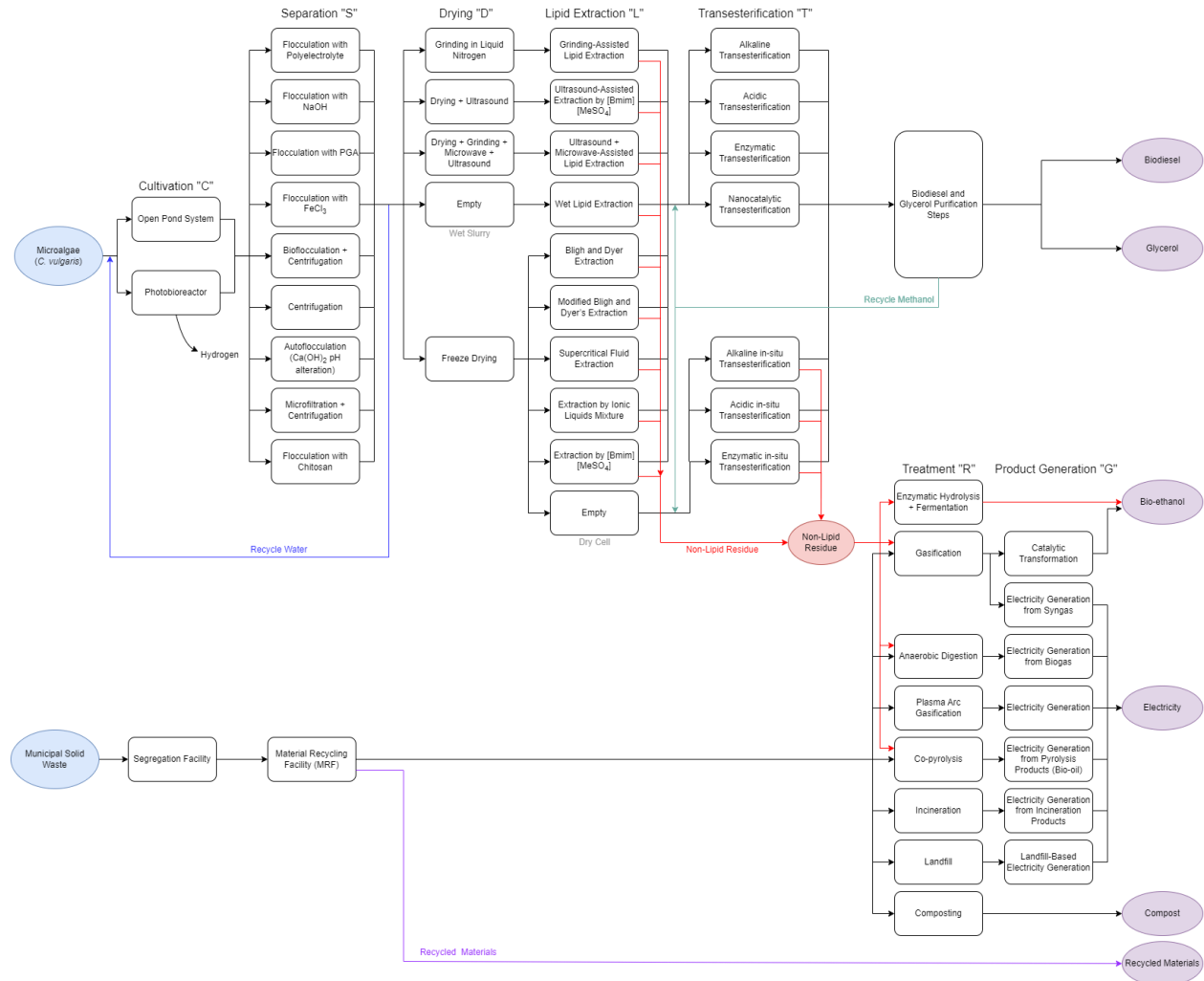


Figure 9 Superstructure of a microalgae + MSW multi-feedstock biorefinery design

From a macroscopic view, there are six processing stages for microalgae and four processing stages for MSW to be converted into final products that are currently of demand worldwide and could be sold. The feedstocks, intermediates and final products are color coded in blue, red and purple, respectively. Rounded squares represent individual processing facility/technology options

that could be selected. The final products from this biorefinery design are biodiesel, glycerol, bioethanol, electricity, compost, and recycled materials. The intermediate products after each process alternative exist yet not represented, except non-lipid residues, in this figure for simplicity. Initially, the two feedstocks enter the processing route separately. However, after certain stages, intermediate products derived from two feedstocks could be processed together and generate valuable products. Table 4 briefly outlines descriptions of microalgae and MSW processing stages.

Table 4 List of microalgae (*C. vulgaris*) and municipal solid waste processing stages

Feedstock	Processing Stage	Index	Description	Technical Alternatives
Microalgae (<i>C. vulgaris</i>)	Cultivation	c	Growth of microalgae in a culture media	Open pond system, Photobioreactor
	Separation	s	Harvesting of cultivated microalgae biomass from culture media	Flocculation with polyelectrolyte, Flocculation with NaOH, Flocculation with PGA, Flocculation with FeCl ₃ , Bioflocculation, Centrifugation, Autoflocculation, Microfiltration, Flocculation with chitosan
	Drying	d	Complete removal of moisture from microalgae biomass, disruption of cell walls to prepare for material extraction	Grinding in liquid nitrogen, Drying+ultrasound, Drying+grinding+microwave+ultrasound, Freeze drying, Empty*
	Lipid Extraction	l	Extraction and isolation of lipid content from biomass	Grinding-assisted, Ultrasound-assisted by [Bmim][MeSO ₄], Ultrasound+microwave-assisted, Bligh and Dyer, Modified Bligh and Dyer, Supercritical fluid extraction, Ionic liquid extraction, Extraction by [Bmim][MeSO ₄], Empty*
	Transesterification	t	Chemical conversion of lipid content into biodiesel and glycerol	Alkaline, Acidic, Enzymatic, Nanocatalytic, Alkaline in-situ, Acidic in-situ, Enzymatic in-situ
	Biodiesel and Glycerol Purification	p	Post-treatment of biodiesel and glycerol into product grade (99% purity)	Biodiesel and glycerol purification steps (distillation+vacuum flash+neutralization+alcohol stripping)
MSW	Segregation Facility	j	Segregation into different categorization of waste material	Segregation facility
	Material Recycling Facility	k	Separation of recyclable materials (plastics, paper, textile, glass, metals)	Material recycling facility (MRF)
Microalgae (<i>C. vulgaris</i>) + MSW	Pre-Treatment	r	Pre-treatment of residues of microalgae and MSW for product generation	Enzymatic hydrolysis+fermentation, Gasification, Anaerobic digestion, Co-pyrolysis, Incineration, Landfill, Composting
	Product Generation	g	Generation of value-added products (bioethanol, electricity, etc.)	Catalytic transformation, electricity generation methods

The combined processes have shown synergistic results in terms of process efficiency and product yield in various studies. For example, co-pyrolysis of rural solid waste with *C. vulgaris* resulted in improved quality of bio-oil product with low cost process requirements (Tang, 2020). Anaerobic co-digestion of microalgae and solid wastes also showed increased biogas yield as well as digester organic loading rate (Solé-Bundó, 2020). The non-recyclable content of MSW and non-lipid content of microalgae will be therefore sent to various treatment and product generation stages to produce bioethanol and electricity (derived from syngas and biogas).

In addition, the directions of arrows represent the sequence of stages. The black arrows are the interconnection of processing options which produces major products from microalgae and MSW, while other colored arrows represent side components of this biorefinery. Table 5 is a list of arrows and their process descriptions.

Table 5 Description of color-coded arrows in the superstructure

Arrow Color	Description
Black	Main processing routes of microalgae (lipid content) and MSW (non-recyclables)
Red	Processing route of non-lipid residue from microalgae biomass after lipid extraction stage
Purple	Recyclable materials production
Blue	Recycling route of separated water content back into microalgae culture media
Green	Recycling of recovered, unreacted methanol back into transesterification stage as a reactant

As shown in the superstructure, scope of this study included discovery and analysis of material recycling and reuse within the biorefinery for possible economic and environmental advantages. Following the blue-colored arrow, the culture media is recovered from biomass culture via separation process and reused again to cultivate biomass again. Recycling of culture media could significantly reduce the operation cost as cultivation of microalgae needs a large amount of water to maintain dilute biomass concentration for maximum cultivation efficiency.

Methanol is another chemical that could be recycled within the process, which is represented as green arrows. Transesterification reaction theoretically requires molar ratio of methanol to lipid to be 3:1, and in most lab and industrial scale reaction excess methanol is added to push the reaction equilibrium further to the right and produce as much biodiesel as possible (Heo & Lee,

2019). Therefore, the unreacted methanol could be recovered during the post-transesterification purification stage and recycled.

In addition, there exists “empty” boxes in the superstructure which represents the entire bypass of the certain stage of process. The purpose of this box is to collect all the intermediate products from the previous stage and send directly to the following stage for further downstream processing in a mathematical model.

Moreover, about the arrows in a microscopic view, the modelling is done in a way that each processing alternative can go to multiple possible subsequent stages, rather than combining all the resulting intermediate products first, then split into multiple stages. The following figures are the detailed microscopic view of how individual alternatives are interconnected with subsequent stage alternatives.

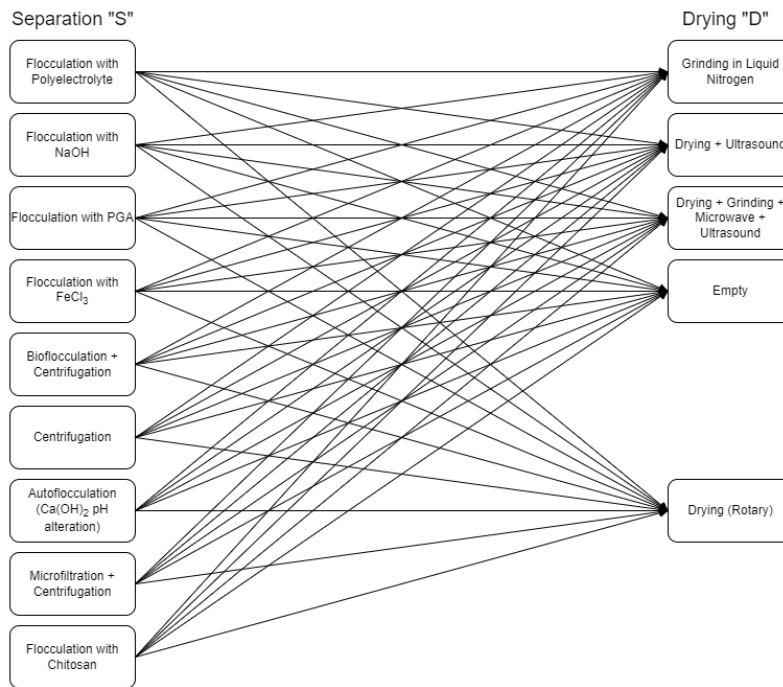


Figure 10 Detailed interconnection representation between separation and drying stages of a biorefinery

As seen in Figure 7, all nine process alternatives in separation stage could be connected to five drying stage alternatives. Therefore, there are five arrows going out from each separation stage alternative.

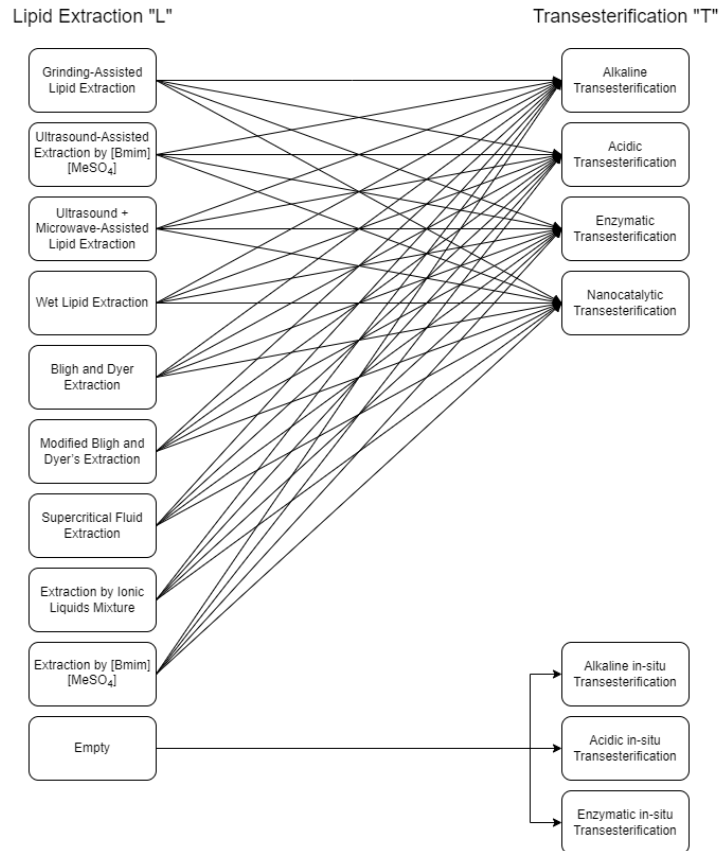


Figure 11 Detailed interconnection representation between lipid extraction and transesterification stages of a biorefinery

Figure 8 indicates that all lipid extraction stage alternatives except the last “empty” process could be connected to the first four transesterification process alternatives. On the other hand, the intermediate products collected at the “empty” box are to be sent to the last three transesterification process alternatives, which are in-situ processes. In-situ means “in the reaction mixture,” so that no separate lipid extraction is required (Velasquez-Orta et al., 2012). Instead, the reaction simultaneously extracts lipid content from microalgal biomass and chemically converts it into biodiesel and glycerol products.

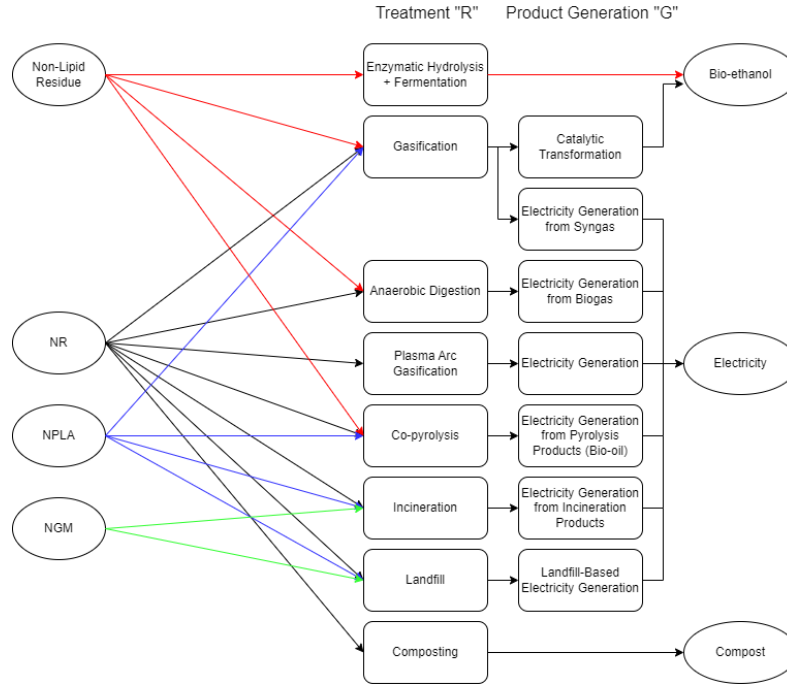


Figure 12 Microscopic Interconnection from intermediate products to treatment stage

Lastly, as shown in Figure 9, non-recyclable contents of MSW are divided into three groups, in terms of which process option they are able to enter. For instance, anaerobic digestion could only convert non-lipid residue from microalgae and NR content from MSW into biogas. A clear representation of how the materials are categorized and sent to the following processing stages could significantly affect the mathematical model that is to be constructed.

3.4 Mathematical Model

Formulations of mathematical model to optimize biorefinery were written for each processing stage. Process aim is profit maximization, with consideration of demand of each product assumptions. Switching constraints for maximum process load is not listed, but included in the GAMS code, if applicable.

$$\max Profit = \max (Sales\ of\ products - feedstock\ cost - production\ cost) \quad (3.1)$$

$$Sales\ of\ products = \sum_{i1} PRODC_{i1} * FPUR_{i1} + \sum_m PRODM_m * FINAL_m + \sum_k RECYC_k * RECYCLE_k \quad (3.2)$$

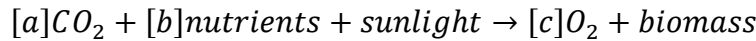
$$Feedstock\ cost = \sum_{ST} FEEDC_{ST} \cdot FEEDF_{ST} \quad \forall ST \quad (3.3)$$

$$\begin{aligned}
\text{Production cost} = & \sum_c \text{COST}C_c * FCO2_c + \sum_s (\text{COST}S_s * \sum_a FSEPI_{s,a}) + \sum_d (\text{COST}D_d * \\
& \sum_{B1} FDRYI_{B1,d}) + \sum_{D1} (\text{COST}D1_{D1} * \sum_{B1} FDRY_{B1,D1}) + \sum_{L2} \text{COST}L2_{L2} * FLIPI_{L2} + \\
& \sum_t \text{COST}T_t * FTRAI_t + (\text{COST}P_p * \sum_t FTRA_t) + \text{COST}G * FEEDF_{st2} + \text{COST}R * \sum_j MSEG_j + \\
& \sum_f \text{COST}F_f * FTREAT_f
\end{aligned} \tag{3.4}$$

Microalgae strain *c. vulgaris* (CV) is considered as a model species for this study as it is widely studied and utilized in many industrial processes. The process data of *c. vulgaris* is taken from the published literature.

- Cultivation of microalgae

The proposed microalgae-based processing network starts with the growth of microalgae.



The amount required for the cultivation of microalgae are calculated on the basis of elemental composition of microalgae [32] described by Dassey et al. [33]. Since carbon takes up about 52% of the microalgae's elemental composition, the amount of carbon dioxide required to produce algal biomass can be calculated to be 1.9g CO₂/g biomass. In addition, the nutrient requirement is assumed to be satisfied by supply water content as well as the remaining nutrients recycled from harvesting stage.

$$\frac{g CO_2}{g biomass} = \frac{44 g/mol \times 52 C\%}{1200 g/mol} = 1.9 g CO_2/g biomass$$

The inlet streams are carbon dioxide, water, and nutrients mixture. The inlet water stream is the combined stream of freshwater and recycled water from other processes within the superstructure. The outlet streams are cultivated microalgal biomass, water and nutrients remaining in the water.

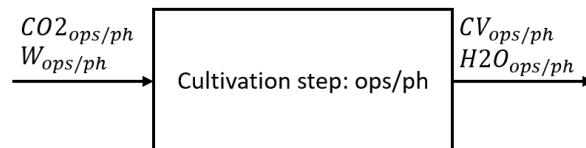


Figure 13 Unit operation of cell cultivation stage

For the case of open pond system, it was assumed that there is a 14% water loss due to evaporation [34,35]. In addition, light is essential for microalgae growth, so only daytime operation is considered for open ponds system.

$$FEEDF_{st1} = \sum_{c \in C} FCO2_c \quad \forall c \quad (3.5)$$

The flowrate of product culture is calculated by mole ratio with carbon dioxide supply.

$$FCULT_{c,a} = FCO2_c \cdot CONV_{C_{c,a}} \cdot YC_c \quad \forall c, a \quad (3.6)$$

- Cell Separation

The concentration of biomass at the inlet of the separation stage depends on the specific alternative selected at the cultivation stage. It is assumed that the concentration of microalgae is 1.5 g/L and 4 g/L for the open pond system and photobioreactor, respectively [3,36]. In addition, 90% of the harvest water with dissolved nutrients is recycled and reused for the growth of microalgae at the previous cultivation stage, while the remaining moisture is further dried in the next drying stage.

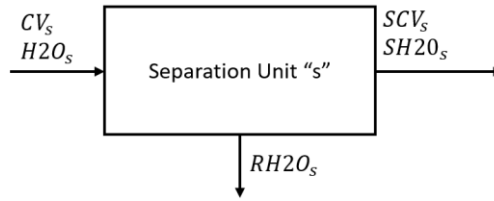


Figure 14 Unit operation of cell separation stage

$$\sum_{c \in C} FCULT_{c,a} = \sum_{s \in S} FSEPI_{s,a} \quad \forall c, s, a \quad (3.7)$$

$$FSEP_{a,s,b} = FSEPI_{s,a} \cdot CONV_{S_{a,s,b}} \cdot YS_s \quad \forall a, s, b \quad (3.8)$$

- Recycling of Spent Culture Medium (Water)

The flowrate of water required in cultivation stage can be expressed in terms of carbon dioxide stream multiplied by specific mass ratio.

$$W_c = WREQ_c \cdot CO2_c \quad \forall c \quad (3.9)$$

To calculate the amount of water recycled from separation stage:

$$FRH2O_{B2} = \sum_{a \in A} \sum_{s \in S} FSEP_{a,s,B2} \quad \forall a, s, B2 \quad (3.10)$$

Water collected after separation stage is combined and recycled in microalgae cultivation. Therefore, the total amount of water that goes into the open pond system and photobioreactor is equal to the sum of total recycle water and fresh water.

$$\sum_{c \in C} W_c = \sum_{b \in B2} FRH2O_{B2} + FH2O \quad (3.11)$$

- Cell Drying

Four technological alternatives are included at the pretreatment stage by considering various combinations of drying, grinding, microwave, and ultra-sonication. Thus, the pretreatment can be performed in a single step or multiple sub-steps, or the pretreatment step can be bypassed entirely which is modeled using empty box. The bypass of this stage is considered for the wet lipid extraction method in the next processing stage.

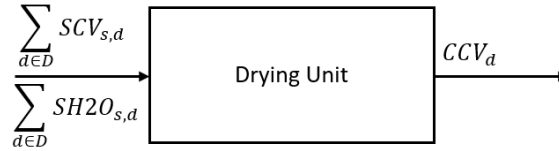


Figure 15 Unit operation of cell drying stage

$$\sum_{a \in A} \sum_{s \in S} FSEP_{a,s,B1} = \sum_{d \in D} FDRYI_{B1,d} \quad \forall a, s, d, B1 \quad (3.12)$$

The output stream from each drying alternative is dried microalgal biomass.

$$FDRY_{B1,d} = FDRYI_{B1,d} \cdot CONVD_{B1,d} \cdot YD_d \quad \forall B1, d \quad (3.13)$$

- Lipid Extraction

For lipid extraction stage, nine technological alternatives are included in the superstructure depending upon the options/conditions of the preceding stage. Empty box, '10,5', is also added in this stage to bypass the extraction of lipids; this option can be coupled with 'in-situ transesterification' included in the subsequent stage of the superstructure model, where both lipid extraction and transesterification occur in a single step. In case if lipid extraction is not bypassed, the outflow from this stage is split into two streams: (1) microalgal lipids, the main process stream, and (2) non-lipid residue which is left over after the extraction of lipids, with the help of

a split factor. The lipid stream is sent to the transesterification stage for conversion into biodiesel whereas the non-lipid contents of microalgae are collected to be sent to other stages for further downstream processing and conversion into the useful products.

For a set of lipid extraction alternatives, it is composed of two different subsets.

$$L = L_1 \cup L_2$$

Where L_1 is a group of alternatives which only have one previous alternative possible, whereas L_2 is a group of alternatives which are connected from empty bypass stage from drying stage.

For $l \in L_1$, the output from previous step is directly sent to the next stage where $l=d$. The stream NLCCV is defined as all the leftover streams including non-lipid residues, chemicals and water that is not lipid.

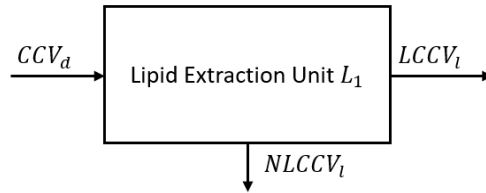


Figure 16 Unit operation of lipid extraction L1 stage

$$LCCV_{L1} = \sum_{b \in B1} FDRY_{B1,D1} \cdot CONVL_{L1} \cdot YL_{L1} \quad \forall L1, B1, D1 \quad (3.14)$$

For $l \in L_2$, there is an initial splitting of incoming stream from freeze drying to each alternative.

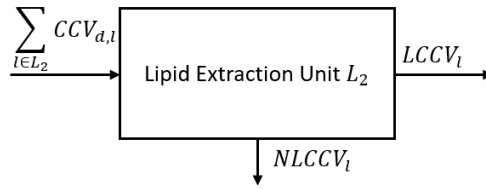


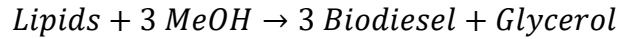
Figure 17 Unit operation of lipid extraction L2 stage

$$\sum_{L2 \in L} FLIPI_{L2} = \sum_{b \in B1} FDRY_{B1,D2} \quad \forall L2, B1, D2 \quad (3.15)$$

$$LCCV_{L2} = FLIPI_{L2} \cdot CONVL_{L2} \cdot YL_{L2} \quad \forall L2 \quad (3.16)$$

- Transesterification

Seven technological alternatives are considered for this stage: four for transesterification, and the rest three for in-situ transesterification. The technological alternatives to carry out in-situ transesterification are selected only if the previous lipid extraction stage is bypassed. Chemical reaction in transesterification can be simplified in terms of major inputs and outputs, as shown below:



Using the given molar ratio, molar mass of materials and known process conversion efficiency, the coefficient multiplied to output variables can be calculated. It is noted that the methanol input requirement is calculated with a basis of 9:1 mole ratio, for excess methanol. For a set of transesterification alternatives, it is composed of two different subsets with different input and output streams.

$$T = T_1 \cup T_2$$

$$T_1 = \{1,2,3,4|\text{transesterification}\}$$

$$T_2 = \{5,6,7|\text{in situ transesterification}\}$$

For T_1 , there is one output stream, which is a mixture of biodiesel, glycerol and other waste material including unreacted lipids and excess methanol.

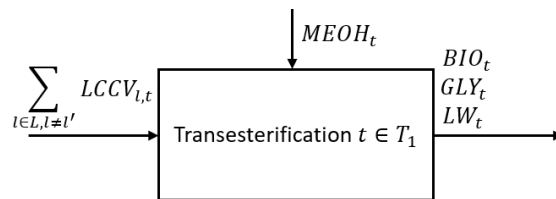


Figure 18 Unit operation of transesterification T1 stage

$$\sum_{t \in T_1} FTRAI_{T1} = \sum_{l \in L_3} LCCV_{L3} \quad \forall T1, L3 \quad (3.17)$$

If in-situ transesterification is selected, then the outflow is split into two streams; (1) biodiesel stream which is composed of biodiesel, glycerol as a byproduct, and waste material including unreacted lipids and excess methanol, and (2) non-lipid microalgae residue.

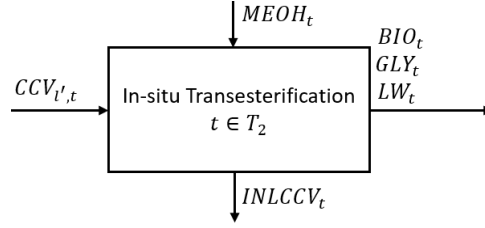


Figure 19 Unit operation of transesterification T2 stage

$$\sum_{t \in T_2} FTRAI_{T_2} = \sum_{l \in L_4} LCCV_{L_4} \quad \forall T_2, L_4 \quad (3.18)$$

Output flowrates are calculated by multiplying the coefficient to the input flowrates.

$$FTRA_{t,h} = FTRAI_t \cdot CONVT_{t,h} \cdot YT_t \quad \forall t, h \quad (3.19)$$

All the non-lipid residue from previous alternatives is combined and sent to be further processed into valuable products in conjunction with MSW. The calculation of total non-lipid residue:

$$NLCCV = \sum_{l \in L_1} (\sum_{b \in B_1} FDRY_{B_1, D_1} \cdot (1 - CONVL_{L_1}) \cdot YL_{L_1}) + \sum_{l \in L_2} (FLIPI_{L_2} \cdot (1 - CONVL_{L_2}) \cdot YL_{L_2}) + \sum_{t \in T_2} (FTRAI_{T_2} \cdot (1 - \sum_{h \in H} CONVT_{T_2, h}) \cdot YT_{T_2}) \quad \forall l, B_1, D_1, T_2, h \quad (3.20)$$

- Biodiesel and Glycerol Purification Steps:

In the previous transesterification steps, lipid content from microalgal biomass is converted into biodiesel and glycerol. However, it is still one large stream of various contents mixed together including catalyst and unreacted methanol. This step includes multiple sub-steps, including methanol recovery, gravity separation, washing and purification of biodiesel layer, washing of glycerol layer, flash separation, to separate the mixture and purify the products. Purified methanol could be combined with fresh methanol supply to be reused for transesterification.

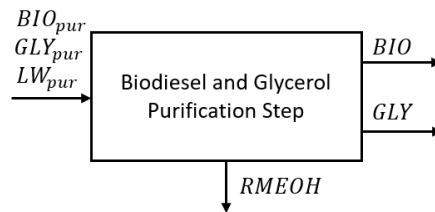


Figure 20 Unit operation of biodiesel and glycerol purification stage

$$FPUR_i = \sum_{t \in T} FTRA_{t,h} \cdot CONVP_{h,i} \cdot YP_p \quad (3.21)$$

- MSW Segregation

Next, the proposed MSW process begins with the segregation of MSW into its constituents. The recyclable components are then recycled in next processing stage.



Figure 21 Unit operation of MSW segregation stage

$$MSEG_j = FEEDF_{st2} \cdot CONVJ_j \cdot YG \quad \forall j, st2 \quad (3.22)$$

- Materials Recycling Facility (MRF)

The recyclable components in MSW (paper, plastic, glass, metal, textile) are recycled first via material recycling facility (MRF), and the remaining waste is sent to next processing stage for the further treatment and conversion into other useful products.

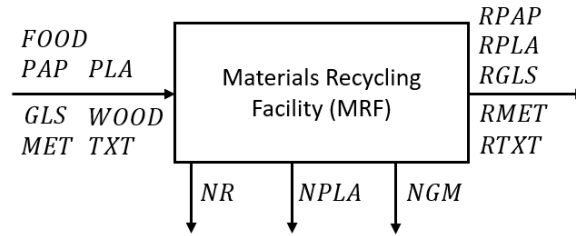


Figure 22 Unit operation of materials recycling facility stage

The remaining recyclable components that are not fully recovered is sent to further processing stages for producing other useful products. Depending on the type of waste, only selected processing stages are able to generate products. Thus, MSW is re-classified into three groups: NR, NPLA, and NGM.

$$NR = FOOD + WOOD + (1 - CONVK_{PAP}) \cdot PAP + (1 - CONVK_{TXT}) \cdot TXT \quad (3.23)$$

$$NPLA = (1 - CONVK_{PLA}) \cdot PLA \quad (3.24)$$

$$NGM = (1 - CONVK_{GLS}) \cdot GLS + (1 - CONVK_{MET}) \cdot MET \quad (3.25)$$

- Treatment and Other Product Generation

Table 6 List of available processing alternatives and their corresponding input materials

Process Alternatives	Input Materials
Enzymatic Hydrolysis (enz)	NLR
Gasification (gas)	NR, NPLA, NLR
Anaerobic Digestion (ad)	NR, NLR
Plasma Arc Gasification (pag)	NR
Co-pyrolysis (py)	NR, NPLA, NLR
Incineration (inc)	NR, NPLA, NGM
Landfill (lf)	NR, NPLA, NGM
Composting (cmp)	NR

Each input must be split into corresponding process alternatives.

$$NLCCV = NLCCV_{enz} + NLCCV_{gas} + NLCCV_{ad} + NLCCV_{py} \quad (3.26)$$

$$NR = NR_{gas} + NR_{ad} + NR_{pag} + NR_{py} + NR_{inc} + NR_{lf} + NR_{cmp} \quad (3.27)$$

$$NPLA = NPLA_{gas} + NPLA_{py} + NPLA_{inc} + NPLA_{lf} \quad (3.28)$$

$$NGM = NGM_{inc} + NGM_{lf} \quad (3.29)$$

Before entering the treatment step, incoming streams are combined into one input for each alternative for model simplicity.

$$FTREAT_{enz} = NLCCV_{enz} \quad (3.30)$$

$$FTREAT_{gas} = NLCCV_{gas} + NR_{gas} + NPLA_{gas} \quad (3.31)$$

$$FTREAT_{ad} = NLCCV_{ad} + NR_{ad} \quad (3.32)$$

$$FTREAT_{pag} = NR_{pag} \quad (3.33)$$

$$FTREAT_{py} = NLCCV_{py} + NPLA_{py} \quad (3.34)$$

$$FTREAT_{inc} = NR_{inc} + NPLA_{inc} + NGM_{inc} \quad (3.35)$$

$$FTREAT_{lf} = NR_{lf} + NPLA_{lf} + NGM_{lf} \quad (3.36)$$

$$FTREAT_{cmp} = NR_{cmp} \quad (3.37)$$

Calculation of output of sequential treatment and final product production are done in one step by multiplying the two conversion factors.

$$FPROD_f = FTREAT_f \cdot CONVF_f \cdot YF_f \quad (3.38)$$

All the numerical values used in computation of the above mathematical model are listed in Appendix A. Descriptions of model equations and variables are listed below.

Table 7 Descriptions of model equations (3.1) to (3.38)

Equation	Description
3.1	Objective function for maximization of profit
3.2	Calculation of total sales of products in \$ per year
3.3	Calculation of total feedstock cost in \$ per year
3.4	Calculation of total production cost in \$ per year
3.5	Mass balance for splitting CO ₂ into cultivation in tonne per year
3.6	Mass balance for cultivation stage outlet in tonne per year
3.7	Mass balance for combining and splitting input into drying unit in tonne per year
3.8	Mass balance for separation stage outlet in tonne per year
3.9	Calculation of water input requirement with respect to CO ₂ source input in tonne per year
3.10	Calculation of combined recycle water RH ₂ O in tonne per year
3.11	Calculation of total water requirement in tonne per year
3.12	Mass balance for combining and splitting input into drying unit in tonne per year
3.13	Mass balance for drying stage outlet in tonne per year
3.14	Mass balance for lipid extraction L1 outlet in tonne per year
3.15	Mass balance for combining and splitting input into lipid extraction L2 in tonne per year
3.16	Mass balance for lipid extraction L2 outlet in tonne per year
3.17	Mass balance for combining and splitting input into transesterification T1 in tonne per year
3.18	Mass balance for combining and splitting input into transesterification T2 in tonne per year
3.19	Mass balance for transesterification stage in tonne per year
3.2	Calculation of total non lipid residue from L1, L2, and T2 in tonne per year
3.21	Mass balance for products of purification stage in tonne per year
3.22	Mass balance for segregation stage in tonne per year
3.23	Calculation of total NR input in tonne per year
3.24	Calculation of total NPLA input in tonne per year
3.25	Calculation of total NGM input in tonne per year
3.26	Mass balance for splitting of NLCCV into respective treatment stages
3.27	Mass balance for splitting of NR into respective treatment stages
3.28	Mass balance for splitting of NPLA into respective treatment stages
3.29	Mass balance for splitting of NGM into respective treatment stages
3.30	Calculation of total enzymatic hydrolysis input in tonne per year
3.31	Calculation of total gasification input in tonne per year
3.32	Calculation of total anaerobic digestion input in tonne per year
3.33	Calculation of total plasma arc gasification input in tonne per year
3.34	Calculation of total fast pyrolysis input in tonne per year
3.35	Calculation of total incineration input in tonne per year
3.36	Calculation of total landfill input in tonne per year
3.37	Calculation of total composting input in tonne per year
3.38	Mass balance for calculating the total output for other product generation stage in tonne per year

Table 8 Descriptions of variables and parameters in model equations

Variable	Description
$FEEDF_{st}$	Amount of CO ₂ and MSW source available in tonne per year
$FCO2_c$	Amount of CO ₂ going into each cultivation stage c in tonne per year
$FCULT_{c,a}$	Amount of outlet a from cultivation stage c in tonne per year
$FSEPI_{s,a}$	Amount of a going into separation stage s in tonne per year
$FSEP_{a,s,b}$	Amount of b outlet from separation stage s in tonne per year
W_c	Total Amount of water supply required in tonne per year
$FRH2O_b$	Amount of recycle water combined in tonne per year
$FH2O$	Amount of fresh water supply in tonne per year
$FDRYI_{b,d}$	Amount of b into drying stage d in tonne per year
$FDRY_{b,d}$	Amount of b outlet from drying stage d in tonne per year
$FLIPI_{L2}$	Amount of dry biomass from freeze drying going into lipid extraction L2 in tonne per year
$LCCV_l$	Amount of lipid out from lipid extraction stage l in tonne per year
$NLCCV$	Total amount of non-lipid out from L1 L2 and T2 in tonne per year
$FTRAI_t$	Amount of lipid into transesterification stage t in tonne per year
$FTRA_{t,h}$	Amount of product h from transesterification step t in tonne per year
$FPUR_i$	Amount of purified products i from purification step p in tonne per year
$MSEG_j$	Amount of MSW segregated product j from segregation stage in tonne per year
$RECYCLE_k$	Amount of recyclable product k produced in tonne per year
NR	Amount of total NR in tonne per year
$NPLA$	Amount of total NPLA in tonne per year
NGM	Amount of total NGM in tonne per year
$FTREAT_f$	Amount of input stream going into treatment stage f for final product in tonne per year
$FPROD_f$	Amount of final product streams out of treatment stage f in tonne per year

Binary Variable	Description
YC_c	Existence of process c at cultivation stage
YS_s	Existence of process s at separation stage
YD_d	Existence of process d at drying stage
YL_l	Existence of process l at lipid extraction stage
YT_t	Existence of process t at transesterification stage
YP_p	Existence of process p at purification stage
YG	Existence of process g at MSW segregation stage
YR	Existence of process r at material recycling facility
YF_f	Existence of treatment stage f

Parameters	Description
$WREQ_c$	Required amount conversion factor of water at c w.r.t CO ₂ input
$CONVC_{c,a}$	Conversion Factor at c to produce a from CO ₂
$CONVS_{a,s,b}$	Conversion Factor at separation stage s to produce b from a
$CONVD_{B1,d}$	Conversion Factor at drying stage d to produce dry biomass from b
$CONVL_l$	Conversion Factor at lipid extraction l to produce lipid from biomass
$CONVT_{t,h}$	Conversion Factor at transesterification stage t to produce h from g
$CONVP_{h,i}$	Conversion Factor at purification stage p to produce i from h
$CONVJ_j$	Conversion Factor at segregation to produce j from MSW source
$CONVK_{J1,k}$	Conversion Factor at MRF to product k from J1

Chapter 4 Case Study Results and Discussions

4.1 Optimization Results

Optimization of the model formulation was performed in GAMS 24.5.6 using CPLEX 11.0.0 as a solver. The solution contained 38 blocks of equations, 49 blocks of variables, 146 single equations, 221 single variables and took 0.087 seconds to solve. With the given parameters and defined equations, the optimal model configuration resulted in \$253,857,000 USD per year in profit. The total revenue obtained from sales of final products was \$1433,859,000 USD per year. All anticipated products except compost were produced in this pathway. Figure 23 shows the optimal pathway configuration to produce end-products from two feedstocks:

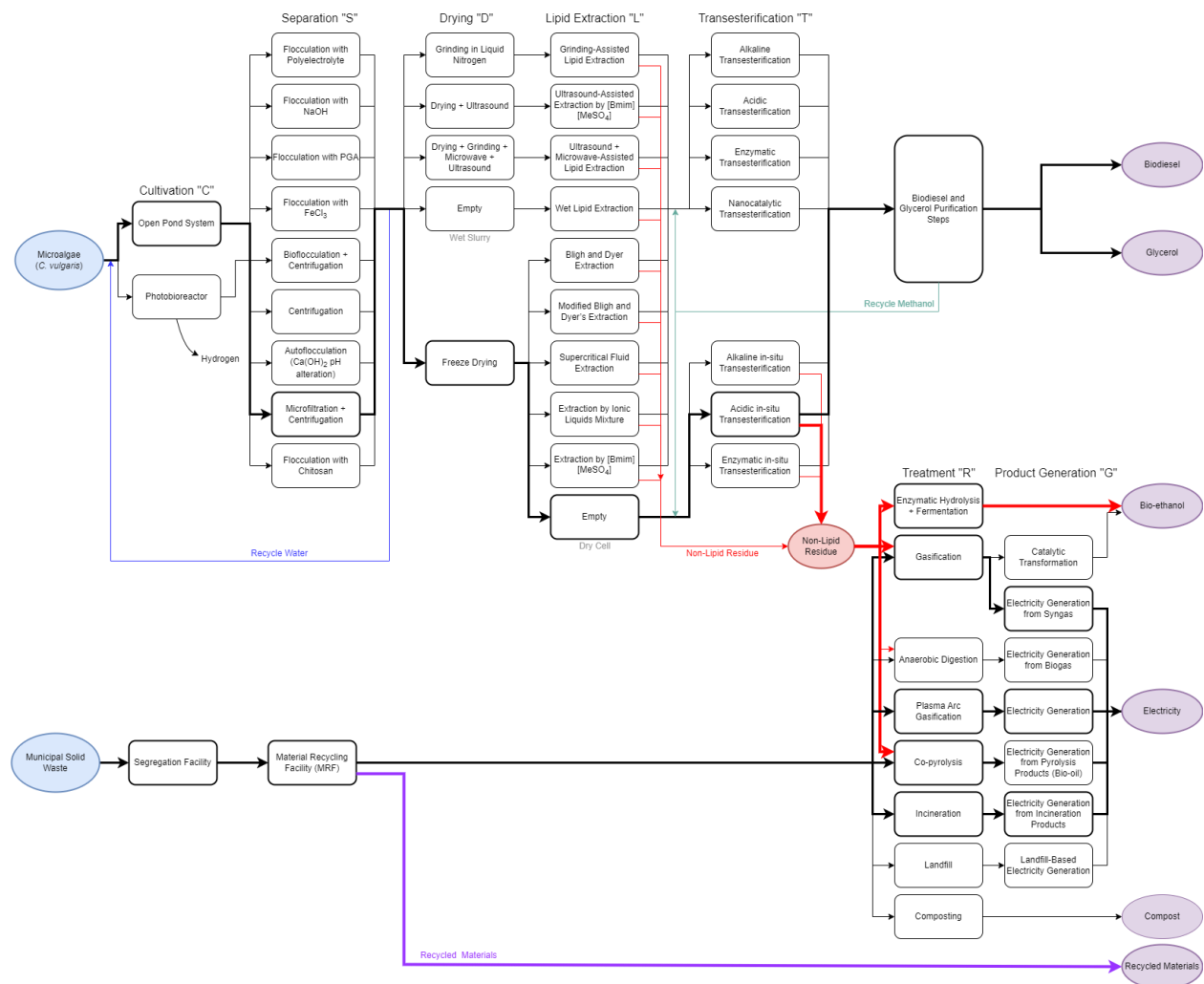


Figure 23 Superstructure of integrated biorefinery with highlighted optimal processing routes

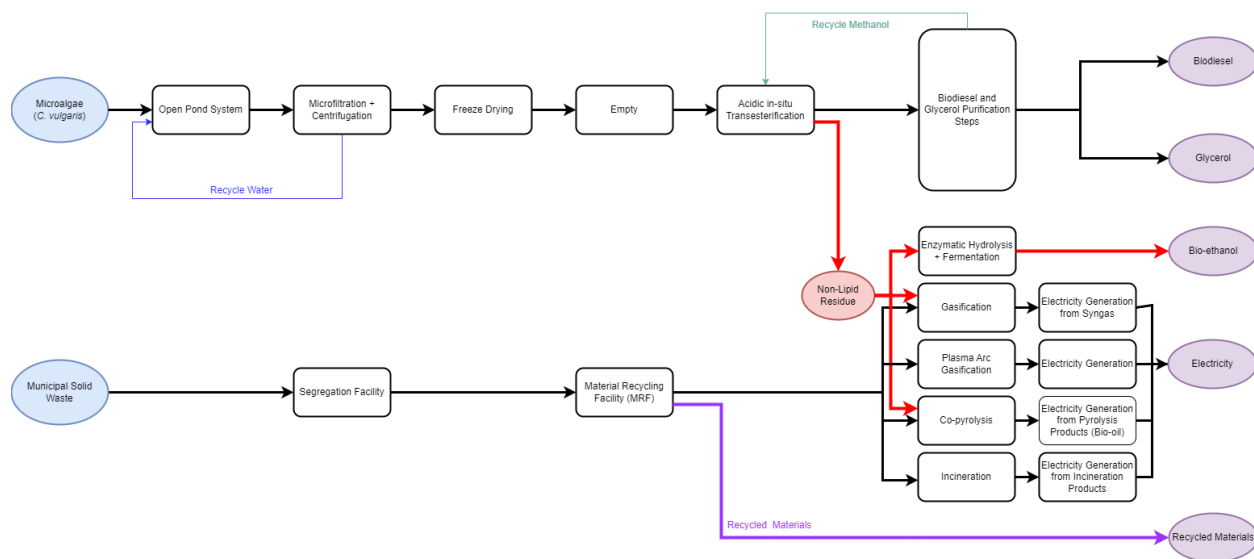


Figure 24 Final superstructure of integrated biorefinery with optimal processing routes

The highlighted arrows represent the optimal pathway configuration that maximizes total profit. For processing lipid content of microalgal biomass, only one technological alternative was selected at each process stage. For microalgal feedstock, the intermediate products after each processing stage do not have market values to be directly sold. Instead, biomass must be fully converted into final value-added products, biodiesel and glycerol. This result suggests that selection and operation of multiple technological alternatives is not economically ideal for microalgal lipid treatment. It was noted that there was one “empty” stage option was selected in the final configuration, at lipid extraction stage. The bypassing of lipid extraction stage always leads to in-situ transesterification, which converts biomass oil into free fatty acids directly from the oil-bearing, non-disrupted biomass. Various reports (Velasquez-Orta, 2012; Ehimen, 2010) have already shown economic and environmental advantages of in-situ transesterification, which was also shown in this optimization result. It eliminates the solvent extraction step required to obtain the oil feedstock as in the conventional method, simplifying and reducing the overall process cost, thus contributing to lowering the final product costs. Process waste generation and pollution could also be reduced by this method.

On the other hand, there exists a process region which multiple alternatives were selected: combined microalgae non-lipid and MSW product generation. Especially, electricity was produced via three different alternatives: gasification, plasma arc gasification, and incineration. In Seoul metropolitan area, electricity is one of the most demanding energy products as it is a

highly industrialized region with packed population. Each electricity generation method having a certain productivity capacity, distributed production of electricity would be more feasible. In addition, the intermediate products from gasification and co-pyrolysis alternatives are syngas and bio-oil, which themselves have market value of \$24.46 to \$90.09 per thousand m³, depending on its gas composition, and \$1.11 per liter, respectively. Although not examined within the scope of study, there exists potential to partially sell syngas and bio-oil as products while the rest could be sent to the next processing stage to produce electricity.

Combination of microalgae and MSW conversion processes is achieved in the solution as well. Gasification and co-pyrolysis were selected to convert both MSW and microalgal non-lipid residues. For more detailed analysis, the numerical values obtained from optimization will be reviewed. Table 9 and 10 listed optimal production levels of intermediate and final products.

Table 9 Optimal production rate of final products

Product	Production Level (tonne per year or MWh per year)
Biodiesel	403,520
Glycerol	42,009
Bioethanol	742,370
Electricity	3,490,500
Compost	0
Recycled Paper	1,141,600
Recycled Plastic	201,810
Recycled Glass	256,850
Recycled Metal	406,680
Recycled Rubber	96,829

Table 10 Optimal Production rate of intermediate products from microalgae processes

Process Stage	Selected Alternative	Intermediate Product	Production Level (tonne per year or MWh per year)
Microalgae Cultivation	Open pond system	Microalgal biomass culture	1,578,900
Microalgae Separation	Microfiltration	Wet biomass	1,547,400
Biomass Drying	Freeze drying	Dry biomass	1,531,200
Lipid Extraction	Empty	Dry biomass bypass	1,531,200
Transesterification	Acidic in-situ	Crude biodiesel	469,210
		Crude glycerol	48,847
		Crude methanol	2,337,200
Purification	Biodiesel and glycerol purification steps	Biodiesel	403,520
		Glycerol	42,009
		Methanol	2,220,300

Optimal production rate in tonne per year for major products have considered the constraint which it must be at least meet the annual demands. Major products for this study were biodiesel and electricity, as these are the two energy products that are of the highest demand in Seoul metropolitan area being a highly developed and industrialized area. For microalgal lipid content, 100% of the material flow was directed to each process alternative as only one option was selected for each stage. At cultivation stage, open pond system was the selected method to cultivate microalgal biomass. With the assumption of open pond system that is composed of multiple raceway ponds that are 4,000 m² in volume, and with continuous supply of CO₂, the system is able to cultivate 1,578,900 tonnes of microalgal biomass per year. As lipid extraction stage is bypassed, the loss of microalgal biomass could be minimized. From literature, process efficiency of other alternatives for lipid extraction ranges from 15% to 92%. Therefore, higher product yield could be achieved through a direct in-situ transesterification. From 1,531,200 tonnes of fully dried microalgal biomass, 469,210 tonnes of crude biodiesel could be produced, and finally 403,520 tonnes of product grade (99% purity) biodiesel is produced annually. Since only 31.5% of the total microalgal biomass is composed on lipid, if the biorefinery is only designed for producing oil products, the economic feasibility could not be justified. However, by adding process alternatives for non-lipid residue as well as MSW, more options to produce other value-added products are available to contribute to greater profit. Table 11 is a list of intermediate products from MSW processes and combined technological approaches.

Table 11 Optimal Production rate of intermediate products from MSW processes

Process Stage	Selected Alternative	Intermediate Product	Production Level (tonne per year or MWh per year)
MSW Segregation	Segregation facility	Food waste	1,365,800
		Wood waste	244,620
		Paper	1,427,000
		Plastic	224,230
		Glass	285,390
		Metal	428,080
		Rubber	101,930
MSW Recycling	Material recycling facility	Non-recyclables	1,973,277
		Recycled paper	1,141,600
		Recycled plastic	201,810
		Recycled glass	256,850
		Recycled metal	406,685
		Recycled rubber	96,828
Pre-Treatment	Ezymatic hydrolysis + Fermentation	Bioethanol	742,370
	Gasification	Syngas	13,835
	Plasma arc gasification	Syngas	3,480,230
	Co-pyrolysis	Bio-oil	44,850
	Incineration	Incinerated Products	49,945
Product Generation	Electricity generation from syngas (gasification)	Electricity	255,040
	Electricity generation from syngas (plasma arc gasification)	Electricity	2,800,870
	Electricity generation from bio-oil (co-pyrolysis)	Electricity	264,780
	Electricity generation from incineration products	Electricity	169,810

From the numerical results obtained for MSW and non-lipid microalgal residue processes, about 41.3% from MSW mixture supply was not able to be recycled. Out of 3,490,500 MWh of total electricity to be produced, about 80.2% was produced via plasma arc gasification. The distribution of non-recyclable MSW was not heavily leaned onto a certain process alternative, however the conversion rate of electricity generation from plasma arc gasification generated syngas was significantly greater than the other alternatives.

Interestingly, out of all projected final products, the annual production rate of compost was 0 tonne as composting was not selected in the optimal solution pathway. In fact, the product price of compost is \$30 USD per tonne, which is much lower than any other possible products. This

result is also ideal for the context of this case study. As mentioned in Section 3.2, Seoul is not an agricultural city. Rather, the area is compactly filled with industrial settings, so producing compost may not be the ideal scenario. If compost were to be produced in this biorefinery, high transportation cost should be taken into account when estimating total profit as compost would be in higher demand in agricultural society, in suburban regions of South Korea.

In addition, landfill option was not included as part of the optimal biorefinery configuration. If minimization of production cost was the objective function of the model, landfill would have been included due to its low process cost. However, actual objective function included revenue from product sales, which makes landfill an unfavorable alternative. As mentioned in Section 3.2, the most urgent task in waste management in Seoul is to reduce landfill in order to reduce geographical space dedicated to landfill and mitigate social rejection. Therefore, this biorefinery configuration not only provides optimal solution to maximize profit, but also suggests a solution to mitigate issues related to landfill.

Lastly, the effectiveness of water and methanol recycle is analyzed. The following table organized the flowrates of materials recycled and fresh supply requirement.

Table 12 Amount of recycled material flows and its fresh supply requirement

Chemical	Total Required Amount (tonne per year)	Recycled Amount (tonne per year)	Fresh Supply Required (tonne per year)
Water	394,740,000	352,804,000	41,936,000
Methanol	3,469,160	2,220,300	1,248,860

As shown in the table, the total required amount of water and methanol to fully run the biorefinery were computed to be 394,740,000 and 3,469,160 tonne per year, respectively. Focusing on the recycled amount of water and methanol, the results show that up to 89.4% and 64.0% of total supply of water and methanol could be fulfilled by recycling process. Maintaining the desired dilute biomass concentration in a cultivation system is crucial for optimal growth rate. In addition, methanol is always added in excess to push the reaction towards the right (product). Methanol could be easily recovered back into 99% purity during the purification process of biodiesel and glycerol. Therefore, by redirecting spent water and purified methanol is expected to save \$116,171,320 USD per year.

4.2 Sensitivity Analysis

The optimal model that included the selections of optimal processing routes are subject to produce different results depending on variations in parameters. A deterministic modeling always carries uncertainties in influential factors such as economic and technological variations. Therefore, investigations to find impactful parameters that could lead to large variations in the optimal results is crucial in an optimization study. Sensitivity analysis is then conducted to consider a range of parameter values and how they affect the final optimal results. In this study with LP model, one parameter will be tested at a time to see its individual effect on the final profit. Out of numerous possible perturbations, the study has considered biodiesel product cost, MSW composition and microalgae cultivation efficiency. The values of these parameter were varied within the range of $\pm 50\%$. The results are shown in Figures 24, 25 and 26.

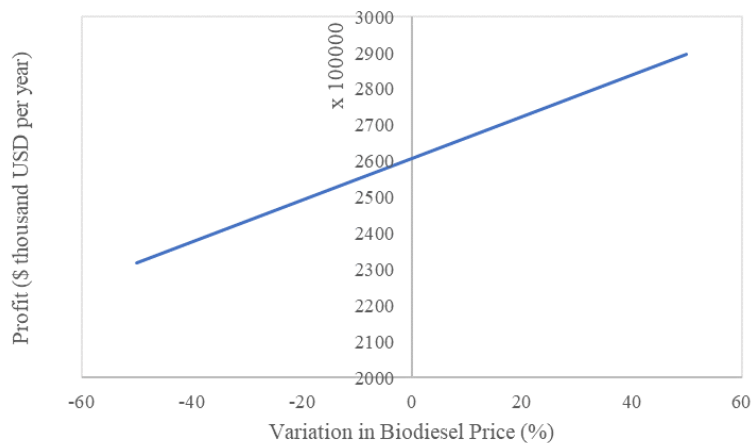


Figure 25 Sensitivity analysis on biodiesel price variation

First, biodiesel selling price was varied between $\pm 50\%$ range from original set price. The sensitivity analysis result shows that biodiesel price was the only parameter that has a linear relationship with the expected profit. With every 10% increase/decrease in biodiesel price, the profit linearly increased/decreased by 2.2%. Currently, the market price of biodiesel is the highest among all anticipated products from integrated biorefinery. Even if biodiesel market price goes below bioethanol market price, which is the second highest, the production rate of each product remained the same in the optimal solution, since all lipid content of microalgae has

only one option of product. Therefore, the profitability of biorefinery is highly dependent on biodiesel price.

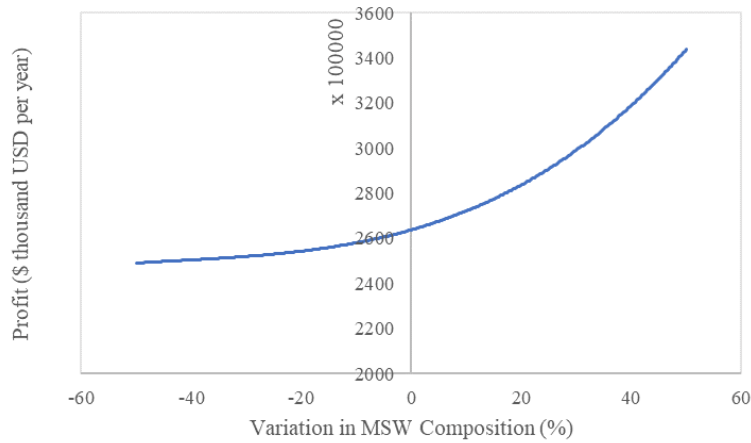


Figure 26 Sensitivity analysis on MSW composition

Sensitivity analysis on MSW composition was based on varying the percentage of non-recyclable component. From the original set value of 41.3% recyclable components, negative variation showed linear relationship while positive variation had exponential relationship with the final profit. Profit increased by 2.5% with 10% from original value but increased by 5.1% from 10% to 20% increase. This result suggests that recycling is the crucial part of this biorefinery design. Segregation and recycling of MSW are the prerequisite steps for all post-processing to produce value added products. These two steps are already highly established in a large scale thus production cost could be saved.

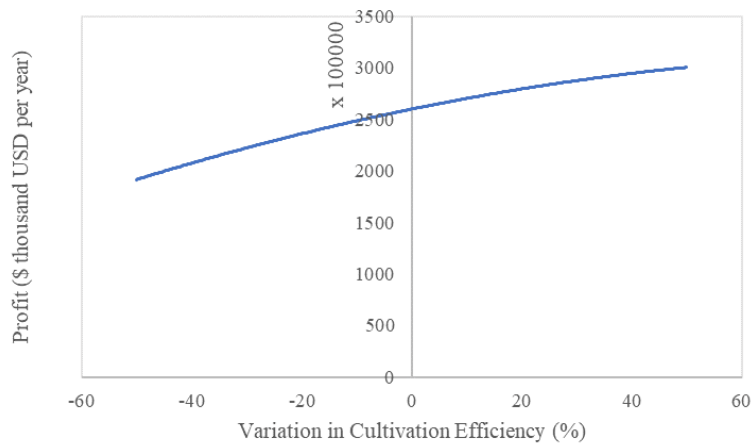


Figure 27 Sensitivity analysis on cultivation efficiency

Lastly, microalgae cultivation efficiency was varied to observe the effect of weather variation on total profit. Microalgae cultivation efficiency would highly depend on the weather condition under open pond system. South Korea is located in temperate zone with four distinct seasons. Its extreme seasons are characterized as cold and dry winter, and hot and humid summer. During extreme conditions, microalgal growth rate could be highly affected. Currently, cultivation efficiency of open pond system is about 35%. Sensitivity analysis indicates that decrease in cultivation efficiency has more drastic effect than the increase. Profit value starts to plateau on the positive variation region, while it linearly decreases on the negative variation region. Therefore, in order to maximize profit, utilization of weather-resistant cultivation methods such as photobioreactor or covered pond system could mitigate low cultivation issue during extreme seasons. To find the most important parameter for the developed model, more thorough sensitivity analysis is suggested.

Chapter 5 Conclusions and Future Recommendations

5.1 Conclusions

The aim of this study was to investigate the economic feasibility of an integrated biorefinery based on two potential feedstocks, microalgae and municipal solid waste (MSW), by employing the superstructure-based optimization approach. This report has presented the development sequence and executions of an optimization model of an integrated biorefinery. First, data from the published literature and other reliable sources showed all possible processing technologies for microalgae and MSW. In addition, possible crosslinking pathways for combined microalgae and MSW processing suggested increased overall product yield and decreased waste to landfill. Based on the literature review, a complete superstructure that incorporates all technological options and connecting pathways was designed. Next, model was written in MILP style, which included an objective function, economic constraints and mass balance. The objective function was defined to maximize total profit of running an integrated biorefinery.

A case study was selected to assess economic feasibility of an integrated biorefinery in Seoul metropolitan area, South Korea. Being a highly industrialized city, solid waste management and energy supply issues have led social and environmental concerns. Given the superstructure-based model and case study parameters, a MILP problem was solved in GAMS for optimization. As a result, the optimal solution included a selection of technological pathways to yield \$253,857,000 USD in and \$1433,859,000 USD in annual profit and revenue, respectively. Top products included 403,520 tonnes of biodiesel, 742,370 tonnes of bioethanol, and 3,490,500 MWh of electricity production annually. The optimal solution omitted landfill of waste, and increase the waste directed to electricity, which were ideal suggestion for the case study scenario. Moreover, recycling of water and methanol within the process cycle could potentially save \$116,171,320 USD per year.

Sensitivity analysis was done with three adjustable parameters: biodiesel market price, MSW composition, and microalgae cultivation efficiency. Biodiesel price was linearly correlated to total profit as it is one of the main products anticipated in this biorefinery. MSW composition caused a noticeable, exponential increase in profit as the proportion of recyclable components increased. Lastly, microalgae cultivation efficiency was selected to observe effects of potential

weather variation on microalgal growth rate, and final profit. Profit value was linearly dependent on negative variation region of cultivation rate. This suggested extreme climate which hinders microalgae growth, could significantly affect the economic feasibility of this biorefinery.

The main contributions of this research include the following aspects:

- Prior to this study, an integrated model for an integrated biorefinery with lignocellulosic feedstock was the main interest in bioenergy system design field. Integration of next-generation feedstocks has never been fully addressed in the literature. This study fills this gap by proposing an integrated modelling of microalgae and MSW as main feedstocks for energy and value-added product generation.
- A systematic design of a multi-feedstock biorefinery could provide meaningful suggestions for a case where a sustainable supply of a single feedstock is limited.
- The modelling was done in a way that multiple technological options could be selected at each level of process stage, so that feedstock flow could be split for optimized yield.
- Recycling of water and methanol was suggested to mitigate high chemical cost for transesterification.

5.2 Future Research Recommendations

Although this research has addressed the modeling and optimization of an integrated biorefinery in a comprehensive manner, still some related work requires further investigations including:

- Possibility to partially sell intermediate products directly to the market while the rest could be sent to further processing. Further studies could focus on discovering more possibilities to a wider range of product types that could be additionally produced via new technological alternatives or produced within the existing configuration.
- Quantification of CO₂ emission to assess environmental feasibility of the model. It is also consumed as a feed for microalgae cultivation. From this study, it was inconclusive if the overall production is carbon positive, negative, or neutral. Therefore, emission data could be collected for each technological alternative to compare with cultivation requirement.
- Conduct a life cycle analysis (LCA) to assess and quantify the environmental impacts associated with this biorefinery design. From this assessment, it is possible to estimate product's ultimate effects on human health, ecosystem function, and natural resource

depletion. The result could be compared with the technological assessment that has been conducted in this study for economic feasibility, and finally conclude if this biorefinery has both economic and environmental benefit to society. ISO 14000 is recommended to be referred in an environmental feasibility study.

- Apply the superstructure model to a different case study with different feed types and compositions to see the effect of feed condition on optimal route selection. Selection of different country/region/climate could highly affect the MSW composition, and type of microalgae strain that could be cultivated. Comparison with the results from this study with other case scenarios could offer deeper knowledge in process optimization strategies for different cases.
- Addition of transportation cost, emission cost and other related expenses into profit objective function for more thorough economic analysis. In real cases, the biorefinery may not be able to be constructed in the same site, rather each process could be scattered around a certain region of study. Therefore, there will be more related cost to be taken into account for more accurate representation of the real case scenario in the study. The longevity and economic sustainability could also be browsed by projecting future expense changes.

References

- Ajeej, A., Thanikal, J.V., Narayanan, C.M. and Kumar, R.S., 2015. An overview of bio augmentation of methane by anaerobic co-digestion of municipal sludge along with microalgae and waste paper. *Renewable and Sustainable Energy Reviews*, 50, pp.270-276.
- Akoh, C.C., Chang, S.W., Lee, G.C. and Shaw, J.F., 2007. Enzymatic approach to biodiesel production. *Journal of agricultural and food chemistry*, 55(22), pp.8995-9005.
- Akubude, V.C., Nwaigwe, K.N. and Dintwa, E., 2019. Production of biodiesel from microalgae via nanocatalyzed transesterification process: A review. *Materials Science for Energy Technologies*, 2(2), pp.216-225.
- Alamgir, M. and Ahsan, A., 2007. Municipal solid waste and recovery potential: Bangladesh perspective. *Journal of Environmental Health Science & Engineering*, 4(2), pp.67-76.
- Alamillo, R., Tucker, M., Chia, M., Pagán-Torres, Y. and Dumesic, J., 2012. The selective hydrogenation of biomass-derived 5-hydroxymethylfurfural using heterogeneous catalysts. *Green Chemistry*, 14(5), pp.1413-1419.
- Amiri, P. and Arabian, D., 2018. Pre-treatment and extraction of oil from *Chlorella vulgaris* microalgae by ultrasound. *Aquatics Physiology and Biotechnology*, 6(3), pp.145-171.
- Azapagic, A., 2014. Sustainability considerations for integrated biorefineries. *Trends in biotechnology*, 32(1), pp.1-4.
- Azman, N.S.B., Ghani, N.A. and Kee, L.M., 2021. Ultrasonication Assisted Extraction of Lipids from *Chlorella vulgaris* with [Bmim][MeSO₄] as an Additive. In *Proceedings of the 6th International Conference on Fundamental and Applied Sciences* (pp. 281-290). Springer, Singapore.
- Balasubramanian, S., Allen, J.D., Kanitkar, A. and Boldor, D., 2011. Oil extraction from *Scenedesmus obliquus* using a continuous microwave system—design, optimization, and quality characterization. *Bioresource technology*, 102(3), pp.3396-3403.
- Barros, A.I., Gonçalves, A.L., Simões, M. and Pires, J.C., 2015. Harvesting techniques applied to microalgae: a review. *Renewable and sustainable energy reviews*, 41, pp.1489-1500.
- Becker, E.W. and Venkataraman, L.V., 1984. Production and utilization of the blue-green alga *Spirulina* in India. *Biomass*, 4(2), pp.105-125.

- Bernaerts, T.M., Gheysen, L., Foubert, I., Hendrickx, M.E. and Van Loey, A.M., 2019. The potential of microalgae and their biopolymers as structuring ingredients in food: A review. *Biotechnology advances*, 37(8), p.107419.
- Fan, J., Budarin, V.L., Macquarrie, D.J., Gomez, L.D., Simister, R., Farmer, T.J., Raverty, W.D., McQueen-Mason, S.J. and Clark, J.H., 2016. A new perspective in bio-refining: levoglucosenone and cleaner lignin from waste biorefinery hydrolysis lignin by selective conversion of residual saccharides. *Energy & Environmental Science*, 9(8), pp.2571-2574.
- Chen, L., Li, R., Ren, X. and Liu, T., 2016. Improved aqueous extraction of microalgal lipid by combined enzymatic and thermal lysis from wet biomass of *Nannochloropsis oceanica*. *Bioresource technology*, 214, pp.138-143.
- Cudjoe, D. and Han, M.S., 2020. Economic and environmental assessment of landfill gas electricity generation in urban districts of Beijing municipality. *Sustainable Production and Consumption*, 23, pp.128-137.
- Damartzis, T., Michailos, S. and Zabaniotou, A., 2012. Energetic assessment of a combined heat and power integrated biomass gasification–internal combustion engine system by using Aspen Plus®. *Fuel processing technology*, 95, pp.37-44.
- Dasan, Y.K., Lam, M.K., Yusup, S., Lim, J.W. and Lee, K.T., 2019. Life cycle evaluation of microalgae biofuels production: Effect of cultivation system on energy, carbon emission and cost balance analysis. *Science of the total environment*, 688, pp.112-128.
- Dassey, A.J. and Theegala, C.S., 2013. Harvesting economics and strategies using centrifugation for cost effective separation of microalgae cells for biodiesel applications. *Bioresource technology*, 128, pp.241-245.
- Davis, R., Aden, A. and Pienkos, P.T., 2011. Techno-economic analysis of autotrophic microalgae for fuel production. *Applied Energy*, 88(10), pp.3524-3531.
- De, S., Bandyopadhyay, S., Assadi, M. and Mukherjee, D.A., 2018. Sustainable energy technology and policies. Singapore: Springer Singapore, pp.E1-E1.
- Dhar, B.R. and Kirtania, K., 2009. Excess methanol recovery in biodiesel production process using a distillation column: a simulation study. *Chemical Engineering Research Bulletin*, 13(2), pp.55-60.

- Dong, J., Tang, Y., Nzihou, A. and Chi, Y., 2019. Key factors influencing the environmental performance of pyrolysis, gasification and incineration Waste-to-Energy technologies. *Energy conversion and management*, 196, pp.497-512.
- Drobež, R., Novak Pintarič, Z., Pahor, B. and Kravanja, Z., 2009. MINLP synthesis of processes for the production of biogas from organic and animal waste. *Chemical and Biochemical Engineering Quarterly*, 23(4), pp.445-459.
- Dubé, M.A., Tremblay, A.Y. and Liu, J., 2007. Biodiesel production using a membrane reactor. *Bioresource technology*, 98(3), pp.639-647.
- Ehimen, E.A., Sun, Z.F. and Carrington, C.G., 2010. Variables affecting the in situ transesterification of microalgae lipids. *Fuel*, 89(3), pp.677-684.
- Escamilla-García, P.E., Camarillo-López, R.H., Carrasco-Hernández, R., Fernández-Rodríguez, E. and Legal-Hernández, J.M., 2020. Technical and economic analysis of energy generation from waste incineration in Mexico. *Energy Strategy Reviews*, 31, p.100542.
- Faried, M., Samer, M., Abdelsalam, E., Yousef, R.S., Attia, Y.A. and Ali, A.S., 2017. Biodiesel production from microalgae: Processes, technologies and recent advancements. *Renewable and sustainable energy reviews*, 79, pp.893-913.
- Fernández-Sevilla, J.M., Acien Fernández, F.G. and Molina Grima, E., 2010. Biotechnological production of lutein and its applications. *Applied microbiology and biotechnology*, 86(1), pp.27-40.
- Vermuë, M.H., Olivieri, G., van den Broek, L.A.M., Barbosa, M.J., Eppink, M.H.M., Wijffels, R.H. and Kleinegris, D.M.M., 2014. Cationic polymers for successful flocculation of marine microalgae. *Bioresource technology*, 169, pp.804-807.
- Gallo, J.M.R. and Trapp, M.A., 2017. The chemical conversion of biomass-derived saccharides: An overview. *Journal of the Brazilian Chemical Society*, 28, pp.1586-1607.
- Ghedini, E., Taghavi, S., Menegazzo, F. and Signoretto, M., 2021. A Review on the Efficient Catalysts for Algae Transesterification to Biodiesel. *Sustainability*, 13(18), p.10479.
- Guieysse, B., Béchet, Q. and Shilton, A., 2013. Variability and uncertainty in water demand and water footprint assessments of fresh algae cultivation based on case studies from five climatic regions. *Bioresource technology*, 128, pp.317-323.

- Guldhe, A., Singh, B., Rawat, I., Ramluckan, K. and Bux, F., 2014. Efficacy of drying and cell disruption techniques on lipid recovery from microalgae for biodiesel production. *Fuel*, 128, pp.46-52.
- Gultom, S.O. and Hu, B., 2013. Review of microalgae harvesting via co-pelletization with filamentous fungus. *Energies*, 6(11), pp.5921-5939.
- Gyeongsangbuk-do, Republic of Korea., 2010. Feasibility Report—Freshwater Microalgae-based Bioenergy Research and Development Project. (in Korean)
- Heo, H.Y., Heo, S. and Lee, J.H., 2019. Comparative techno-economic analysis of transesterification technologies for microalgal biodiesel production. *Industrial & Engineering Chemistry Research*, 58(40), pp.18772-18779.
- Hong, J.W., Jo, S.W. and Yoon, H.S., 2015. Research and development for algae-based technologies in Korea: a review of algae biofuel production. *Photosynthesis research*, 123(3), pp.297-303.
- Huang, H.J., Ramaswamy, S., Tschirner, U.W. and Ramarao, B.V., 2008. A review of separation technologies in current and future biorefineries. *Separation and purification technology*, 62(1), pp.1-21.
- Huang, W.C. and Kim, J.D., 2013. Cationic surfactant-based method for simultaneous harvesting and cell disruption of a microalgal biomass. *Bioresource technology*, 149, pp.579-581.
- IEA., 2021. Key World Energy Statistics 2021, Paris: IEA. Retrieved from <https://www.iea.org/reports/key-world-energy-statistics-2021>
- Ismail, I.M. and Nizami, A.S., 2016. ENV-617: WASTE-BASED BIOREFINERIES IN DEVELOPING COUNTRIES: AN IMPERATIVE NEED OF TIME.
- Jeon, J.M., Choi, H.W., Yoo, G.C., Choi, Y.K., Choi, K.Y., Park, H.Y., Park, S.H., Kim, Y.G., Kim, H.J., Lee, S.H. and Lee, Y.K., 2013. New mixture composition of organic solvents for efficient extraction of lipids from *Chlorella vulgaris*. *Biomass and Bioenergy*, 59, pp.279-284.
- Jiang, L.Y. and Zhu, J.M., 2016. Separation technologies for current and future biorefineries—status and potential of membrane-based separation. *Advances in Bioenergy: The Sustainability Challenge*, pp.193-208.
- Kamm, B. and Kamm, M.J.A.M., 2004. Principles of biorefineries. *Applied microbiology and biotechnology*, 64(2), pp.137-145.

- Korea Institute of Energy Technology Evaluation and Planning (KETEP)., 2011. Green Energy Strategic Roadmap 2011.
- Khan, M.I., Shin, J.H. and Kim, J.D., 2018. The promising future of microalgae: current status, challenges, and optimization of a sustainable and renewable industry for biofuels, feed, and other products. *Microbial cell factories*, 17(1), pp.1-21.
- Khan, M.M.U.H., Jain, S., Vaezi, M. and Kumar, A., 2016. Development of a decision model for the techno-economic assessment of municipal solid waste utilization pathways. *Waste management*, 48, pp.548-564.
- khorrandashti, M.S., Giri, M.S. and Majidian, N., 2021. Extraction lipids from chlorella vulgaris by supercritical CO₂ for biodiesel production. *South African Journal of Chemical Engineering*, 38(1), pp.121-131.
- Kim, B., Heo, H.Y., Son, J., Yang, J., Chang, Y.K., Lee, J.H. and Lee, J.W., 2019. Simplifying biodiesel production from microalgae via wet in situ transesterification: A review in current research and future prospects. *Algal Research*, 41, p.101557.
- Kim, Y.H., Choi, Y.K., Park, J., Lee, S., Yang, Y.H., Kim, H.J., Park, T.J., Kim, Y.H. and Lee, S.H., 2012. Ionic liquid-mediated extraction of lipids from algal biomass. *Bioresource technology*, 109, pp.312-315.
- Kim, Y.H., Park, S., Kim, M.H., Choi, Y.K., Yang, Y.H., Kim, H.J., Kim, H., Kim, H.S., Song, K.G. and Lee, S.H., 2013. Ultrasound-assisted extraction of lipids from *Chlorella vulgaris* using [Bmim][MeSO₄]. *Biomass and bioenergy*, 56, pp.99-103.
- Korean Statistical Information Service., 2022. Population Statistics Based on Resident Registration. Korean Statistical Information Service.
- Köse, Ö., Tüter, M. and Aksoy, H.A., 2002. Immobilized *Candida antarctica* lipase-catalyzed alcoholysis of cotton seed oil in a solvent-free medium. *Bioresource technology*, 83(2), pp.125-129.
- Kotasthane, T., 2017. Potential of microalgae for sustainable biofuel production. *J. Mar. Sci. Res. Dev*, 7(01).
- Krishnan, S., Abd Ghani, N., Aminuddin, N.F., Quraishi, K.S., Azman, N.S., Cravotto, G. and Leveque, J.M., 2020. Microwave-assisted lipid extraction from *Chlorella vulgaris* in water with 0.5%–2.5% of imidazolium based ionic liquid as additive. *Renewable Energy*, 149, pp.244-252.

- Kumar, V., Arora, N., Nanda, M. and Pruthi, V., 2019. Different cell disruption and lipid extraction methods from microalgae for biodiesel production. In *Microalgae biotechnology for development of biofuel and wastewater treatment* (pp. 265-292). Springer, Singapore.
- Lakshmikandan, M., Murugesan, A.G., Wang, S., Abomohra, A.E.F., Jovita, P.A. and Kiruthiga, S., 2020. Sustainable biomass production under CO₂ conditions and effective wet microalgae lipid extraction for biodiesel production. *Journal of Cleaner Production*, 247, p.119398.
- Laurens, L.M.L., Nagle, N., Davis, R., Sweeney, N., Van Wychen, S., Lowell, A. and Pienkos, P.T., 2015. Acid-catalyzed algal biomass pretreatment for integrated lipid and carbohydrate-based biofuels production. *Green Chemistry*, 17(2), pp.1145-1158.
- Lecina, M., Nadal, G., Solà, C., Prat, J. and Cairó, J.J., 2016. Optimization of ferric chloride concentration and pH to improve both cell growth and flocculation in *Chlorella vulgaris* cultures. Application to medium reuse in an integrated continuous culture bioprocess. *Bioresource technology*, 216, pp.211-218.
- Lee, A.K., Lewis, D.M. and Ashman, P.J., 2012. Disruption of microalgal cells for the extraction of lipids for biofuels: Processes and specific energy requirements. *Biomass and bioenergy*, 46, pp.89-101.
- Lee, I. and Han, J.I., 2015. Simultaneous treatment (cell disruption and lipid extraction) of wet microalgae using hydrodynamic cavitation for enhancing the lipid yield. *Bioresource Technology*, 186, pp.246-251.
- Li, C., Liu, Y.H., Luo, A.X., Ruan, R.S. and Liu, C.M., 2008. New two-step method of producing biodiesel from waste cooking oil. *Cereals Oils Process*.
- Li, T., Strous, M. and Melkonian, M., 2017. Biofilm-based photobioreactors: their design and improving productivity through efficient supply of dissolved inorganic carbon. *FEMS Microbiology Letters*, 364(24), p.fnx218.
- Liu, S., Gifuni, I., Mear, H., Frappart, M. and Couallier, E., 2021. Recovery of soluble proteins from *Chlorella vulgaris* by bead-milling and microfiltration: Impact of the concentration and the physicochemical conditions during the cell disruption on the whole process. *Process Biochemistry*, 108, pp.34-47.
- Lundquist, T.J., Woertz, I.C., Quinn, N.W.T. and Benemann, J.R., 2010. A realistic technology and engineering assessment of algae biofuel production. *Energy Biosciences Institute*, p.1.

- Luo, S., Xu, T., Chen, L., Chen, J., Rao, C., Xiao, X., Wan, Y., Zeng, G., Long, F., Liu, C. and Liu, Y., 2012. Endophyte-assisted promotion of biomass production and metal-uptake of energy crop sweet sorghum by plant-growth-promoting endophyte *Bacillus* sp. SLS18. *Applied Microbiology and Biotechnology*, 93(4), pp.1745-1753.
- Luque, R. and Speight, J.G., 2015. Gasification and synthetic liquid fuel production: an overview. *Gasification for Synthetic Fuel Production*, pp.3-27.
- Ma, X., Zheng, H., Zhou, W., Liu, Y., Chen, P. and Ruan, R., 2016. Enhanced harvesting of *Chlorella vulgaris* using combined flocculants. *Applied biochemistry and biotechnology*, 180(4), pp.791-804.
- Mallick, N., Bagchi, S.K., Koley, S. and Singh, A.K., 2016. Progress and challenges in microalgal biodiesel production. *Frontiers in microbiology*, 7, p.1019.
- Martin, M. and Grossmann, I.E., 2012. Simultaneous optimization and heat integration for biodiesel production from cooking oil and algae. *Industrial & engineering chemistry research*, 51(23), pp.7998-8014.
- Mathimani, T. and Mallick, N., 2018. A comprehensive review on harvesting of microalgae for biodiesel—key challenges and future directions. *Renewable and Sustainable Energy Reviews*, 91, pp.1103-1120.
- Mencarelli, L., Chen, Q., Pagot, A. and Grossmann, I.E., 2020. A review on superstructure optimization approaches in process system engineering. *Computers & Chemical Engineering*, 136, p.106808.
- Mian, M.M., Zeng, X., Nasry, A.A.N.B. and Al-Hamadani, S.M., 2017. Municipal solid waste management in China: a comparative analysis. *Journal of material cycles and waste management*, 19(3), pp.1127-1135.
- Ministry of Environment, 2014. Ministry of Environment, 2013 National Waste Generation and Disposal Status.
- Minutillo, M., Perna, A. and Sorce, A., 2019. Combined hydrogen, heat and electricity generation via biogas reforming: Energy and economic assessments. *International Journal of Hydrogen Energy*, 44(43), pp.23880-23898.
- Mussatto, S.I. and Dragone, G.M., 2016. Biomass pretreatment, biorefineries, and potential products for a bioeconomy development. In *Biomass fractionation technologies for a lignocellulosic feedstock based biorefinery* (pp. 1-22). Elsevier.
- Nagler, A. and Gerace, S., 2020. First and second generation biofuels. *Fuel*, 6, p.12.

- Natarajan, R., Ang, W.M.R., Chen, X., Voigtmann, M. and Lau, R., 2014. Lipid releasing characteristics of microalgae species through continuous ultrasonication. *Bioresource technology*, 158, pp.7-11.
- Ndikubwimana, T., Zeng, X., Murwanashyaka, T., Manirafasha, E., He, N., Shao, W. and Lu, Y., 2016. Harvesting of freshwater microalgae with microbial bioflocculant: a pilot-scale study. *Biotechnology for biofuels*, 9(1), pp.1-11.
- Nelson, L.A., Foglia, T.A. and Marmer, W.N., 1996. Lipase-catalyzed production of biodiesel. *Journal of the American Oil Chemists' Society*, 73(9), pp.1191-1195.
- Nguyen, T.D.P., Frappart, M., Jaouen, P., Pruvost, J. and Bourseau, P., 2014. Harvesting *Chlorella vulgaris* by natural increase in pH: effect of medium composition. *Environmental technology*, 35(11), pp.1378-1388.
- OECD., 2022. *KOREA: INVENTORY OF ESTIMATED BUDGETARY SUPPORT AND TAX EXPENDITURES FOR FOSSIL-FUELS*.
- Ohri, A. and Singh, P.K., 2011. Decision Support Tool for Segregation of Municipal Solid Waste Management.
- Olmstead, I.L., Kentish, S.E., Scales, P.J. and Martin, G.J., 2013. Low solvent, low temperature method for extracting biodiesel lipids from concentrated microalgal biomass. *Bioresource technology*, 148, pp.615-619.
- Ouda, O.K., Raza, S.A., Nizami, A.S., Rehan, M., Al-Waked, R. and Korres, N.E., 2016. Waste to energy potential: a case study of Saudi Arabia. *Renewable and Sustainable Energy Reviews*, 61, pp.328-340.
- Park, J.Y., Nam, B., Choi, S.A., Oh, Y.K. and Lee, J.S., 2014. Effects of anionic surfactant on extraction of free fatty acid from *Chlorella vulgaris*. *Bioresource technology*, 166, pp.620-624.
- Park, J.Y., Oh, Y.K., Lee, J.S., Lee, K., Jeong, M.J. and Choi, S.A., 2014. Acid-catalyzed hot-water extraction of lipids from *Chlorella vulgaris*. *Bioresource technology*, 153, pp.408-412.
- Pasquet, V., Chérouvrier, J.R., Farhat, F., Thiéry, V., Piot, J.M., Bérard, J.B., Kaas, R., Serive, B., Patrice, T., Cadoret, J.P. and Picot, L., 2011. Study on the microalgal pigments extraction process: Performance of microwave assisted extraction. *Process Biochemistry*, 46(1), pp.59-67.
- Paulino, R.F.S., Essiptchouk, A.M. and Silveira, J.L., 2020. The use of syngas from biomedical waste plasma gasification systems for electricity production in internal combustion: Thermodynamic and economic issues. *Energy*, 199, p.117419.

- Pishgar, Z., Samimi, A., Mohebbi-Kalhari, D. and Shokrollahzadeh, S., 2020. Comparative study on the harvesting of marine *Chlorella vulgaris* microalgae from a dilute slurry using autoflocculation-sedimentation and electrocoagulation-flotation methods. *International Journal of Environmental Research*, 14(6), pp.615-628.
- Plata, V., Kafarov, V. and Moreno, N., 2010. Optimization of third generation biofuels production: biodiesel from microalgae oil by homogeneous transesterification. *Chemical Engineering*, 21.
- Podstawczyk, D., Witek-Krowiak, A., Chojnacka, K. and Sadowski, Z., 2014. Biosorption of malachite green by eggshells: mechanism identification and process optimization. *Bioresource Technology*, 160, pp.161-165.
- Pokoo-Aikins, G., Nadim, A., El-Halwagi, M.M. and Mahalec, V., 2010. Design and analysis of biodiesel production from algae grown through carbon sequestration. *Clean Technologies and Environmental Policy*, 12(3), pp.239-254.
- Praveenkumar, R., Kim, B., Choi, E., Lee, K., Cho, S., Hyun, J.S., Park, J.Y., Lee, Y.C., Lee, H.U., Lee, J.S. and Oh, Y.K., 2014. Mixotrophic cultivation of oleaginous *Chlorella* sp. KR-1 mediated by actual coal-fired flue gas for biodiesel production. *Bioprocess and biosystems engineering*, 37(10), pp.2083-2094.
- Qdais, H.A., Hamoda, M. and Newham, J., 1997. Analysis of residential solid waste at generation sites. *Waste management & research*, 15(4), pp.395-406.
- Quesada-Salas, M.C., Delfau-Bonnet, G., Willig, G., Pr eat, N., Allais, F. and Ioannou, I., 2021. Optimization and comparison of three cell disruption processes on lipid extraction from microalgae. *Processes*, 9(2), p.369.
- Ramos, A. and Rouboa, A., 2022. Life cycle thinking of plasma gasification as a waste-to-energy tool: Review on environmental, economic and social aspects. *Renewable and Sustainable Energy Reviews*, 153, p.111762.
- Ranjith Kumar, R., Hanumantha Rao, P. and Arumugam, M., 2015. Lipid extraction methods from microalgae: a comprehensive review. *Frontiers in Energy Research*, 2, p.61.
- Rentizelas, A., Karellas, S., Kakaras, E. and Tatsiopoulou, I., 2009. Comparative techno-economic analysis of ORC and gasification for bioenergy applications. *Energy Conversion and Management*, 50(3), pp.674-681.

- Richardson, J.W., Johnson, M.D. and Outlaw, J.L., 2012. Economic comparison of open pond raceways to photo bio-reactors for profitable production of algae for transportation fuels in the Southwest. *Algal Research*, 1(1), pp.93-100.
- Rizwan, M., Lee, J.H. and Gani, R., 2013. Optimal processing pathway for the production of biodiesel from microalgal biomass: a superstructure based approach. *Computers & chemical engineering*, 58, pp.305-314.
- Rizwan, M., Lee, J.H. and Gani, R., 2015. Optimal design of microalgae-based biorefinery: Economics, opportunities and challenges. *Applied Energy*, 150, pp.69-79.
- Lee, R.A. and Lavoie, J.M., 2013. From first-to third-generation biofuels: Challenges of producing a commodity from a biomass of increasing complexity. *Animal Frontiers*, 3(2), pp.6-11.
- Royon, D., Daz, M., Ellenrieder, G. and Locatelli, S., 2007. Enzymatic production of biodiesel from cotton seed oil using t-butanol as a solvent. *Bioresource technology*, 98(3), pp.648-653.
- Ruggieri, L., Cadena, E., Martínez-Blanco, J., Gasol, C.M., Rieradevall, J., Gabarrell, X., Gea, T., Sort, X. and Sánchez, A., 2009. Recovery of organic wastes in the Spanish wine industry. Technical, economic and environmental analyses of the composting process. *Journal of cleaner production*, 17(9), pp.830-838.
- Sabki, M.H., Lee, C.T., Bong, C.P. and Klemes, J.J., 2018. A review on the economic feasibility of composting for organic waste management in Asian countries. *Chemical Engineering Transactions*, 70, pp.49-54.
- Sadef, Y., Nizami, A.S., Batool, S.A., Chaudary, M.N., Ouda, O.K.M., Asam, Z.U.Z., Habib, K., Rehan, M. and Demirbas, A., 2016. Waste-to-energy and recycling value for developing integrated solid waste management plan in Lahore. *Energy Sources, Part B: Economics, Planning, and Policy*, 11(7), pp.569-579.
- Sassner, P., Galbe, M. and Zacchi, G., 2008. Techno-economic evaluation of bioethanol production from three different lignocellulosic materials. *Biomass and bioenergy*, 32(5), pp.422-430.
- Sen, S.M., Binder, J.B., Raines, R.T. and Maravelias, C.T., 2012. Conversion of biomass to sugars via ionic liquid hydrolysis: process synthesis and economic evaluation. *Biofuels, Bioproducts and Biorefining*, 6(4), pp.444-452.

- Seo, J.Y., Praveenkumar, R., Kim, B., Seo, J.C., Park, J.Y., Na, J.G., Jeon, S.G., Park, S.B., Lee, K. and Oh, Y.K., 2016. Downstream integration of microalgae harvesting and cell disruption by means of cationic surfactant-decorated Fe₃O₄ nanoparticles. *Green Chemistry*, 18(14), pp.3981-3989.
- Shuba, E.S. and Kifle, D., 2018. Microalgae to biofuels: 'Promising' alternative and renewable energy, review. *Renewable and Sustainable Energy Reviews*, 81, pp.743-755.
- Sim, T.S., Goh, A. and Becker, E.W., 1988. Comparison of centrifugation, dissolved air flotation and drum filtration techniques for harvesting sewage-grown algae. *Biomass*, 16(1), pp.51-62.
- Singh, G. and Patidar, S.K., 2018. Microalgae harvesting techniques: A review. *Journal of environmental management*, 217, pp.499-508.
- Siva, S. and Marimuthu, C., 2015. Production of biodiesel by transesterification of algae oil with an assistance of nano-CaO catalyst derived from egg shell. *International Journal of ChemTech Research*, 7(4), pp.2112-2116.
- Slegers, P.M., Koetzier, B.J., Fasaei, F., Wijffels, R.H., Van Straten, G. and Van Boxtel, A.J.B., 2014. A model-based combinatorial optimisation approach for energy-efficient processing of microalgae. *Algal Research*, 5, pp.140-157.
- Soeder, C.J., 1980. Massive cultivation of microalgae: results and prospects. *Hydrobiologia*, 72(1), pp.197-209.
- Srirangan, K., Akawi, L., Moo-Young, M. and Chou, C.P., 2012. Towards sustainable production of clean energy carriers from biomass resources. *Applied energy*, 100, pp.172-186.
- Sun, Y., Qin, Z., Tang, Y., Huang, T., Ding, S. and Ma, X., 2021. Techno-environmental-economic evaluation on municipal solid waste (MSW) to power/fuel by gasification-based and incineration-based routes. *Journal of Environmental Chemical Engineering*, 9(5), p.106108.
- Suparmaniam, U., Lam, M.K., Uemura, Y., Lim, J.W., Lee, K.T. and Shuit, S.H., 2019. Insights into the microalgae cultivation technology and harvesting process for biofuel production: A review. *Renewable and Sustainable Energy Reviews*, 115, p.109361.
- Taher, H., Al-Zuhair, S., Al-Marzouqi, A.H., Haik, Y. and Farid, M.M., 2011. A review of enzymatic transesterification of microalgal oil-based biodiesel using supercritical technology. *Enzyme research*, 2011.

- Takkellapati, S., Li, T. and Gonzalez, M.A., 2018. An overview of biorefinery-derived platform chemicals from a cellulose and hemicellulose biorefinery. *Clean technologies and environmental policy*, 20(7), pp.1615-1630.
- Taleb, A., Kandilian, R., Touchard, R., Montalescot, V., Rinaldi, T., Taha, S., Takache, H., Marchal, L., Legrand, J. and Pruvost, J., 2016. Screening of freshwater and seawater microalgae strains in fully controlled photobioreactors for biodiesel production. *Bioresource Technology*, 218, pp.480-490.
- Tan, K.T., Lee, K.T. and Mohamed, A.R., 2009. Production of FAME by palm oil transesterification via supercritical methanol technology. *Biomass and Bioenergy*, 33(8), pp.1096-1099.
- Tan, X.B., Lam, M.K., Uemura, Y., Lim, J.W., Wong, C.Y. and Lee, K.T., 2018. Cultivation of microalgae for biodiesel production: a review on upstream and downstream processing. *Chinese Journal of Chemical Engineering*, 26(1), pp.17-30.
- Tan, X.B., Lam, M.K., Uemura, Y., Lim, J.W., Wong, C.Y. and Lee, K.T., 2018. Cultivation of microalgae for biodiesel production: a review on upstream and downstream processing. *Chinese Journal of Chemical Engineering*, 26(1), pp.17-30.
- Teo, S.H., Islam, A. and Taufiq-Yap, Y.H., 2016. Algae derived biodiesel using nanocatalytic transesterification process. *Chemical engineering research and design*, 111, pp.362-370.
- Ursu, A.V., Marcati, A., Sayd, T., Sante-Lhoutellier, V., Djelveh, G. and Michaud, P., 2014. Extraction, fractionation and functional properties of proteins from the microalgae *Chlorella vulgaris*. *Bioresource technology*, 157, pp.134-139.
- Van Haver, L. and Nayar, S., 2017. Polyelectrolyte flocculants in harvesting microalgal biomass for food and feed applications. *Algal Research*, 24, pp.167-180.
- Vandamme, D., Foubert, I., Fraeye, I., Meesschaert, B. and Muylaert, K., 2012. Flocculation of *Chlorella vulgaris* induced by high pH: role of magnesium and calcium and practical implications. *Bioresource technology*, 105, pp.114-119.
- Vandamme, D., Foubert, I. and Muylaert, K., 2013. Flocculation as a low-cost method for harvesting microalgae for bulk biomass production. *Trends in biotechnology*, 31(4), pp.233-239.
- Vandamme, D., Pontes, S.C.V., Goiris, K., Foubert, I., Pinoy, L.J.J. and Muylaert, K., 2011. Evaluation of electro-coagulation–flocculation for harvesting marine and freshwater microalgae. *Biotechnology and bioengineering*, 108(10), pp.2320-2329.

- Velasquez-Orta, S.B., Lee, J.G.M. and Harvey, A., 2012. Alkaline in situ transesterification of *Chlorella vulgaris*. *Fuel*, 94, pp.544-550.
- Vicente, G., Martinez, M. and Aracil, J., 2004. Integrated biodiesel production: a comparison of different homogeneous catalysts systems. *Bioresource technology*, 92(3), pp.297-305.
- Wang, B., Lan, C.Q. and Horsman, M., 2012. Closed photobioreactors for production of microalgal biomasses. *Biotechnology advances*, 30(4), pp.904-912.
- Wang, X., Ruan, Z., Sheridan, P., Boileau, D., Liu, Y. and Liao, W., 2015. Two-stage photoautotrophic cultivation to improve carbohydrate production in *Chlamydomonas reinhardtii*. *biomass and bioenergy*, 74, pp.280-287.
- Wang, H., Pu, Y., Ragauskas, A. and Yang, B., 2019. From lignin to valuable products—strategies, challenges, and prospects. *Bioresource technology*, 271, pp.449-461.
- Yi, S., Yoo, K.Y. and Hanaki, K., 2011. Characteristics of MSW and heat energy recovery between residential and commercial areas in Seoul. *Waste management*, 31(3), pp.595-602.
- Yoon H-S., 2012. International and domestic trends in biofuel production via microalgae. *Bioin Special Webzine 27*, Biotech Policy Research Center (in Korean)
- Yue, H., Ma, X. and Gong, J., 2014. An alternative synthetic approach for efficient catalytic conversion of syngas to ethanol. *Accounts of chemical research*, 47(5), pp.1483-1492.
- Zeller, M.A., Hunt, R., Jones, A. and Sharma, S., 2013. Bioplastics and their thermoplastic blends from *Spirulina* and *Chlorella* microalgae. *Journal of Applied Polymer Science*, 130(5), pp.3263-3275.
- Zheng, H., Yin, J., Gao, Z., Huang, H., Ji, X. and Dou, C., 2011. Disruption of *Chlorella vulgaris* cells for the release of biodiesel-producing lipids: a comparison of grinding, ultrasonication, bead milling, enzymatic lysis, and microwaves. *Applied biochemistry and biotechnology*, 164(7), pp.1215-1224.
- Zhou, W., Wang, Z., Alam, M., Xu, J., Zhu, S., Yuan, Z., Huo, S., Guo, Y., Qin, L. and Ma, L., 2019. Repeated utilization of ionic liquid to extract lipid from algal biomass. *International Journal of Polymer Science*, 2019.
- Zullaikah, S., Utomo, A.T., Yasmin, M., Ong, L.K. and Ju, Y.H., 2019. Ecofuel conversion technology of inedible lipid feedstocks to renewable fuel. In *Advances in Eco-Fuels for a Sustainable Environment* (pp. 237-276). Woodhead Publishing.

Appendix A Numerical Data for Model Parameters

Table 13 Approximated cost factor at microalgae cultivation stage c

Main Input	Processing	Product	\$/tonne	Reference
CO2	Open Pond System	Microalgal Biomass Suspension	410	Slade, R., & Bauen, A. (2013).
CO2	Photobioreactor	Microalgal Biomass Suspension	3800	Slade, R., & Bauen, A. (2013).

Table 14 Approximated conversion factor at microalgae cultivation stage c

Processing	Main Input	Outlet	Conversion Factor (kg/kg main input)	Reference
Open Pond System	Carbon dioxide	Microalgae	0.18421	Richardson et al. (2012).
	Carbon dioxide	Culture Media	122.667	
Photobioreactor	Carbon dioxide	Microalgae	0.394737	Richardson et al. (2012).
	Carbon dioxide	Culture Media	98.68425	

*Assumed output has 1.5 g/L and 4 g/L concentration in culture media for each processing alternative. Open pond system and photobioreactor have 35% and 75% efficiency, respectively.

Table 15 Approximated cost factor at microalgae separation stage s

Main Input	Processing	Product	\$/tonne	Reference
Microalgal Biomass Suspension	Floc. With Polyelectrolyte	Wet Microalgal Biomass	501	Van Haver & Nayar (2017).
Microalgal Biomass Suspension	Floc. With NaOH	Wet Microalgal Biomass	212.6	Nguyen et al. (2014).
Microalgal Biomass Suspension	Floc. With PGA	Wet Microalgal Biomass	532.6	Ma et al. (2016).
Microalgal Biomass Suspension	Floc. With FeCl3	Wet Microalgal Biomass	517	Lecina et al. (2016).
Microalgal Biomass Suspension	Biofloc.+Centrifugation	Wet Microalgal Biomass	984	Ndikubwimana et al. (2016).
Microalgal Biomass Suspension	Centrifugation	Wet Microalgal Biomass	864	Dassey & Theegala (2013).
Microalgal Biomass Suspension	Autofloc. With Ca(OH)2 pH Alteration	Wet Microalgal Biomass	133.5	Pishgar et al. (2020).
Microalgal Biomass Suspension	Microfiltration+Centrifugation	Wet Microalgal Biomass	2050	Liu et al. (2021).
Microalgal Biomass Suspension	Floc. With Chitosan	Wet Microalgal Biomass	514	Rashid et al. (2013)

Table 16 Approximated conversion factor at microalgae separation stage s

Processing	Main Input	Outlet	Conversion Factor (kg/kg main input)	Reference
Floc. With Polyelectrolyte	Microalgae	Wet Biomass	0.94	Van Haver & Nayar (2017).
	Culture Media	Water	0.1	
Floc. With NaOH	Microalgae	Wet Biomass	0.98	Nguyen et al. (2014).
	Culture Media	Water	0.1	
Floc. With PGA	Microalgae	Wet Biomass	0.95	Ma et al. (2016).
	Culture Media	Water	0.1	
Floc. With FeCl3	Microalgae	Wet Biomass	0.95	Lecina et al. (2016).
	Culture Media	Water	0.1	
Biofloc.+Centrifugation	Microalgae	Wet Biomass	0.4	Ndikubwimana et al. (2016).
	Culture Media	Water	0.1	
Centrifugation	Microalgae	Wet Biomass	0.95	Dassey & Theegala (2013).
	Culture Media	Water	0.1	
Autofloc. With Ca(OH) ₂ pH Alteration	Microalgae	Wet Biomass	0.75	Pishgar et al. (2020).
	Culture Media	Water	0.1	
Microfiltration+Centrifugation	Microalgae	Wet Biomass	0.98	Liu et al. (2021).
	Culture Media	Water	0.1	
Floc. With Chitosan	Microalgae	Wet Biomass	0.91	Rashid et al. (2013).
	Culture Media	Water	0.1	

Table 17 Approximated cost factor at microalgae drying stage d

Main Input	Processing	Product	\$/tonne	Reference
Wet Microalgal Biomass	Grinding in Liq. Nitrogen	Microalgal Biomass Slurry	112	Kumar et al. (2019).
Wet Microalgal Biomass	Drying+Ultrasound	Microalgal Biomass Slurry	240	Quesada-Salas et al. (2021).
Wet Microalgal Biomass	Drying+Grinding+Microwave+Ultrasound	Microalgal Biomass Slurry	345.1	Quesada-Salas et al. (2021).
Wet Microalgal Biomass	Empty	Wet Microalgal Biomass	0	-
Wet Microalgal Biomass	Freeze Drying	Microalgal Biomass Slurry	52.8	Guldhe et al. (2014).

Table 18 Approximated conversion factor at microalgae drying stage d

Processing	Main Input	Outlet	Conversion Factor (kg/kg main input)	Reference
Grinding in Liq. Nitrogen	Wet Biomass	Dry Biomass	1	Kumar et al. (2019).
Drying+Ultrasound	Wet Biomass	Dry Biomass	1	Quesada-Salas et al. (2021).
Drying+Grinding+Microwave+Ultrasound	Wet Biomass	Dry Biomass	1	Quesada-Salas et al. (2021).
Freeze Drying	Wet Biomass	Dry Biomass	1	Guldhe et al. (2014).

Table 19 Approximated cost factor at microalgae lipid extraction stage 1

Main Input	Processing	Product	\$/tonne	Reference
Microalgal Biomass Slurry	Grinding-Assisted	Lipid	405	Krishnan et al. (2020).
Microalgal Biomass Slurry	Ultrasound-Assisted+[Bmim][MeSO4]	Lipid	1421	Azman et al. (2021).
Microalgal Biomass Slurry	Ultrasound+Microwave	Lipid	260	Amiri & Arabian (2018).
Wet Microalgal Biomass	Wet Lipid Extraction	Lipid	921	Lakshmikandan et al. (2020).
Microalgal Biomass Slurry	Bligh and Dyer Extraction	Lipid	284	Jeon et al. (2013).
Microalgal Biomass Slurry	Modified Bligh and Dyer	Lipid	284	Jeon et al. (2013).
Microalgal Biomass Slurry	Supercritical Fluid Extraction	Lipid	441.7	khorrandashti et al. (2021).
Microalgal Biomass Slurry	Ionic Liquids Mixture	Lipid	2650	Zhou et al. (2019).
Microalgal Biomass Slurry	Extraction by [Bmim][MeSO4]	Lipid	1320	Azman et al. (2021).
Microalgal Biomass Slurry	Empty	Microalgal Biomass Slurry	0	-

Table 20 Approximated conversion factor at microalgae lipid extraction stage 1

Processing	Main Input	Outlet	Conversion Factor (kg/kg main input)	Reference
Grinding-Assisted	Dry Biomass	Lipid	0.289989	Krishnan et al. (2020).
Ultrasound-Assisted+[Bmim][MeSO4]	Dry Biomass	Lipid	0.074025	Azman et al. (2021).
Ultrasound+Microwave	Dry Biomass	Lipid	0.10017	Amiri & Arabian (2018).
Wet Lipid Extraction	Wet Biomass	Lipid	0.289485	Lakshmikandan et al. (2020).
Bligh and Dyer Extraction	Dry Biomass	Lipid	0.0672525	Jeon et al. (2013).
Modified Bligh and Dyer	Dry Biomass	Lipid	0.0843885	Jeon et al. (2013).
Supercritical Fluid Extraction	Dry Biomass	Lipid	0.1300005	khorrandashti et al. (2021).
Ionic Liquids Mixture	Dry Biomass	Lipid	0.255717	Zhou et al. (2019).
Extraction by [Bmim][MeSO4]	Dry Biomass	Lipid	0.04725	Azman et al. (2021).

* Assumed 31.5% of microalgal biomass is composed of lipid content (*C. vulgaris*) and the rest is classified as non-lipid residue. Therefore, the conversion factor is the multiplied value of process efficiency to 31.5%.

Table 21 Approximated cost factor at transesterification stage t

Main Input	Processing	Product	\$/tonne	Reference
Lipid	Alkaline Transesterification	Biodiesel + Glycerol + Residue	520	Heo & Lee (2019).
Lipid	Acidic Transesterification	Biodiesel + Glycerol + Residue	610	Heo & Lee (2019).
Lipid	Enzymatic Transesterification	Biodiesel + Glycerol + Residue	1250	Heo & Lee (2019).
Lipid	Nanocatalytic Transesterification	Biodiesel + Glycerol + Residue	1100	Teo et al. (2016).
Microalgal Biomass Slurry	Alkaline in-situ Transesterification	Biodiesel + Glycerol + Residue	762	Velasquez-Orta et al. (2012).
Microalgal Biomass Slurry	Acidic in-situ Transesterification	Biodiesel + Glycerol + Residue	850	Velasquez-Orta et al. (2012).
Microalgal Biomass Slurry	Enzymatic in-situ Transesterification	Biodiesel + Glycerol + Residue	1340	Kim et al. (2019).

Table 22 Approximated conversion factor at transesterification stage t

Processing	Main Input	Outlet	Conversion Factor (kg/kg main input)	Reference
Alkaline Transesterification	Lipid	Biodiesel	0.9690	Heo & Lee (2019).
	Lipid	Glycerol	0.1009	
	Lipid	Methanol	0.0988	
Acidic Transesterification	Lipid	Biodiesel	0.9391	Heo & Lee (2019).
	Lipid	Glycerol	0.0978	
	Lipid	Methanol	0.4988	
Enzymatic Transesterification	Lipid	Biodiesel	0.7172	Heo & Lee (2019).
	Lipid	Glycerol	0.0747	
	Lipid	Methanol	0.0949	
Nanocatalytic Transesterification	Lipid	Biodiesel	0.9620	Teo et al. (2016).
	Lipid	Glycerol	0.1002	
	Lipid	Methanol	0.2171	
Alkaline in-situ Transesterification	Dry Biomass	Biodiesel	0.2273	Velasquez-Orta et al. (2012).
	Dry Biomass	Glycerol	0.0237	
	Dry Biomass	Methanol	1.5104	
Acidic in-situ Transesterification	Dry Biomass	Biodiesel	0.3032	Velasquez-Orta et al. (2012).
	Dry Biomass	Glycerol	0.0316	
	Dry Biomass	Methanol	1.5104	
Enzymatic in-situ Transesterification	Dry Biomass	Biodiesel	0.2612	Kim et al. (2019).
	Dry Biomass	Glycerol	0.0272	
	Dry Biomass	Methanol	0.2288	

* Based on the chemical reaction equation, biodiesel and glycerol are produced in 3 times and 1 time factor in mole ratio from lipid content. Also, it was assumed that methanol was added 9 times factor in mole ratio to lipid where, by theory, only requires by 3 times factor. Therefore, the outlet methanol amount is 2/3 of the originally added methanol input. Process efficiency from literature was also multiplied into the conversion factor.

Table 23 Approximated cost factor at biodiesel and glycerol purification stage p

Main Input	Processing	Product	\$/tonne	Reference
Biodiesel + Glycerol + Residue	methanol recovery, gravity separation, washing and purification, flash separation	Biodiesel	1518	Dhar & Kirtania (2009).

Table 24 Approximated conversion factor at biodiesel and glycerol purification stage p

Processing	Main Input	Outlet	Conversion Factor (kg/kg main input)	Reference
Biodiesel+Glycerol Purification Steps	Biodiesel	Biodiesel Product	0.86	Dhar & Kirtania (2009).
	Glycerol	Glycerol Product	0.86	
	Methanol	Methanol Recovery	0.95	

Table 25 Approximated cost factor at MSW processing stages

Main Input	Processing	Product	\$/tonne	Reference
MSW	Segregation Facility	Recyclables + Waste	25	Yap & Nixon (2015).
Recyclables + Waste	Material Recycling Facility (MRF)	Waste Mixture (divided into 3 groups)	34.8	Mian et al. (2017).
Non-Lipid Residue	Enzy. Hydrolysis + Fermentation	Bioethanol	777.45	Chen & Fu (2016).
Non-Lipid Residue + Waste	Gasification	Syngas	383.73	Liz, Han & Gu (2018).
Syngas	Catalytic Transformation	Bioethanol	113.11	Yue, Ma, X & Gong (2014).
Syngas	Elec. Gen. from Syngas	Electricity	71.16	Paulino et al. (2020).
Non-Lipid Residue + Waste	Anaerobic Digestion	Biogas	45.9	Ajeej et al. (2015).
Biogas	Elec. Gen. from Biogas	Electricity	63	Minutillo, Perna, & Sorce (2019).
Waste	Plasma Arc Gasification	Syngas	96.34	Munir et al. (2019).
Syngas	Elec. Gen. from PAG	Electricity	41	Ramos & Rouboa (2022).
Non-Lipid Residue + Waste	Pyrolysis	Biooil	15.6	Treedet & Suntivarakorn (2018).
Biooil	Elec. Gen from Biooil	Electricity	8.82	Dong et al. (2019).
Waste	Incineration	Incinerated Products	24.5	Sun et al. (2021).
Incinerated Products	Elec. Gen from Incinerated Products	Electricity	29.68	Escamilla-García et al. (2020).
Waste	Landfill	Landfill	7.15	Chong, Matsufuji & Hassan (2005).
Landfill	Elec. Gen from Landfill	Electricity	31.2	Cudjoe & Han (2020).
Waste	Composting	Compost	12	Sabki et al. (2018).

Table 26 Approximated conversion factor at segregation and recycling stages

Processing	Main Input	Outlet	Conversion Factor (kg/kg main input)	Reference
MSW Segregation	MSW	Food Waste	0.335	Yi et al. (2011).
	MSW	Paper	0.35	
	MSW	Plastics	0.055	
	MSW	Glass	0.07	
	MSW	Metals	0.105	
	MSW	Wood Waste	0.06	
	MSW	Textiles	0.025	
MSW Materials Recycling Facility	Paper	Recyclable paper	0.8	Yi et al. (2011).
	Plastics	Recyclable plastics	0.9	
	Glass	Recyclable glass	0.9	
	Metals	Recyclable metals	0.95	
	Rubbers	Recyclable rubber	0.95	

Table 27 Approximated conversion factor at MSW processing stages

Processing	Main Input	Outlet	Conversion Factor (kg/kg main input)	Reference
Enzy. Hydrolysis + Fermentation	Non-Lipid Residue	Bioethanol	0.26	Chen & Fu (2016).
Gasification	Non-Lipid Residue + Waste	Syngas	0.38	Liz, Han & Gu (2018).
Catalytic Transformation	Syngas	Bioethanol	0.31	Yue, Ma, X & Gong (2014).
Elec. Gen. from Syngas	Syngas	Electricity	1843.37	Paulino et al. (2020).
Anaerobic Digestion	Non-Lipid Residue + Waste	Biogas	0.617	Ajeej et al. (2015).
Elec. Gen. from Biogas	Biogas	Electricity	1907.3	Minutillo, Perna, & Sorce (2019).
Plasma Arc Gasification	Waste	Plasma Arc Gas	1.845	Munir et al. (2019).
Elec. Gen. from PAG	Syngas	Electricity	983.13	Ramos & Rouboa (2022).
Pyrolysis	Non-Lipid Residue + Waste	Biooil	0.53	Treedet & Suntivarakorn (2018).
Elec. Gen. from Biooil	Biooil	Electricity	590.36	Dong et al. (2019).
Incineration	Waste	Incinerated Products	1	Sun et al. (2021).
Elec. Gen. from Incinerated Products	Incinerated Products	Electricity	340	Escamilla-García et al. (2020).
Landfill	Waste	Landfill	1	Chong, Matsufuji & Hassan (2005).
Elec. Gen. from Landfill	Landfill	Electricity	162	Cudjoe & Han (2020).
Composting	Waste	Compost	0.423	Sabki et al. (2018).

* Note that the conversion factors for gas products and electricity are in terms of m³/kg main input and kWh/kg main input, respectively.

Appendix B GAMS Code

```
$title Microalgae_MSW_Combined

* This model has been developed for the optimal utilization and conversion of microalgae and
* municipal solid waste (MSW) into useful energy products
* Written by Kyuyeon Kim, 2022, University of Waterloo.

SETS
*FEED
ST Feed storage /CO2ST, MSWST/
st1(ST) CO2 storage location /CO2ST/
st2(ST) MSW Storage Location /MSWST/

*PROCESS ALTERNATIVES
c Cultivation of Microalgae /OPS, PHOTO/
s Separation of Microalgae /FLOC-PE, FLOC-NAOH, FLOC-PGA, FLOC-FE, BIOFLOC, CENT, AUTO, MICRO, FLOC-CHI/
d Drying of Microalgae /LIQ-N, ULTRA, MICRO-ULTRA, D-EMPTY, FREEZE/
D1(d) Normal Drying and Empty Bypass of Microalgae /LIQ-N, ULTRA, MICRO-ULTRA, D-EMPTY/
D2(d) Freeze Drying of Microalgae /FREEZE/
l Lipid Extraction /GRIND, ULTRA-BMIM, ULTRA-MICRO-EXT, WET, BND, MOD-BND, SUPFLUID, IONLIQ, BMIM, L-EMPTY/
L1(l) Normal Lipid & Wet Extraction /GRIND, ULTRA-BMIM, ULTRA-MICRO-EXT, WET/
L2(l) Lipid Extraction after Freeze Drying /BND, MOD-BND, SUPFLUID, IONLIQ, BMIM, L-EMPTY/
L3(l) Lipid Extraction group 1 /GRIND, ULTRA-BMIM, ULTRA-MICRO-EXT, WET, BND, MOD-BND, SUPFLUID, IONLIQ, BMIM/
L4(l) Lipid Extraction group 2 empty /L-EMPTY/
t Transesterification /ALKALINE, ACIDIC, ENZYME, NANO, ALKALINE-IS, ACIDIC-IS, ENZYME-IS/
T1(t) Normal Transesterification /ALKALINE, ACIDIC, ENZYME, NANO/
T2(t) In-situ Transesterification /ALKALINE-IS, ACIDIC-IS, ENZYME-IS/
p Biodiesel and Glycerol Purification /PURIFICATION/
g MSW Segregation /RECYCLING/
r Recycling Facility /MRF/
f MSW Other Treatment /ENZ, GASIFCAT, GASIFELEC, ANAEROBICE, PAGASE, COPYE, INCINE, LANDE, COMPOSTING/
F1(f) /ENZ/
F2(f) /GASIFCAT/
F3(f) /GASIFELEC/
F4(f) /ANAEROBICE/
F5(f) /PAGASE/
F6(f) /COPYE/
F7(f) /INCINE/
F8(f) /LANDE/
F9(f) /COMPOSTING/

*Products
a Cultivation Products /CV,H2O/
b Separation Products /SCV, RH2O/
B1(b) Separation Products to next stage /SCV/
B2(b) Separation Product Recycle Water /RH2O/
h Transesterification Products /RBIO, RGLY, RMEOH/
I1(h) Purification Final PRODUCTS /RBIO, RGLY/
j MSW Segregation Products /FOOD, WOOD, PAP, PLA, GLS, MET, TXT/
J1(j) Recyclables /PAP, PLA, GLS, MET, TXT/
JK1(J1) NR recyclables /PAP, TXT/
JK2(J1) NPLA recyclables /PLA/
JK3(J1) NGM recyclables /GLS, MET/
J2(j) Nonrecyclables /FOOD, WOOD/
k Recyclable Final PRODUCTS /RPAP, RPLA, RGLS, RMET, RTXT/
K1(k) Part of NR /RPAP, RTXT/
K2(k) Part of NPLA /RPLA/
K3(k) Part of NGM /RGLS, RMET/
m FINAL MSW NLCCV PRODUCTS /BIOETHANOL, ELECTRICITY, COMPOST/
M1(m) Ethanol /BIOETHANOL/
M2(m) Compost /COMPOST/
M3(m) Electricity /ELECTRICITY/
;
```

VARIABLES

sales sales of products
biomasscost biomass cost
prodcost production cost
profit net profit of overall process
;

POSITIVE VARIABLES

FEEDF(ST) Amount of CO2 and MSW source available at source location
FCO2(c) Amount of CO2 going into each cultivation stage
FCULT(c,a) Amount of a out from cultivation stage c
W(c) Total Amount of water supply required
FSEPI(s,a) Amount of a going into separation stage s
FSEP(a,s,b) Amount of b out from separation stage s
FRH2O(B2) Amount of recycle water combined
FH2O Amount of fresh water supply
FDRYI(B1,d) Amount of B1 into drying stage d
FDRY(B1,d) Amount of B1 out from drying stage d
LIPIDIN(D2) arbitrary lipid input storage
FLIPI(L2) Amount of CCV from freeze drying going into lipid extraction
LCCV(l) Amount of lipid out from lipid extraction stage l
NLCCV Amount of non-lipid out L1 L2 and T2
FTRAI(t) Amount of LCCV into trasesterification
FTRA(t,h) Amount of products h from transesterification step t
FPUR(h) Amount of purified products i from purification step p
MSEG(j) Amount of MSW segregated products from segregation stage
RECYCLE(J1) Amount of recyclable products
NR Amount of total NR
NPLA Amount of total NPLA
NGM Amount of total NGM
FENZ Amount of NLCCV going into EZNYME FERMENTATION
FNR Amount of NR going into treatment
FNPLA Amount of NPLA going into treatment
FNGM Amount of NGM going into treatment
FA1 NLCCV to GASIF
FA2 NLCCV to ANAEROBIC
FA4 NLCCV to COPY
FB1 NR to GASIF
FB2 NR to ANAEROBIC
FB3 NR to PAGAS
FB4 NR to COPY
FB5 NR to INCIN
FB6 NR to LAND
FB7 NR to COMPOST
FC1 NPLA to GASIF
FC4 NPLA to COPY
FC5 NPLA to INCIN

FC6 NPLA to LAND
FD5 NGM to INCIN
FD6 NGM to LAND
FTREAT(f) Amount of input stream going into treatment stage f for final product
FPROD(f) Amount of final product streams out of treatment stage f
FINAL(m) Amount of final products combined
;

BINARY VARIABLES

YC(c) Existence of process c at cultivation stage
YS(s) Existence of process s at separation stage
YD(d) Existence of process d at drying stage
YL(l) Existence of process l at lipid extraction stage
YT(t) Existence of process t at transesterification stage
YP(p) Existence of process p at purification stage
YG(g) Existence of process g at MSW segregation stage
YR(r) Existence of process r at material recycling facility
YF(f) Existence of treatment stage f
;

EQUATIONS

feedavail available amount of each feed at the beginning
demandreq(I1) demand requirement for microalgae products
demandreq(R1) demand requirement for microalgae MSW combined products

**MICROALGAE*

mb1(st1) splitting mass balance of CO2 into cultivation
recy1(c) calculation of water input requirement with respect to CO2 source input
mb3(c,a) mass balance for cultivation stage outlet
mb4(a) combining and splitting mass balance of a into drying unit s
mb5(a,s,b) mass balance for separation stage outlet
recy2(B2) combining recycle water RH2O
recy3 Total water=recycle+fresh water supply
mb6(B1) combining and splitting mass balance of b into drying unit d
mb7(B1,d) mass balance for drying stage outlet
mb8(D1,L1) mass balance for Normal Lipid Extraction stage L1
mb9(D2) combining and splitting mass balance of CCV into lipid unit L2 from freeze drying
mb9l lipid input splitting mass balance
mb10(L2) mass balance for lipid extraction stage L2
mb11 combining and splitting mass balance of LCCV into transesterification T1
mb12 splitting of empty bypass stage L4 LCCV into transesterification T2
mb13(t,h) mass balance for transesterification stage
mb14 calculation of total non lipid residue from lipid extraction stage from L1 L2 T2
mb15(h) mass balance for products of purification stage p

**MSW*

mb16(j) mass balance for segregation stage
mb17(J1) mass balance for recyclables at MRF stage
mb18 calculation of NR
mb19 calculation of NPLA
mb20 calculation of NGM
mb21 splitting of NLCCV into respective treatment stages
mb22 splitting of NR
mb23 splitting of NPLA
mb24 splitting of NGM
mb25 calculation of gasification input
mb26 calculation of anaerobic digestion input
mb27 calculation of co pyrolysis input
mb28 calculation of incineration input
mb29 calculation of landfill input
mb30(f) mass balance of treatment stage process f
mb31 calculation of final bioethanol product
mb32 calculation of final compost product
mb33 calculation of final electricity product

salesofprodeq equation for sales of products
biomasscosteq equation for biomass cost
prodcosteq equation for process production cost
Profiteq equation for profit

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mb1(st1).. FEEDF(st1) =e= sum(c, FCO2(c));
recyl(c).. W(c) =e= FCO2(c)*WREQ(c);
mb3(c,a).. FCO2(c)*CONVC(c,a)*YC(c) =e= FCULT(c,a);
mb4(a).. sum(c,FCULT(c,a)) =e= sum(s,FSEPI(s,a));
mb5(a,s,b).. FSEPI(s,a)*CONVS(a,s,b)*YS(s) =e= FSEP(a,s,b);
recy2(B2).. FRH2O(B2) =e= sum(a,sum(s,FSEP(a,s,B2)));
recy3.. sum(B2,FRH2O(B2))+FH2O =e= sum(c,W(c));
mb6(B1).. sum(a,sum(s,FSEP(a,s,B1))) =e= sum(d,FDRYI(B1,d));
mb7(B1,d).. FDRYI(B1,d)*CONVD(B1,d)*YD(d) =e= FDRY(B1,d);
mb8(D1,L1).. sum(B1,FDRY(B1,D1))*CONVL(L1)*YL(L1) =e= LCCV(L1);
mb9(D2).. sum(B1,FDRY(B1,D2)) =e= LIPIDIN(D2);
mb91.. sum(D2,LIPIDIN(D2)) =e= sum(L2,FLIPI(L2));
mb10(L2).. FLIPI(L2)*CONVL(L2)*YL(L2) =e= LCCV(L2);
mb11.. sum(L3,LCCV(L3)) =e= sum(T1,FTRAI(T1));
mb12.. sum(L4,LCCV(L4)) =e= sum(T2,FTRAI(T2));
mb13(t,h).. FTRAI(t)*CONVT(t,h)*YT(t) =e= FTRA(t,h);
mb14(D1).. sum(L1,sum(B1,FDRY(B1,D1))*(1-CONVL(L1))*YL(L1))+sum(L2,FLIPI(L2))*(1-CONVL(L2))*YL(L2)
+sum(T2,FTRAI(T2))*sum(h,CONVT(T2,h))*YT(T2) =e= NLCCV;
mb15(h).. sum(t,FTRA(t,h))*CONVP(h)*sum(p,YP(p)) =e= FPUR(h);

mb16(j).. sum(st2,FEEDF(st2))*CONVJ(j)*sum(g,YG(g)) =e= MSEG(j);
mb17(J1).. MSEG(J1)*CONVK(J1)*sum(x,YR(x)) =e= RECYCLE(J1);
mb18.. sum(J2,MSEG(J2))+ sum(JK1,MSEG(JK1))*(1-CONVK(JK1))*sum(x,YR(x)) =e= NR;
mb19.. sum(JK2,MSEG(JK2))*(1-CONVK(JK2))*sum(x,YR(x)) =e= NPLA;
mb20.. sum(JK3,MSEG(JK3))*(1-CONVK(JK3))*sum(x,YR(x)) =e= NGM;
mb21(F1).. NLCCV =e= FTREAT(F1)+FA1+FA2+FA4;
mb22(F5,F9).. NR =e= FB1+FB2+FTREAT(F5)+FB4+FB5+FB6+FTREAT(F9);
mb23.. NPLA =e= FC1+FC4+FC5+FC6;
mb24.. NGM =e= FD5+FD6;
mb25(F2,F3).. FA1+FB1+FC1 =e= FTREAT(F2)+FTREAT(F3);
mb26(F4).. FA2+FB2 =e= FTREAT(F4);
mb27(F6).. FA4+FB4+FC4 =e= FTREAT(F6);
mb28(F7).. FB5+FC5+FD5 =e= FTREAT(F7);
mb29(F8).. FB6+FC6+FD6 =e= FTREAT(F8);
mb30(f).. FTREAT(f)*CONVF(f)*YF(f) =e= FPROD(f);
mb31(M1,F1,F2).. FINAL(M1) =e= FPROD(F1)+FPROD(F2);
mb32(M2,F9).. FINAL(M2) =e= FPROD(F9);
mb33(M3,F3,F4,F5,F6,F7,F8).. FINAL(M3) =e= FPROD(F3)+FPROD(F4)+FPROD(F5)+FPROD(F6)+FPROD(F7)+FPROD(F8);

salesofprodeq.. sales =e= sum(I1, PRODC(I1))*FPUR(I1))+sum(m, PRODM(m)*FINAL(m))+sum(J1,RECYC(J1))*RECYCLE(J1));
biomasscosteq.. biomasscost =e= sum(ST, FEEDC(ST))*FEEDF(ST);
prodcosteq.. prodcost =e= sum(c,COSTC(c)*FCO2(c))+sum(s,COSTS(s)*sum(a,FSEPI(s,a))+sum(d,COSTD(d)*sum(B1,FDRYI(B1,d))
+sum(D1,COSTD1(D1))*sum(B1,FDRY(B1,D1))+sum(L2,COSTL2(L2))*FLIPI(L2)
+sum(t,COSTT(t))*FTRAI(t))+sum(p,COSTP(p))*sum(h,sum(t,FTRA(t,h))))
+sum(g,COSTG(g))*sum(st2,FEEDF(st2))+sum(x,COSTR(x))*sum(j,MSEG(j))+sum(f,COSTF(f))*FTREAT(f));

Profiteq.. profit =e= sales - biomasscost - prodcost;

profit.lo = 0 ;

model integratedrefinery /all/;
solve integratedrefinery using minlp maximizing sales;

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