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Review

Importance of Microalgae and Municipal Waste in Bioenergy Products Hierarchy—Integration of Biorefineries for Microalgae and Municipal Waste Processing: A Review

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Abstract: In the context of global advancements, the imperative of a sustainable energy supply looms large. Biomass, an adaptable and renewable resource, has garnered attention for its potential contributions, although economic uncertainties persist due to the intricate web of processing pathways. In response, the biorefinery concept emerges as a structured strategy to optimize the processing of microalgae and municipal solid waste (MSW), capitalizing on their multifaceted potential to yield diverse end-products. This review underscores the critical significance of a cohesive biorefinery paradigm that unites the processing of microalgae and MSW, unveiling their capacity to generate a spectrum of high-value products. The utilization of mixed-integer linear programming paves the way for an optimal biorefinery model that navigates through complex decisions. Challenges encompass the array of diverse feedstocks and the preliminary nature of data availability. The overarching goal of this research is to discern optimal pathways for the conversion of MSW and microalgae into energy and valuable products, with a focus on enhancing waste utilization and augmenting the energy supply. In the broader landscape, this comprehensive review advances strategies for sustainable energy generation and waste management, invigorating innovative approaches to shape future progress. By illuminating pathways towards maximizing the potential of biomass resources, this review contributes to the ongoing discourse on sustainable energy and waste utilization.

Keywords: biorefinery; microalgae processing; municipal solid waste; superstructure formation; optimization top of form

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1. Introduction

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. Over the last couple of decades, biorefinery has received much interest as the most strategically important and prospective industry, as it could be associated with many aspects of social development and a sustainable future, as opposed to the fossil fuels. Fossil fuels presently stand as the predominant global energy source, having propelled worldwide economic progress throughout the last century. Yet, they are finite resources and can also irreversibly harm the environment. The current situation of climate change and problems related to the use of fossil fuels could be mitigated by replacing them with other renewable resources [1]. On the other hand, biomass resources are evenly available

worldwide and biomass-derived products are renewable. Biofuels are also welcomed in the transportation sector due to their high energy density and similarity to conventional transportation fuels such as gasoline and diesel. Furthermore, biorefinery 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 the food, pharmaceutical, cosmetics, and packing industries [2].

Despite continuous approaches to research and development on biorefineries, there are still a number of challenges to be addressed before commercialization. In 2017, biomass fuels contributed approximately 5% to the United States' overall primary energy consumption. The formidable challenges lie in the elevated expenses linked to biomass feedstock, alongside the intricacies of their transportation and processing. Moreover, the technologies involved in converting, harnessing, and recycling alternative renewable energy sources remain in a state of ongoing development. Recently, there have been more types of raw resources identified as substitutive feedstocks that are sufficient for producing meaningful products. With more options in the selection of feedstocks and processing methods, the current focus of process engineering research is about integrating multiple process routes and optimizing the pathways to improve economic feasibility, transformation efficiency, and final product yield [3]. Potential development could focus on optimizing unit operations and plants, or applying process, energy, water, and waste integration. Published studies established the combined optimization approach in techno-economic analysis for the production of bioethanol [4], biogas [5], biodiesel [6], and mixed biofuels [7]. Many studies identify the most optimal pathways from the superstructure flowsheets using a mixed-integer nonlinear programming (MINLP) model. For instance, Slegers et al. [8] introduced a model-centric combinatorial strategy to enhance the energy-efficient conversion of microalgae into biodiesel. Martin and Grossman [9] formulated a MINLP model to evaluate a superstructure for biodiesel production from cooking oil and algae, considering heat and water integration. Rizwan et al. [10] proposed a superstructure-based modeling framework for the production of biodiesel from microalgae. In their follow-up study [11], the optimization was extended by adding microalgae residue processing and water recycling for wider aspects of process economics.

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 should 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) the inconsistent and preliminary nature of technological and economic data. Especially, the research in the field of biorefineries based on second- and third-generation feedstocks, including municipal solid waste (MSW) and microalgae, are at an early phase of study with a limited amount of reliable data for each processing step. In addition, there remains a lack of comprehensive exploration into the possibilities of integrating biofuel production from MSW and microalgae with various waste treatment methodologies. Therefore, this review will cover the potential technological alternatives available for converting MSW and microalgae into various energy and valuable products as well as the handling and/or recycling of waste materials. To increase the understanding of the overall process, a brief review about MSW and microalgae as feedstocks and major biorefinery routes will be explained. The objective of this paper is to review and summarize up-to-date information on currently developing or available technological processing alternatives for microalgae and MSW biorefineries. The identified unit operation options will be later considered to synthesize an integrated superstructure for both microalgae and MSW. In addition, the review will also explore potential value-added products that could be generated other than biofuels to exhaust the remaining solid wastes, thus increasing the conversion rate and contributing towards the primary energy supply.

It should be noted that the integration of microalgae and municipal waste treatment within the framework of a biorefinery concept offers a promising avenue for addressing

multifaceted environmental and resource challenges. This amalgamation capitalizes on the unique attributes of both microalgae and municipal waste, presenting numerous benefits:

1. Resource Synergy: Microalgae possess the remarkable ability to metabolize various organic materials, including those present in municipal waste streams. Integrating these two processes allows for a symbiotic relationship wherein microalgae can consume nutrients from the waste, aiding its decomposition, while simultaneously aiding in waste treatment.
2. Waste Valorization: The integration enables the transformation of organic components within municipal waste into valuable resources, such as biofuels, bioplastics, and high-protein biomass, through microalgae cultivation. This transforms waste management from a disposal-focused practice into a resource recovery approach [12].
3. Carbon Capture and Utilization: Microalgae efficiently capture carbon dioxide (CO_2) during their growth. By coupling this CO_2 sequestration with municipal waste processing, the integration mitigates greenhouse gas emissions and contributes to carbon neutrality.
4. Enhanced Efficiency: Microalgae cultivation can enhance the overall efficiency of municipal waste treatment processes. The microorganisms can contribute to breaking down complex organic compounds and accelerating waste decomposition.
5. Circular Economy: The integrated system aligns with the principles of a circular economy by creating closed-loop cycles, wherein waste is repurposed into valuable products. This minimizes resource depletion and waste generation.
6. Sustainable Energy Production: The integration can yield bioenergy from microalgae biomass, offering an alternative to fossil fuels. This sustainable energy source contributes to reducing dependence on non-renewable resources.
7. Environmental Remediation: Microalgae have the potential to remediate pollutants from wastewater streams generated during municipal waste treatment, further enhancing the environmental impact of the integrated process.
8. Economic Viability: By converting waste into valuable products and generating energy, the integrated approach can potentially create economic opportunities and job prospects in the waste management and bioenergy sectors.

In summary, the integration of microalgae and municipal waste treatment within the biorefinery concept aligns with the principles of sustainability, the circular economy, and resource efficiency. This synergy transforms waste management into a dynamic process that generates value and contributes to a cleaner environment and a more sustainable future.

2. Biomass Feedstocks and Their Characteristics

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 refers 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" [13]. Historically, biomass stands as humanity's most ancient energy source, still providing up to 14% of the global energy supply today. The energy harbored within biomass, originating from diverse forms of carbonaceous compounds, essentially embodies solar energy. For instance, through photosynthesis, plants harness the sun's energy. Biomass can be directly combusted or transformed into biofuels or biogas, subsequently serving as combustible fuels [14].

- Biomass covers a wide range of energy forms. Forestry and agricultural products including wood from trees, grass, crops, and oilseeds were the common forms of biomass in the past. Biomass also includes plant residues, biomass processing residues,

animal manure, and even municipal solid waste (MSW). The following items are brief explanations of common biomass resources.

- Energy crops are non-consumable crops that can be harvested even on malnutritional land, on 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 include 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 re-stimulate wildlife habitat and circulate water and soil quality, thus improving the overall crop land productivity.
- Residues from forest and agricultural crops also have the 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, the periodic removal of organic residues in forests and fields also aids in ecosystem restoration, functional vitality, and structural resilience.
- Other organic wastes produced by humankind 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 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 generating bioenergy. Utilizing organic wastes is an emerging opportunity to produce bioenergy and reduce significantly the volume of landfills.
- Algae are defined as a group of photosynthetic phytoplankton typically found in freshwater and marine systems. Recent studies have discovered the potential to harvest bioenergy from algal biomass due to their lipid-rich compositions. They also contain 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 the opportunity for wastewater recycling and utilization in a biorefinery concept.

From the presented sources of biomass, it can be concluded that biomass is widely available all over the world and is easy to acquire. Thus, one of the main considerations during the systems planning should be the determination of the proper 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 [15]:

- First-generation biofuels: They are mainly derived from agricultural products such as crops, sugarcane, and oilseed. These types of feedstocks are naturally abundant and are known to be very high in carbohydrate or energy content, needed 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 types 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 such a drastically increased demand for energy recently that

the first-generation feedstock is no longer considered ideal. Crop cultivation results in nitrogen oxides (NOx), which are gaseous chemicals that accelerate the greenhouse effect [16]. The shift from food crop cultivation to biofuel crop production has the potential to lower food availability and consequently impact food prices. Furthermore, the competition for crop supply between food and fuel production increased the crop purchasing price up to USD 338/ton in 2012 [17], ultimately decreasing the 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 desolate land. In addition, agricultural, municipal, and institutional by-products and waste also fall under the second-generation biofuel feedstocks category [18]. The price value for lignocellulosic biomass ranges between USD 60–100/ton, and municipal solid waste costs between USD 0 and USD 60/ton [17]. These feedstocks can be categorized based on their homogeneity: homogenous, quasi-homogeneous, or non-homogeneous. Despite their advantages, the process used to convert them 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 comprehensive research, this prospect could evolve into an advantageous foundation for establishing a "biorefinery," offering the potential to derive a multitude of products from a single feedstock. Thus, more research and development are required for efficient bioenergy production. Still, underlying environmental concerns for land use and potential ecosystem interference are crucial considerations if fertilizer is used for farming.
- Third-generation biofuels: Third-generation biofuels are derived from algae, which have a very distinctive and rapid growth pattern compared to other traditional feedstocks. They have a diverse biochemical composition including carbohydrates, lipids, and proteins, which allows for the 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 of up to 70% [19]. 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 a water shortage or low temperature climate. In technical aspects, their high water content requires a significant dewatering process, as well as complex stages of filtration and transesterification for lipids to be further processed for biodiesel production [20].

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 resources, and high feedstock cost, have accelerated recent attention towards the next-generation biofuels [21]. As many other types of resources have been proposed as future generations of biorefinery feedstock, the future of biorefinery may not only be the production of multiple bioproducts from one feedstock, but also a combination of multiple generations of feedstocks to maximize the yield and sustainability.

Meanwhile, in the context of integrated biorefineries, the complementary traits of microalgae and MSW offer the potential for synergistic solutions, transforming waste into valuable products and sustainable energy sources, while addressing environmental challenges. Some information on the characteristics of microalgae is provided here:

1. Rapid Growth Rate: Microalgae are tiny single-celled organisms that exhibit rapid growth rates compared to traditional terrestrial crops. They can double their biomass in a matter of hours under optimal conditions.

2. High Biomass Yield: Microalgae can yield a significantly higher biomass per unit area compared to traditional crops. This makes them an efficient source of biomass for various applications.
3. Nutrient Utilization: Microalgae have the ability to utilize nutrients such as nitrogen and phosphorus effectively, which can be beneficial for nutrient removal from wastewater or effluents.
4. CO_2 Sequestration: Microalgae are highly efficient in capturing carbon dioxide (CO_2) from the atmosphere during photosynthesis. This trait is of great interest for mitigating greenhouse gas emissions.
5. Biochemical Composition: Microalgae have a diverse biochemical composition, containing proteins, lipids, carbohydrates, and other valuable compounds. This composition can vary based on species, growth conditions, and cultivation methods.
6. Value-Added Products: Microalgae can be used to produce a range of valuable products, including biofuels (biodiesel, bioethanol), bioplastics, pigments, nutraceuticals, and animal feed supplements.

On the other hand, for municipal solid waste (MSW), the following main characteristics can be mentioned:

1. Diverse Composition: MSW is a complex mixture of organic, inorganic, and potentially hazardous materials. It includes paper, plastics, food waste, glass, metals, and more.
2. Energy Content: The organic fraction of MSW, such as food waste and paper, contains a significant energy content that can be harnessed through various conversion processes.
3. Waste-to-Energy Potential: MSW can be incinerated to generate heat and electricity, contributing to waste management and energy production simultaneously.
4. Challenges: The heterogeneity of MSW poses challenges in processing and separation. Contamination and variable composition can affect the efficiency of conversion processes.
5. Resource Recovery: MSW can be a source of valuable materials. Recycling and recovery efforts can extract metals, plastics, and other recyclables, reducing the need for virgin resources.
6. Anaerobic Digestion: The organic fraction of MSW can undergo anaerobic digestion to produce biogas (methane), which can be used as a renewable energy source.
7. Landfill Diversion: The effective utilization of MSW as biomass feedstock can divert waste from landfills, reducing environmental pollution and promoting sustainable waste management.

3. Bioenergy Products and Conversion Methods

With a wide range of biomass feedstock options and processing methods, a variety of possible biomass-derived products can 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 the biorefinery process is worth being studied and commercialized. Table 1 summarizes a list of common biomass-derived products and conventional fossil fuels.

As summarized above, the first section of the product list is raw biomass, commonly found in agricultural and forestry landscapes. In the past, this type of biomass was directly burned, heated, or cooked to generate energy, which led to low energy efficiency. However, if the raw biomass materials are converted into biofuels (listed in the second section of the table) like ethanol, methanol, biodiesel, and pyrolysis oil, the values show that both bulk density and volumetric energy increase, 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 increase, transportation and distribution costs could be saved compared to raw biomass. Thus, transforming biomass feedstocks into higher-energy applications in the most economical, energy-efficient, and eco-friendly manner would be the main objective for a biorefinery concept.

Table 1. Bulk density and volumetric energy of biomass and conventional fuels [22].

Product	Bulk Density (Kg/m^3)	Volumetric Energy (GJ/m^3)
Rice Hulls	130	2.1
Straw	160–300	2.6–4.9
Softwood	200–340	1.0–6.8
Agricultural Residues	50–200	0.8–3.6
Hardwood	280–480	5.3–9.1
Bagasse	160	2.8
Pyrolysis Oil	1280	10.6
Methanol	790	17.6
Ethanol	790	23.5
Biodiesel	900	35.4
Coal	600–900	11–33
Gasoline	740	35.7
Diesel	850	39.1

Biomass conversion methods can be classified into three main process technologies: (i) chemical, (ii) thermo-chemical, and (iii) biochemical conversions [23]. Figure 1 presents an overview of common bioenergy conversion methods and their expected bioproducts, classified into three categories.

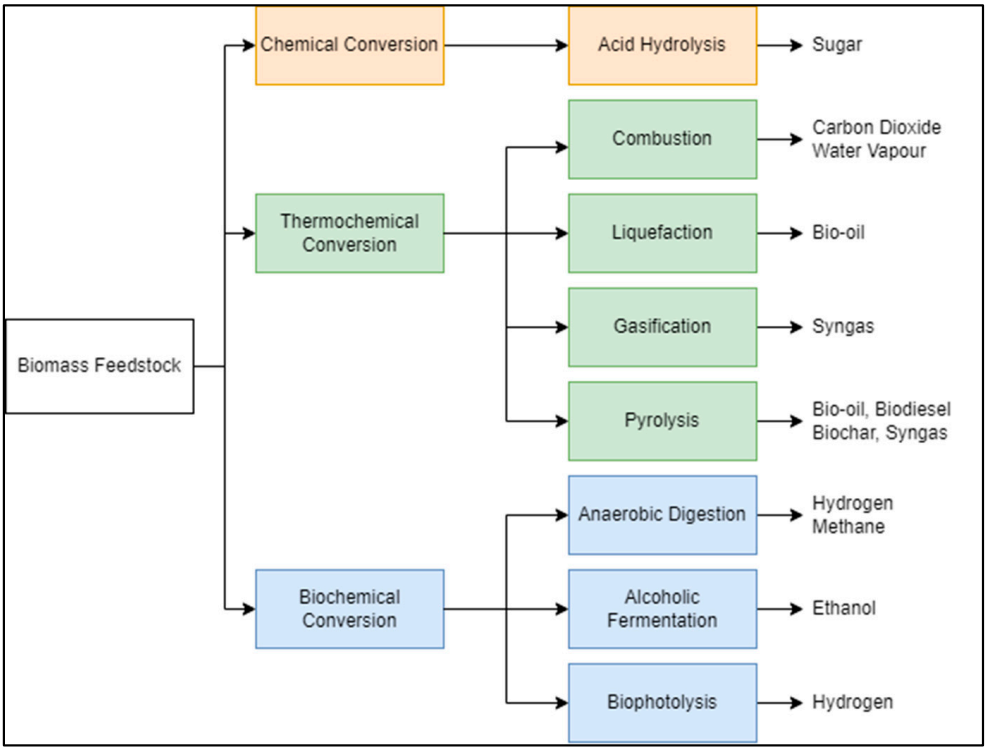


Figure 1. Biomass conversion methods pathway (adapted from [23]).

3.1. 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 taken [24]. Hydrolysis is a term to describe a conversion process that breaks down a compound due to a reaction with water. Specifically, acid-catalyzed hydrolysis stands as the extensively researched and firmly established process for chemically breaking down cellulose into glucose and hemicellulose into xylose. Lignin, on the other hand, is a complex

polymer with random aromatic structures, which will likely remain as a polymer by-product after extraction. A number of studies are currently focusing on developing ways to obtain valuable chemicals to be used for other purposes [24].

Depending on the acid concentration, different process settings are required. With a strong acid, a low temperature of around 40 °C is ideal to result in a high sugar yield, up to 90%. However, equipment corrosion and high energy consumption from acid recovery processes are disadvantageous. Therefore, dilute acid or mild acid reaction conditions are more favored in industrial processes. With mild acidity, the reaction must be carried out at a relatively high temperature of around 200 °C. Another concern is that glucose, xylose, and other sugar monomers could react again via a dehydration reaction to produce unwanted by-products [25]. 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 serve as intermediates for the synthesis of vital chemicals referred to as platform molecules. For instance, employing a Ru/CeOx catalyst for the selective hydrogenation of HMF can yield dihydroxymethyltetrahydrofuran—a precursor for solvents and monomers. Furthermore, utilizing a CuRu/C catalyst with HMF can yield the fuel additive 2,5-dimethylfuran (DMF). Another platform molecule, furfural, can be converted into tetrahydrofuran via decarbonylation with Pd/SiO_2 [26]. Therefore, different catalysts and reaction condition settings could be determined depending on the desired products. Utilizing reaction simulation software, such as Aspen Plus, CHEMCAD, BioSTEAM, could aid in calculating the expected product and by-product yield to plan the sequential processes.

3.2. Thermochemical Conversion Methods

Thermochemical conversion is defined as a degradation process of biomass structure involving high temperatures under aerobic or anaerobic conditions [27]. Depending on the conversion mechanism and reaction condition, there are four main processes, which are explained below.

3.2.1. Combustion

Combustion is defined as a process wherein a substance is rapidly burned in the presence of oxygen, releasing a significant amount of heat energy. Biomass resources, comprising carbon, hydrogen, and oxygen, yield carbon dioxide and water vapor as the principal oxidation by-products. Advantages of combusting biomass over coal include higher fuel reactivity and lower greenhouse gas emissions. With this conversion method, the production of unwanted intermediates and by-products could be prevented. For combustion to take place, the moisture content of biomass feedstock must be less than 50%. If not, an additional dewatering and drying step before combustion is required to remove excess moisture [28].

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 pieces of equipment, including a 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 ranges between 25% and 40%, and the higher efficiency is achieved with systems over 100 MW [28]. Co-combustion is another strategy to increase the conversion efficiency. A study by [29] showed improved thermal efficiency when the biomass is co-combusted in a coal-fired power plant.

3.2.2. 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 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 the 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 carbon dioxide gas, solid bio-char trace, bio-oil, and traces of aqueous phase [30]. 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 the liquefaction process is that its efficiency could reach up to 85–90%, since it does not require too much additional energy taken from the feedstock.

3.2.3. Gasification

Gasification involves the partial oxidation of biomass feedstock under high pressure and temperatures to produce a 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 [31]. The gasification process is also considered highly efficient since it allows biomass sources to produce both chemical products and energy. This provides a possibility for biomass products to take over the role of natural gas and fossil fuels in the energy sector. It is also gaining attention due to its ability to process solid wastes into useful energy forms [32]. The overall efficiency of a gasification system has been improved over decades, recently reaching 40–55%, from the study by BIOCAP Canada (2006) [33]. However, optimization in pre- and post-treatment stages is still incomplete, which has been causing slow development and implementation of biomass gasification. Meanwhile, syngas can be further processed in various ways for different desired final products. To produce heat and power, a combined heat and power (CHP) system can be selected to further process syngas. Other processing options like a methanol production system and the Fischer–Tropsch system could produce chemicals and liquid fuels, respectively.

3.2.4. 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 [34]. Depending on the biomass type, catalyst, rate of temperature increase, and maximum temperature reached, different pyrolysis products could be produced. The rate of temperature change is an important variable for producing desired products. In the case of fast pyrolysis, the time required for heating biomass feedstock is short. The residence time is also short, so the rapid quenching of condensable products results in the production of bio-oil. On the other hand, slow pyrolysis with a lower heating rate and longer residence time will offer more condensation and predominantly produce bio-chars [35].

3.3. Biochemical Conversion Methods

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

3.3.1. Anaerobic Digestion (AD)

Anaerobic digestion involves the biological breakdown of organic materials like polysaccharides, proteins, and lipids by microorganisms in an oxygen-deprived envi-

ronment. This process yields a product known as biogas, comprising up to 60% methane (CH_4), 35% carbon dioxide (CO_2), and trace gases. The conversion of biomass feedstock into biogas through anaerobic digestion exhibits a relatively modest efficiency, typically ranging around 15–20%.

Although the process seems to have a low efficiency, the 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. Virtually all forms of organic biomass sources have either exhibited favorable digestion traits or can be pre-treated to enhance their digestibility. Studies presented in [36], and much more research, discovered that co-digestion of various types of biomass with waste streams can increase the C/N ratio of a feedstock and accelerate bacterial activity. These studies showed higher methane production and increased organic loading rates 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. Finally, AD is considered an alternative for a conventional landfill process for organic wastes. Released methane gas from landfills contribute to a buildup of greenhouse gases (GHGs) in the atmosphere. By replacing landfill processes with AD, GHG issues can be mitigated by directly capturing biogas and utilizing it as a fuel for a turbine to produce power (electricity).

3.3.2. Fermentation

Fermentation is a biological decomposition of sugar-containing organic substrates by enzymes produced by microorganisms under anaerobic conditions [37]. The production of ethanol is the major application of the fermentation process. Starch and cellulose, which are rigid polysaccharide structures, can also be fermented after they are first converted into sugar by a hydrolysis reaction. After post-treatment processes, which are distillation and dehydration processes, a 99% purity ethanol could be acquired [28].

There are several factors to consider for a large-scale commercial biomass fermentation process. An aseptic condition is required for most fermentation processes, which could be difficult and costly to achieve in an industrial-scale operation. After a separation and post-treatment of an 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 the fermentation process or reused in other biological processes without noticeable disadvantages over fresh water [37]. Therefore, extensive studies on wastewater recycling systems within a biorefinery design is highly suggested.

3.3.3. Biophotolysis

Biophotolysis is a biological process to produce hydrogen gas using a photosynthetic apparatus [38]. The biomass feedstock for hydrogen production with this technique is only limited to eukaryotic microalgae and prokaryotic cyanobacteria, which possess light-harvesting pigments. Photosynthesis occurs within chloroplasts or thylakoid membranes, initiating electron transfer across membranes through both photosystems, which generates ATP. This process is accompanied by water splitting, leading to hydrogen generation. The reaction is catalyzed by a hydrogenase enzyme [39]. A simplified chemical reaction equation is as below:

$$2\,H_2O + \text{light energy} \rightarrow 2\,H_2 + O_2 \quad (1)$$

Multiple factors influence photo-biological hydrogen production. Foremost among these is light intensity, which is recognized as the primary determinant impacting the efficiency of microbial hydrogen production [38]. Under strong artificial light illumination, cells can show altered metabolic capacity and reduced efficiency. On the other hand, if the environment is too dark, cells can experience light inhibition, also resulting in reduced process efficiency. Second, basic essential macro- and micronutrients such as vitamins, nitrogen sources, carbon sources, 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 [38].

4. Microalgae-Based Biorefinery Conversion Techniques

Microalgae are microorganisms growing through photosynthesis, which requires light, carbon dioxide, water, and nutrients [7]. Microalgae's primary chemical constituents encompass lipids, proteins, and carbohydrates, each stored within the cell with distinct compositions contingent upon their strains. Minor contents include pigments, vitamins, and polyunsaturated fatty acids, which are value-added chemicals used in the pharmaceutical, food, and cosmetics industries [4]. The microalgae-based biorefinery process comprises eight primary processing stages: (1) microalgae cultivation, (2) microalgal biomass harvesting, (3) pre-treatment (including drying and cell disruption), (4) lipid extraction, (5) transesterification, (6) post-transesterification purification, (7) residue pre-treatment, and (8) residue conversion into additional value-added products [10]. 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.

4.1. Cultivation of Microalgae

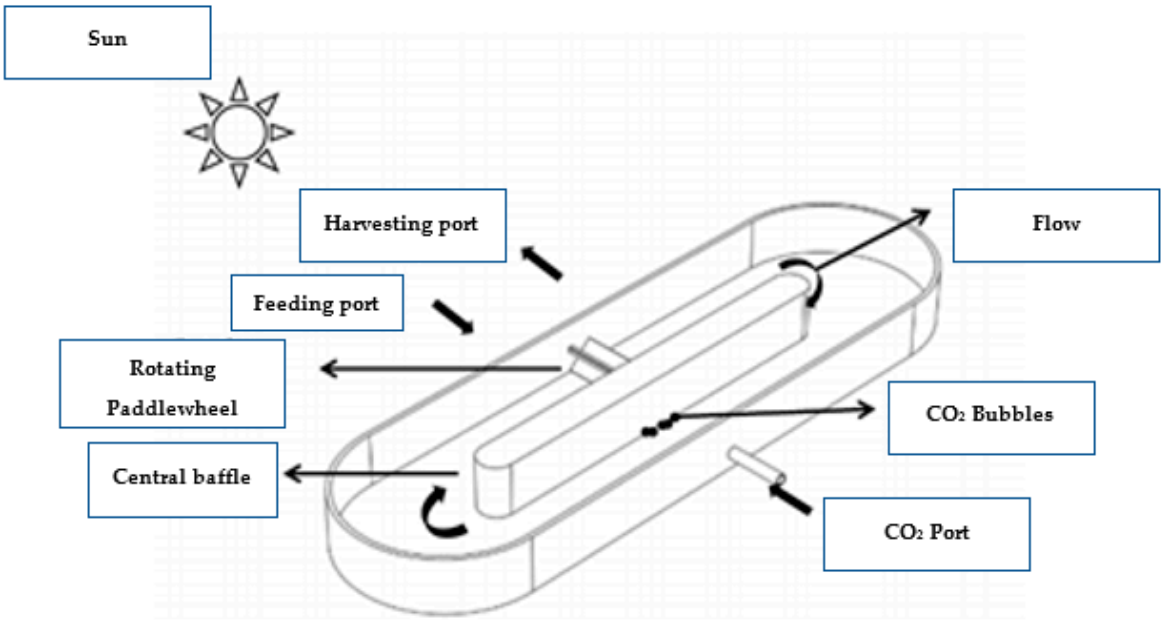
The initiation of a microalgae-based biorefinery hinges upon microalgae cultivation. The growth of microalgae is influenced by cultivation conditions encompassing factors such as light, carbon dioxide, temperature, pH, and nutrient availability, which collectively impact the microalgae's characteristics. 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 temperatures will hinder biomass production [40]. 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. Exploring the utilization of wastewater in microalgae cultivation is a viable option, given its typical enrichment with phosphorus and nitrogen nutrients. Additionally, this approach holds potential for diminishing contaminants present in the wastewater [41]. If wastewater is being contemplated as an alternative nutrient source, a systematic analysis becomes imperative to assess its viability [42]. Employing a photoautotrophic method, microalgae biomass can be cultivated commercially in largely two different types of setting, either in open ponds or an enclosed photobioreactor (PBR).

4.1.1. Open and Closed Pond Systems

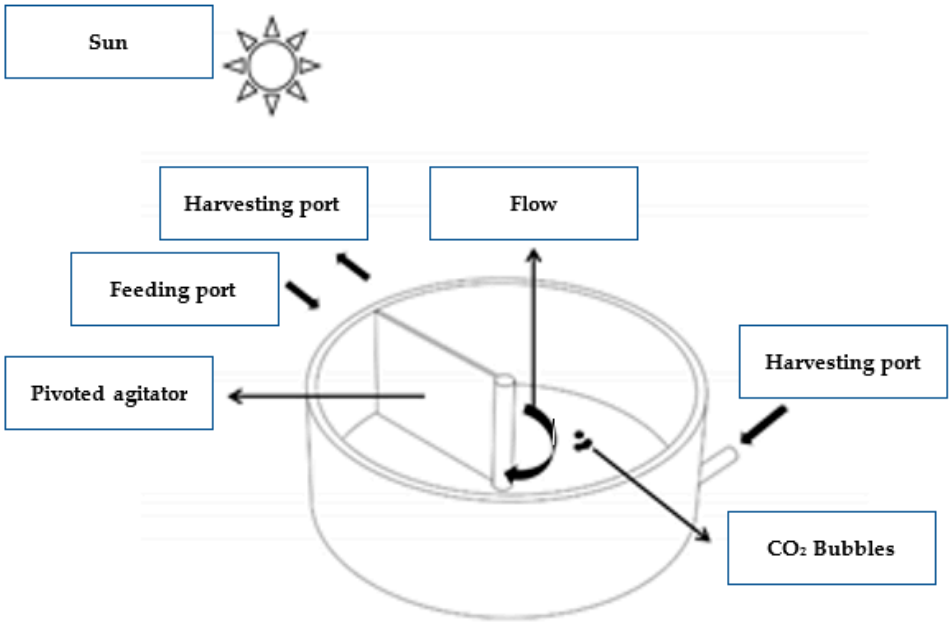
Cultivation of microalgae in open ponds can be carried out either in open or under a covered surface, and in natural waters or artificial sinks. The open pond system has a great economic advantage and ease of scalability, since it utilizes natural sunlight and the atmosphere. Also, sewage or wastewater treatment plants can incorporate into their cultivation systems the use of wastewater as a water and nutrient supply for microalgae, thus minimizing upstream processing costs [43]. However, this system could be contaminated easily, and it is difficult to control the environment. Difficulty in controlling the culture temperature results in loss of water due to evaporation. Guieysse et al., in [44], conducted a case study of water evaporation prediction in five typical climatic zones to quantify the variable water demand in each region. In addition, the 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 moderate climate zones. Therefore, careful study of land selection is essential before the construction of a biorefinery system.

Open ponds are commonly constructed in either circular or raceway configurations. In raceway ponds, microalgae biomass is recirculated around a track loop, as shown in Figure 2a [43]. The depth of the pond is approximately 0.3 m to increase exposure to sunlight, thus increasing the growth of the 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 the constant addition of carbon dioxide and nutrients from the feed ports. The 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 m^2 due to the limitation of effective mixing offered by the rotating arm [43].



(**a**) Open raceway pond cultivation system



(**b**) Circular pond cultivation system

Figure 2. Different pond cultivation systems (retrieved from [43]).

On the other hand, the 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 a greenhouse. This method could minimize water and carbon dioxide loss and enhance cell growth rates. The building material is often Plexiglas, which is

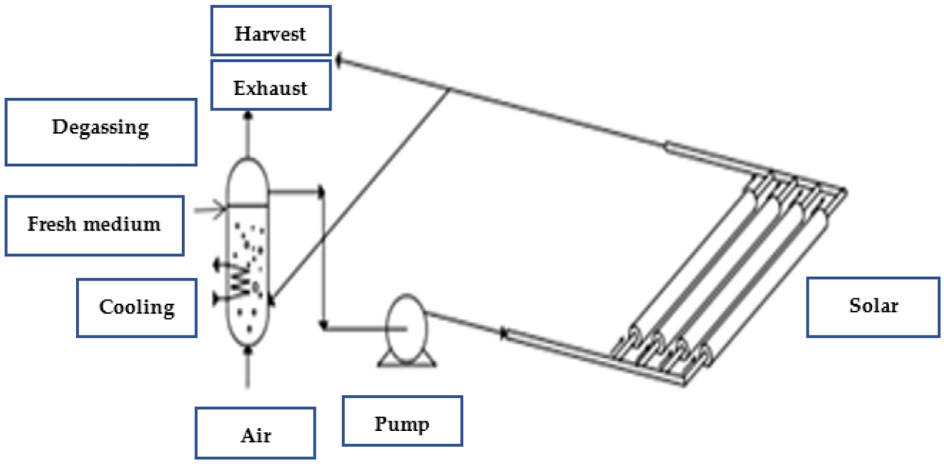
more expensive than the open pond's concrete material, but cheaper than constructing a photobioreactor system.

4.1.2. Photobioreactor (PBR)

A photobioreactor is an enclosed vessel with a supply of artificial and/or solar light as an 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 [41]. Due to the limitations with artificial lighting systems, PBRs often incorporate the utilization of natural sunlight. To enhance the microalgae production rate, various photobioreactor configurations have been developed [45]. Currently, the tubular PRB is the most common industrial configuration (Figure 3a). A tubular PBR consists of a parallel array of horizontal, vertical, or inclined tubes made of glass or plastic, such that they are exposed to the maximum amount of sunlight, depending on the outdoor condition [46]. 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 the mass transfer of carbon dioxide, nutrients, and culture within the system. In addition, temperature control may be difficult in such a 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 [43].

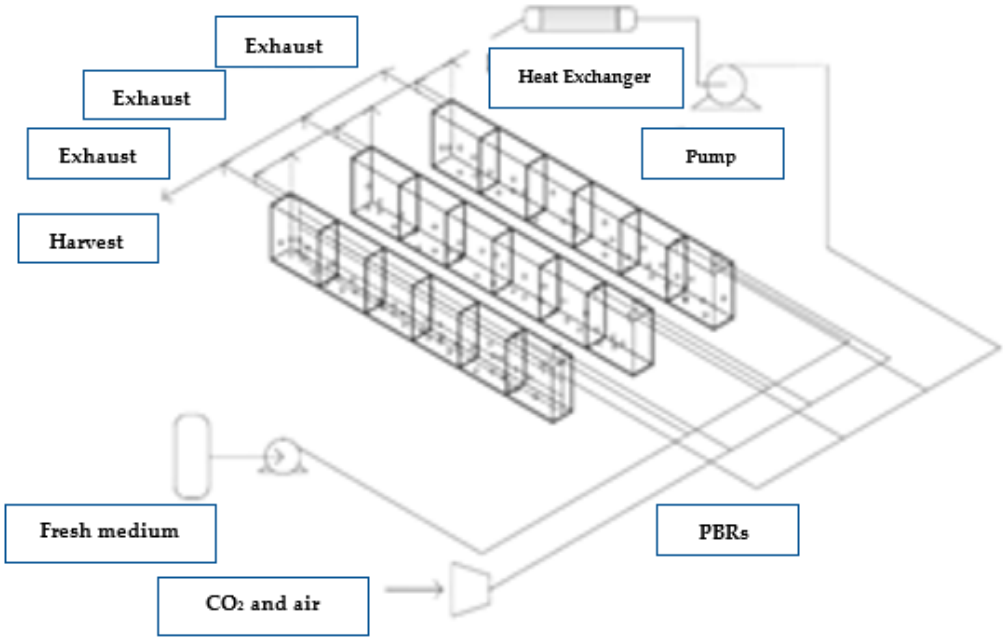
The flat panel PBR is another common configuration, commonly used for lab-scale studies of algae cultivation (Figure 3b). The most prominent advantage of this type is a high surface-to-volume ratio. The configuration also makes the light path very short and evenly distributed across the reactor, resulting in high light efficiency. It is relatively easy to alter the 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. The sparging method involves the dilution or recirculation of the produced gas, resulting in a higher risk of gas leak. The stirring method is very energy intensive, requiring a much higher energy input [47]. Therefore, agitation method selection should focus on the main objective of microalgae cultivation.

It should be noted that for commercial processes, both open ponds and PBRs are feasible alternatives for microalgae cultivation. Open ponds are more cost-effective and less energy intensive, only requiring 4 W/m^3 compared to 2000–3000 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 [48].



(**a**) Tubular PBR

Figure 3. *Cont.*



(**b**) Flat panel PBR

Figure 3. Different types of PBRs (retrieved from [43,48]).

4.2. Harvesting of Microalgae Biomass

The goal of the 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 [49]. Factors including the biomass recovery rate, operating and maintenance costs, and energy consumption must all be considered in the alternatives selection. The process must also be non-toxic, as the residual biomass after lipid extraction has the 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 the water and 55% of the nitrate required [42]. The harvesting step of microalgae is more complex than that of macroalgae since it involves the concentration of the microalgae culture followed by dewatering. The mass and concentration of the microalgae culture can be estimated in terms of dry weight. The harvesting techniques can be largely categorized into mechanical and chemical methods, and often a combination of two technologies could be applied for higher separation efficiency [50].

4.2.1. Gravitational Sedimentation

The gravitational sedimentation method is the oldest method that has been used to separate culture from media [49]. It uses the natural gravitational force to settle down microalgae based on density and the radial sizes of cells. Although it is the most inexpensive and simple method, the sedimentation process is highly time-consuming and inefficient. The prolonged duration of harvesting can significantly affect the biological and chemical activity of cells, such that biomass can start deteriorating and alter its composition, which is not favorable for biofuel production [51]. Therefore, it is currently not the favored method to be considered in most biorefineries.

4.2.2. Centrifugation

Centrifugation is similar to gravitational sedimentation, wherein centrifugal force replaces gravity as a separation force [52]. The 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; disk stack centrifuges are currently the most used in industrial settings.

It is capable of concentrating microalgae between 3 and 30 µm in size. It was also suggested that a hydrocyclone centrifuge could be primarily used to pre-concentrate microalgae to remove the majority of the medium, then another high-energy-requiring centrifuge could be utilized to remove the remaining moisture [52].

In general, centrifugation is widely known for its high separation efficiency of greater than 90% under low flow rates and its high energy intake. With high energy utilization, the process is relatively fast and effective, regardless of microalgae cell types [53]. However, it is highly energy-demanding and requires high operation and maintenance costs. For a large-scale operation, the maintenance, capital, and operation costs are especially high in order to reach high efficiency.

4.2.3. Floatation

Flotation involves a gravity separation mechanism that utilizes gas bubbles traversing through a liquid–solid suspension. [54]. Microalgae cells are then absorbed onto bubbles and floated to the top of a liquid surface. This method is especially fast and effective for the separation of microalgal species with low density and self-float characteristics. Factors that affect floatation efficiency include the type of surfactant or flocculant used, pH, the ionic strength of the medium, air tank pressure, hydraulic retention time, and particle floating rates [55]. The size of the bubbles and particles significantly affects the process efficiency, as lighter particles (preferably less than 500 microns) will more easily float to the top of the medium [56]. A study by Hantou et al. [57] 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, the addition of surfactants or flocculants could be a solution.

The flotation method can be categorized based on the bubble production technique. Among the prominent flotation methods are dissolved air flotation (DAF), dispersed air flotation (DiAF), and ozonation-dispersed flotation (ODF). 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.

4.2.4. Filtration

In a filtration method, microalgae culture is passed through filters with the aid of gravity, pressure, or vacuum force [43]. The resulting microalgae culture remains as a thick paste form on the membrane. Depending on the hydrodynamic conditions and solvent/solute properties, the correct selection of the 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 a 70 mm pore size could be used in conjunction with flocculation by flocculating smaller cells into bigger flocs [43]. Advanced from the conventional method, microfiltration and ultrafiltration, with much smaller pore sizes, are widely used to recover more particles, even shear-sensitive species [58].

The advantages of filtration methods are low energy consumption, high cost efficiency, and high recovery efficiency. Also, the quality of the harvested microalgae cells is relatively good, without significant cell disruption, compared to other methods. Moreover, it demonstrates an environmentally conscious approach by functioning without the necessity for extra chemicals. Thus, the recycling of spent media is much easier [59]. On the other hand, membrane fouling and clogging are major issues of the filtration method. Regular cleaning and replacement of membranes could be costly and must be included in cost estimation.

4.2.5. 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 [59]. Microalgae cells are negatively charged due to the ionized functional groups on their

surface, which causes a repulsive force between cells. Therefore, flocculants must be able to overcome such forces to enable cell aggregation [60]. Inorganic flocculants, such as $Fe_2(SO_4)_3$, $FeCl_3$, and trivalent metal sulfates are widely used, but caution must be employed due to their toxicity and sludge generation, which further require dewatering steps. They can also be hazardous to the environment and even cause contamination of microalgal biomass. Therefore, the careful selection of chemicals would be crucial in a biorefinery study [59]. Farooq et al., in [61], studied the cultivation efficiency of *C. vulgaris* using chemical flocculation with $FeCl_3$ and alum, compared to a reference centrifugation method, in terms of cost and energy factors. The study showed that centrifugation and flocculation with ferric chloride were suitable for microalgae harvesting due to their high harvesting efficiencies of up to 90%. Table 2 shows the comparison of major chemical flocculants in terms of their unit price [62].

Table 2. Price comparison of common chemical flocculants (retrieved from [62]).

Type of Chemical Flocculants	Name	Price/kg (US$)	Cost for 1000 L (US$)
Inorganic	$FeCl_3$	14.1	0.7
	$Al_2(SO_4)_3$	5.6	0.3
	$CaCl_2$	60.7	3.7
Organic	Chitosan	207.2	31.1
	Carboxymethyl cellulose	18.3	2.2
	Starch	0.7	0.1

Other than utilizing flocculants for cell flocculation, different methods have been developed over the years. The electro-flocculation method uses a set of nonreactive anodes and a sacrificial cathode to draw negatively charged microalgae cells towards the charged anode via electrophoretic motion [50]. As a consequence, cells experience charge neutralization and come together to form aggregates known as flocs. In [50], Mathimani et al. used aluminum electrodes to supply 2 kWh/kg of energy to freshwater *C. vulgaris*, which showed 93.6% flocculation efficiency in 30 min of settling time. When it was combined with the dispersed-air floatation (DAF) method, the recovery rate increased up to 99% [63]. The efficiency of the process largely depends on the electrode material, processing time, density, and pH, resulting in a biomass recovery efficiency ranging between 80–95% [64].

Furthermore, auto-flocculation 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 [63]. In particular, pH alteration is commonly selected, as a pH change can be easily induced by adding inexpensive hydroxides. At a higher pH, calcium and magnesium precipitates are formed from microalgae cells, which subsequently induces flocculation. This is considered a cheap, safe, and low-energy method. In [63], Vandamme et al. demonstrated auto-flocculation of *C. vulgaris* using various techniques and showed that the addition of calcium hydroxide increased the biomass concentration by 50 times. This method reached up to 98% biomass recovery within 30 min of flocculation. It should be noted that the effects of the bases and acids used in adjusting pH must be considered in economic feasibility and environmental issues analyses.

On the other hand, bio-flocculation is induced by co-cultivation of microalgae along with other microorganisms, such as bacteria or fungi. This method may be cost-effective, as it does not require alternation of culture condition or the use of expensive and/or toxic flocculants [65]. However, the reaction mechanism must be thoroughly understood to establish this method on 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 bio-flocculants, 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.

4.3. Drying

After the harvesting of microalgal biomass through separation from culture media, the resulting product is a dewatered slurry. The algae biomass must be fully dried prior to lipid extraction to produce biodiesel. The 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 [66]. Therefore, the most feasible drying technique must be selected to not only prevent the deterioration of cells and lowering of cell quality but also produce bioproducts with reasonable cost. The main considerations in method selection would be cost, simplicity, and energy requirement.

4.3.1. Rotary Drying

Rotary drying employs an inclined rotating cylinder to facilitate the continuous movement of algae from one end to the other through the force of gravity. With this method, it is possible to achieve both drying the samples and breaking the cell walls (cell disruption). In [67], Soeder and Pabst conducted an evaluation of the energy demand for drying algae with a 4% water content, determining it to be 15.7 Mcal for the evaporation of 18.2 kg of water per kg of dry algae product. An 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 kWh for such a system. Drying algae in a drum dryer is advantageous as it can simultaneously sterilize samples and break cell walls, reducing additional disruption stages. To minimize the energy cost, users should aim to maintain a relatively higher water content for the final product.

4.3.2. Air and Vacuum Drying

Air drying utilizes cross-flow air to dry out moisture in biomass slurry kept in an oven or on a shelf. Similarly to vacuum drying, biomass is kept in a vacuum oven. In the study presented in [68], the process effectiveness of air and vacuum drying were compared. A wet slurry of microalgae culture with a 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 samples was dried to 4% water content in a vacuum-shelf dryer at 50–65 °C and 0.06 atm. Unlike the rotary drying method, the cell wall was found to be undisrupted after drying.

4.4. 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 lipids, proteins, and pigments. The 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 are assessed to select the optimal option [69]. Recently, studies have been focusing on cell disruption methods applied directly on wet biomass to reduce economic concerns about additional drying steps.

4.4.1. Mechanical Disruption

Common mechanical disruption techniques include bead milling, ultrasound, and homogenization. These methods are energy-intensive and are 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. The compression of cells is caused by solid beads agitated at high velocities in a rotating chamber unit. In [70], Taleb et al. assessed the efficiency of the disruption 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 presented in [71] reported 45% 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 [72].

4.4.2. Non-Mechanical Disruption

Non-mechanical methods involve chemical or biological additives that directly act on the 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 (USD 185/ton) [73]. In [74], Park et al. treated *C. vulgaris* with sulfuric-acid-catalyzed hot water. A less than 1% sulfuric acid concentration was maintained at 120 °C for 60 min, which resulted in a 337 mg/g cell and 935 mg/g lipid extraction yield.

Ionic liquids consist of salts in liquid form, characterized by relatively large asymmetric organic cations intricately combined with smaller anions [75]. They are known for non-flammability, thermal stability, high heat capacity, reusability, and short reaction time. Kim et al., in [76], extracted lipids from *C. vulgaris* using [Bmim] CF_3SO_3 with methanol as a co-solvent, resulting in 19.0% of the total lipid content extracted. Compared to the 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 surfaces and cause disruption. In [74], Park et al. tested the effects of sodium dodecyl benzene sulfonate (SDBS) in conjunction with a 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 a cavitation mechanism. Solvent is required for the extraction of lipids, including hexane, chloroform, dichloromethane, and sodium sulfate. In [77], Balasubramanian et al. 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 a liquid medium. Similar to the microwave disruption method, it uses a cavitation mechanism to break the cell wall as microbubbles gradually grow in size and eventually collapse violently [73]. When these bubbles collapse on the cell wall, the temperature and pressure can rise up to 5000 K and several hundred atmospheres, effectively disrupting the 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 requirements are necessary for effective performance.

The biological disruption method involves enzyme treatments (lysis). This method is operated at non-extreme conditions with low energy requirements. In [78], Chen et al. used cellulose, lipase, protease, and a 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.

4.5. Lipid Extraction

After biomass is dried, lipid content is extracted from concentrated algae or directly from the 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 solvents have shown greater efficiency in lipid extraction [79]. However, lipid extraction is still a challenge in the commercial production of microalgal oil as part of a downstream biorefinery, even though there are multiple extraction methods studied in the literature. The biosafety of extraction solvents could be a concern in selecting biocompatible and non-toxic processes. In addition, the lack of a standard extraction method for fatty acids analysis raises the importance of browsing all possible oil extraction methods and determining the yield and suitability.

4.5.1. Bligh and Dyer Method

First published in 1959, Bligh and Dyer extraction is one of the most common and oldest lipid extraction methods 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 in an exact ratio, then a sufficient amount of water is added. This causes the formation of a biphasic system, leading to the partitioning into a water-methanol-rich upper layer containing protein and carbohydrates, and a chloroform-rich lower layer containing lipids. A clear separation into two phases is then easy to achieve. Among all the lipid extraction methods available, the 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 phase separation is based on gravimetric force, a long settling time could be required in a large-scale application.

4.5.2. Modified Bligh and Dyer Method

In order to improve the above method, modifications were proposed to replace these toxic solvents. Especially, environmentally safer solvents have been alternatively selected. A modified Bligh and Dyer method introduced in [80] used n-hexane/isopropanol in a ratio of 3:2 v/v to extract lipids from biological samples. In [81], Smedes later proposed the use of an 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.

4.5.3. Supercritical Fluid Extraction (SFE)

Supercritical extraction separates lipids from the biological sample, utilizing supercritical carbon dioxide (CO_2) as the extracting solvent. In the SFE process, carbon dioxide diffuses into the biological sample matrices and dissolves valuable chemicals using its solvent density properties. It is operated at a moderate temperature and pressure for the separation stage. Then, a depressurizing setup releases the final product to be solvent-free. Depending on the pressure and temperature, the properties of carbon dioxide can be altered; thus, this method could offer a wide range of extraction selectivity. In addition, a study presented in [82] 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 a higher lipid yield of up to 90%.

4.5.4. 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 and can successfully substitute for 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 samples with hydrogen bonding at cell boundaries are mixed. With ILs, direct lipid

extraction from wet and undisrupted biomass is also possible. A study introduced in [83] extracted lipids from unbroken wet *Chlorella* sp. using choline chloride-acetic acid with a reaction time of 60 min at 110 °C.

[Bmim][$MeSO_4$] 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 them easily isolated. Furthermore, ultrasound irradiation could highly enhance the extraction rate and yield with ILs by strengthening the mass transfer of liquid–liquid systems. A study presented in [84] compared the lipid extraction efficiency by [Bmim][$MeSO_4$] 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 concern 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.

4.6. 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 that, large and branched fatty acids (FA) are converted into smaller, straight-chained fatty acid alkyl esters (FAME) (i.e., biodiesel) and glycerol via a reaction with alcohol in the presence of a catalyst [85]. Among possible alcohols, methanol is the most frequently used. For the transesterification process, catalysis and in situ methods are widely studied and commercialized. There are three most known types of catalysts: alkalis, acids, and enzymes.

4.6.1. Catalytic Transesterification

Most commercial biodiesel production requires the use of a catalyst to accelerate the reaction, which later requires a separation step to recover pure biodiesel from the 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 sulfuric acid. By using a solid acid catalyst, an additional separation step is unnecessary, and the solid catalyst can be reused again. In the study introduced in [86], a mixture of methanol and sulfuric acid is added into lipids in a ratio of 3:1 and reacted for about 2 h 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 (pH > 7) such as sodium hydroxide, potassium hydroxide, and sodium methoxide. It can be performed at low temperature ranges close to alcohol's boiling point, and results in a high conversion rate within a short time. Meanwhile, homogeneous transesterification of lipids extracted from *Chlorella vulgaris* using 0.42 wt% sodium hydroxide in methanol at 43 °C for 90 min was also demonstrated. After distillation, the final free fatty acid yield was 98% [87].

Enzymatic transesterification commonly refers to the addition of lipase, which catalyzes methanolysis reactions. They do not form emulsions, which means that additional washing and purification steps are required 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., in [88], demonstrated a lipase-catalyzed transesterification with methanol in the presence of Novozym 435. The reaction proceeded at 50 °C, with a 1:4 lipid-to-alcohol ratio and a 30 wt% enzyme concentration. The final product conversion rate was 92% after 24 h. Similarly, a study by Royon et al. [89] used Novozym 435 at the same condition, but with tert-butanol as a solvent, which resulted in a 97% conversion rate after 24 h. A long reaction time and higher catalyst cost hinder this method for selection for industrial processes.

Nanocatalysts have emerged as a novel material, as they convert crude lipids into FFA through a cheaper and simpler process with lower water consumption [90]. CaO is

one of the most common nanocatalysts explored for algae biodiesel production. Siva and Marimuthu, in [91], used CaO extracted from eggshell to catalyze methanol transesterification. The reaction was set up to be at a 9:1 methanol to oil ratio, 1.25 wt%, and catalyst loading at 55 °C, which resulted in a 96.3% conversion rate. The fact that CaO is produced from eggshell suggests a potential to incorporate the use of residual biomass from MSW.

4.6.2. In Situ Transesterification

In situ transesterification reacts biomass directly with alcohol without a lipid extraction step. The oil-bearing biomass is the base and reacts directly with the alcohol and catalyst to produce biodiesel. Simultaneous transesterification is shown to generate higher FFA yield [92]. Based on the research by [93], in situ technology is used to extract and produce biodiesel from microalgae biomass with acid catalysts, BF_3, H_2SO_4, 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 all be used similarly to the conventional transesterification methods.

4.7. Post-Treatment Stages of Lipid Products

Following the transesterification of the 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 the pure biodiesel product. The purification step is already highly standardized.

The first step of purification is the separation of crude glycerol and alcohol [94]. 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. The glycerol phase is re-neutralized and salts are generated by the addition of hydrochloric or sulfuric acids. A vacuum flash process is then operated to vaporize unreacted alcohol. It is then condensed back into liquid and reused in the process. Additional distillation stages could recover 99% or higher purity glycerol.

Once separated from the glycerol phase, crude biodiesel comprises residual catalyst, water, unreacted alcohol, residual glycerol, and biodiesel. The mixture enters a neutralization step for the catalyst, and the alcohol stripping process [95]. The 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 the remaining catalysts. After washing multiple times, the biodiesel and water phases are separated.

4.8. Production of Other By-Products

The leftover microalgae biomass post lipid extraction retains significant value due to its abundant protein content and other commercially relevant compounds. Instead of being disposed of, 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 of incorporating various biomass options in a biorefinery design.

4.8.1. 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 [96]. Hydrolysis of *Chlorella* carbohydrates by dilute sulfuric acid pretreatment was shown as an efficient strategy to increase total biomass utilization, based on the study by [97]. This strategy generates fermentable sugars while rendering the lipid and protein fractions more accessible for extraction. The resulting sugar solution can be isolated

from the remaining biomass using solid–liquid extraction with a hexane solution. The remaining slurry after pre-treatment was filtered and fermented with *Zymomonas mobilis* at a pH of 5.8 at 33 °C for 29 h. The final ethanol yield was 78 wt% relative to the theoretical number of the fermentable sugar content.

4.8.2. Protein

Microalgae biomass originally has up to 60% protein content. The protein derived from microalgae holds considerable promise across diverse applications, encompassing food additives, enzymes, nutraceuticals, and probiotics. The purification of proteins can be accomplished through methods such as precipitation, ultrafiltration-based concentration, High-Performance Liquid Chromatography (HPLC), and foam fractionation. A study conducted by [98] tested protein extraction efficiency via precipitation and concentration using tangential ultrafiltration (300 kDa MWCO). With the first method, cell residue after lipid extraction was solubilized into an alkaline solution, then pH was progressively reduced 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 that isoelectric precipitation by pH shifting yielded 76 wt% of protein extraction.

4.8.3. 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 color to plants. Chlorophylls are hydrophobic pigments present in photosynthetic organisms. Finally, phycobiliproteins are the major photosynthetic pigments in microalgae, with antioxidant, antiviral, and anti-inflammatory properties [99]. Various separation and purification methods are currently available and are combined with the lipid extraction step. In [100], Pasquet et al. extracted chlorophyll via a suspension with acetone under an argon atmosphere to inhibit photo-oxidation. The extract was filtered onto PVDF membrane filters and purified by HPLC.

4.8.4. Biopolymers/Bioplastics

Biopolymers are organic-driven materials extracted 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 [99]. 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 an elevated temperature and pressure to form a composite material. In [101], Zeller et al. successfully extracted protein-based bioplastics from *S. platensis* and *C. vulgaris* using compression molding at 150 °C for 20 min.

5. Municipal Solid Waste (MSW)-Based Biorefinery

Municipal solid waste (MSW) refers to solid waste originating from residential and commercial establishments. 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 [102]. Since MSW is composed of a large variety of materials, a hierarchy in processing order is proposed: (1) reduce waste, (2) reuse, (3) recycle recyclable components, (4) treatment and heat recovery, and (5) landfill disposal [103].

Currently, the majority of MSW is landfilled in most countries. However, the 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 the increasing demand for energy.

5.1. MSW Segregation

About 1/3 of MSW consists of various solid components, including food waste, paper, plastic, wood waste, glass, metal, textile, etc. [102]. The segregation step is to primarily recover recyclable components. Such valuable components will be collected based on the final purpose, then sent to the treatment stage.

Segregation or sorting is the process of separating MSW into groups of organic, inorganic, recyclable, 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, and collecting and stockpiling of the remains [104]. Size reduction of waste through shredders and crushers, and separation based on size, density, and magnetic forces using screening devices, can be carried out when applying a fully mechanized sorting process [103]. Depending on the region, climate, and population density, the MSW component varies drastically. Therefore, most studies used solid assumptions on their MSW composition, landfill area, and other parameters to design their optimal segregation facilities [105].

5.2. 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 a material recycling facility (MRF). The MRF is where all solid wastes are further separated, processed, and stored for later use as raw materials for manufacturing and reprocessing [60]. In addition, the classification of MSW and availability for recycling could vary depending on legislation. The study by [60] estimated MRFs in New York City to encompass 16 acres of land and cost USD 127 per ton of solid wastes, based on an assumption of a 150-tons-per-hour processing rate. This would correspond to about USD 46 million savings annually in waste management.

5.3. Treatment and Conversion of MSW

The recovery of value-added chemicals from MSW is crucial for reducing the amount and cost of landfill disposal. The 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 processed will be sent to compost facilities or landfills. The following section will explain various processing alternatives and their resulting yields for energy production.

5.3.1. Gasification (Syngas)

Gasification is a thermochemical process involving partial oxidation, which transforms carbonaceous materials into carbon monoxide, hydrogen, and methane. This reaction occurs at temperatures exceeding 700 °C, utilizing a controlled quantity of oxygen and/or steam [105]. The gasification process is used to produce syngas through methyl carbonylation and hydrogenolysis reactions. Most biomass gasification uses air instead of oxygen, which significantly reduces processing costs for large plants. Syngas is generated through a sequence of three successive processes: (1) synthesis gas production, (2) recovery of waste heat, 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.

The gasification of MSW has been applied to generate other valuable products, including electricity, heat, and ethanol. Especially, the concept of trigeneration refers to the simultaneous generation of electricity, heat, and cooling as an extension of cogeneration. In [106], Rentizelas et al. conducted research on a trigeneration biomass gasification plant featuring a gasifier within a rotating fluidized bed, yielding approximately 2.0 MW of electrical energy and 4.5 MW of thermal energy. In addition, the Combined Heat and Power (CHP) process combines biomass gasification and a gas engine for heat and power produc-

tion, and has a high biomass-to-power efficiency potential of 35–40%. In [107], Damartzis et al. utilize CHP biomass bubbling fluidized bed gasification unit in conjunction with an internal combustion engine (ICE) based on an Aspen Plus simulation.

5.3.2. Anaerobic Digestion (Biogas)

The organic fraction of MSW could be processed via anaerobic digestion to degrade the organic matter into biogas. In 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 [27]. The AD process is considered 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.

5.3.3. Plasma Arc Gasification (Syngas)

Plasma arc gasification is a thermal process at a very elevated temperature, between 2000 to 14,000 °C, using 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 [108]. Especially, plasma gasification converts nitrogen and sulfur content in the feedstock to nitrogen gas and hydrogen sulfide, without forming GHGs like nitrogen oxide and sulfur 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.

5.3.4. Pyrolysis (Bio-Oil)

In 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 s at the maximum reaction temperature [35]. 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 temperatures and residence time must also be applied for different samples to reach the optimal processing pathway.

5.3.5. Incineration

With the drastic increase in waste due to continued population growth and the industrial revolution, incineration is one of the oldest MSW management systems applied commercially [35]. Some advantages of the 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 currently strictly control 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 the re-circulation of flue gases, which increases thermal capacity and reduces GHG generation during combustion. The use of catalysts has also aided in suppressing the formation of NO_x and SO_x gases.

5.3.6. Composting

The remaining organic materials are decomposed under controlled aerobic conditions with temperatures of 55 °C or higher [109]. The final product of this process is called compost. Composting is considered a sustainable management of organic waste, since the organic compost matter reduces in volume and the process avoids the risk of pathogen

infections if it is directly waste-to-landfill. Some industries, such as farming, sugar, and wine industries use compost as a fertilizer or organic amendment, which saves in cost for commercial chemical fertilizers. Multiple factors must be considered for the composting environment, such as an initial water content between 45–75%, air humidity below 75%, turning frequency, and a carbon-to-nitrogen ratio of 50:1 [110]. Currently, the windrow technique is the simplest and the most accomplished method, performed with standard equipment. Specialized windrow aeration equipment is developed and used for processes with large amounts of waste. Studies presented by [110,111] demonstrated the environmental and economic modeling of the composting process. The cost data encompass site development, pre-development expenses, operational costs, gas capture expenses, and post-closure expenditures.

5.3.7. Landfill

For the materials that could not be further processed to produce value-added products, the remaining waste could be landfilled [112]. Landfill still remains 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 in landfill settlement, so the deformation will lower the structural strength of the land. Also, gas and leachate generation could be a significant environmental issue [112]. Therefore, the careful selection of landfill location as well as the predictions of settlement are key issues in designing and constructing landfill sites.

6. Waste Management Options for Biorefineries

Currently the way countries deal with urban waste and its disposal is the key towards moving to a sustainable future while dealing with climate change and carbon emissions. Solid waste management is critical and becoming a challenge for developing countries. By 2025, urban cities around the world are projected to produce up to 2.2 billion tons of solid waste [113]. Ismail's studies in [114] underscore that within numerous developing nations, the notion of waste biorefineries holds considerable relevance and urgency. This stems from the environmental and economic strains imposed by the prevailing waste disposal practices, as well as the imperative to meet escalating energy needs. Simultaneously, waste biorefineries pave the way for new enterprises, employment opportunities, and enhancements in public health and local environments.

Meanwhile, it should be noted that the integration of microalgae and municipal solid waste (MSW) biorefineries represents a pioneering approach that addresses pressing environmental, energy, and waste management challenges. This integration capitalizes on the unique attributes of both microalgae and MSW, offering a plethora of benefits that contribute to sustainability and resource optimization. In other words, the integration of microalgae and MSW biorefineries represents a transformative solution that leverages the strengths of both feedstocks. By simultaneously addressing waste management, resource recovery, energy generation, and environmental concerns, this integration contributes to a more sustainable and resilient future. The importance of this subject can be highlighted as:

1. Holistic Waste Management: MSW poses a significant environmental challenge, requiring efficient and sustainable disposal strategies. Integrating microalgae and MSW biorefineries offers a novel approach to converting waste into valuable resources, thereby mitigating the burden on landfills and reducing environmental pollution.
2. Resource Synergy: Microalgae are proficient in absorbing nutrients and CO_2 from wastewater streams, while MSW provides organic matter that can serve as a nutrient source for microalgae growth. This synergy enhances waste treatment efficiency and nutrient recovery.
3. Circular Economy: The integration embodies the principles of a circular economy by transforming waste into valuable products. It embodies a paradigm shift from linear "take-make-dispose" practices to resource-efficient closed-loop systems.

4. Sustainable Energy Generation: The combined biorefinery approach can yield bioenergy in the form of biogas from MSW and biofuels from microalgae. This contributes to the diversification of energy sources and reduces reliance on fossil fuels.

Moreover, some potential benefits of this integration are:

1. Waste Valorization: Integrating microalgae and MSW biorefineries converts organic components in MSW into biofuels, bioplastics, and other value-added products through microalgae cultivation. This approach transforms waste management into a resource recovery process.
2. Carbon Sequestration: Microalgae capture CO_2 during growth, and integrating them with MSW processing can further enhance carbon sequestration, aiding in climate change mitigation.
3. Nutrient Recycling: Microalgae can extract nutrients such as nitrogen and phosphorus from wastewater, contributing to wastewater treatment and nutrient recycling.
4. Economic Opportunities: The integration opens avenues for revenue generation through the production of biofuels, biogas, and high-value products from microalgae. It also reduces waste management costs.
5. Environmental Remediation: Microalgae possess the potential to remediate pollutants from wastewater streams generated during MSW processing, enhancing the overall environmental impact of the integrated process.
6. Community Engagement: Community involvement in waste collection and microalgae cultivation can enhance awareness about waste management and sustainable practices.

Challenges for Integrated Biorefineries

Key catalysts driving the progress of integrated biorefineries include concerns regarding power supply security and the escalating costs associated with conventional fuels [115]. Biorefineries are very capital intensive in nature; they are largely dependent on the price of the feedstocks and how much energy can be generated through their processes.

A hybrid or integrated biorefinery can effectively yield both types of outcomes, with the added versatility of adapting to diverse substrates when necessary, as demonstrated in a study conducted by Ouda et al. in [116]. Traditionally, only direct countable monetary costs have been included in waste management costs; however, nonmonetary costs should also be included to represent the load that the system puts on the society. If nonmonetary costs of environmental and human damage are included, the costs of waste management could easily increase by 50–100%. Environmental costs represent the monetary value of the environmental loads caused by the system which can cause indirect harm to society, such as a decline in air quality, which can lead to respiratory diseases, and global warming. The possible solutions for capital cost reduction include having multiple feedstocks and performing techno-economic analyses on the available biorefinery technologies as a part of an initial phase design analysis, as described in study conducted by Nizami et al. in [117].

7. Biorefinery Optimization Approaches and Challenges

Lockhart and Johnson, in [118], 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 the assistance of quantitative tools, models 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 much more valuable information. By considering feedstock costs, chemical costs, operational costs, and capital costs for the facilities, the final profit of a biorefinery system could be estimated as well.

Published studies have established the combined optimization approach in techno-economic analyses for the 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 mixed-integer programming. For instance,

in [8], Slegers et al. introduced a model-driven combinatorial approach aimed at the energy-efficient conversion of microalgae into biodiesel. Elia et al., in [119], 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, in [9], formulated a mixed-integer nonlinear programming (MINLP) model to evaluate a superstructure for biodiesel production from cooking oil and algae, considering heat and water integration. Rizwan et al., in [10], 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 presented in [11], the optimization was extended by adding microalgae residue processing and water recycling for wider aspects of process economics. Hytoenen and Stuart, in [120], 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 a 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 supplies to produce multiple valuable products. In addition, its multi-feedstock nature helps secure feedstock availability under continuous operation throughout the year. Due to the complexity of its network, an optimization study could be an effective method to optimize such a process design. Recent studies that focused on the integration of multiple feedstock sources to produce multiple products are organized in Table 3.

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 a 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 formations of other types of feedstocks, including microalgae and MSW. Differences in feedstocks' chemical compositions and conversion technologies may also provide opportunities to recycle and reuse waste from one process to another.

Table 3. Multi-feedstock multi-product biorefinery studies.

Feedstocks	Combined Processes	Major Products
Lignocellulosic biomass	Hydrothermal conversion	Lignin, syngas, bio-oil
cassava	Microalgae cultivation	Biogas
Microalgae		
Sewage sludge	-	Biodiesel
Edible waste oil		
Microalgae		
Poultry litter	Gasification	Biodiesel, gasoline, natural gas, electricity
Forest residue		
Corn Stover	Dilute-acid Pretreatment	Bioethanol
Winter Wheat Straw		

Table 3. *Cont.*

Feedstocks	Combined Processes	Major Products
Microalgae strains	Chemical conversions	Omega-3 acids, chlorophylls, lutein, etc.
Lignocellulosic residue	Hydrothermal pretreatment, enzymatic hydrolysis	Glucose
Lignocellulosic biomass	Bioethanol processing stage	Bioethanol
switchgrass	Bioethanol processing stage	Bioethanol
Crop residue		
Woody materials		

8. Methodology and Problem Definition

A goal of this section is to introduce the systems design methodology, which can be utilized for the integration of biorefineries for microalgae and municipal waste processing. Therefore, process synthesis approaches including superstructure development are discussed here.

8.1. Process Synthesis Methodology

Conceptual process design in chemical engineering deals with defining, simulating, optimizing, and controlling 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. The design task then involves the integration of the unit blocks to represent a complex chemical process. During recent 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 [121]. 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 [122].

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 [123] and superstructure synthesis [124,125]. First, hierarchical decomposition requires a sequential procedure of progressively defining a process at each stage or level. At each level, heuristic rules and engineering judgements are involved to determine changes in the flowsheet that may lead to an improved solution. Studies introduced in [126–128] show thorough reviews of the hierarchical decomposition method. Although this approach provides simplicity in implementation, it is difficult to interact between different levels and can lead to sub-optimal designs.

On the other hand, the superstructure synthesis method involves solving a simultaneous optimization problem using mathematical programming [125]. This approach comprises three primary sequential stages: (i) formulating a superstructure; (ii) converting the superstructure into a mathematical programming model; and (iii) determining an optimal solution through the resolution of the mathematical model. A successful superstructure must include all possible alternatives that can be potentially selected in the final flowsheet, as well as the correct interconnection between the alternatives. As it involves solving a mathematical model, a poorly constructed superstructure may lead to the omission of several feasible and/or optimal solutions. Therefore, it is important to depict the problem as accurately 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 integrated into an optimization problem, wherein an objective function is defined, such as minimizing costs or maximizing profits. Finally, the computation of an optimization problem can be 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 preferred for its ability to systematically evaluate many structural alternatives. Figure 4 depicts the sequential steps taken to find the optimal solution in this study using superstructure synthesis methodology.

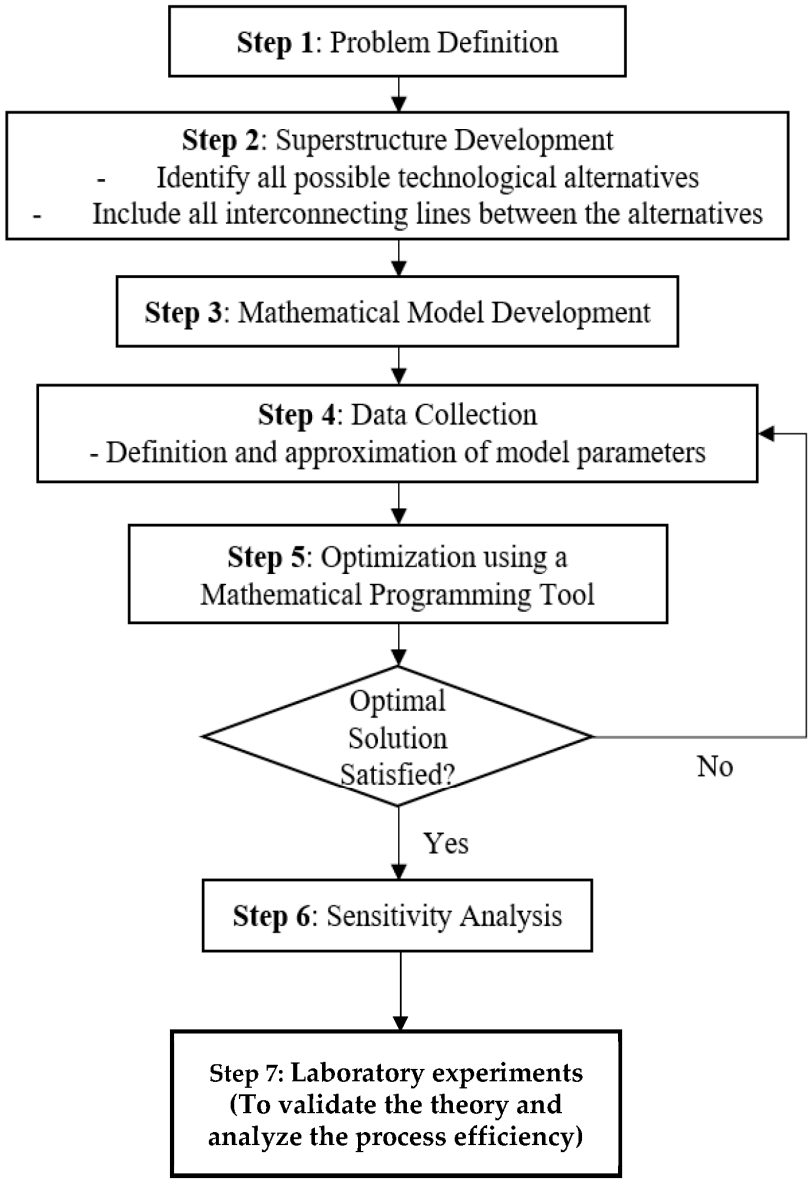


Figure 4. Sequential steps for superstructure synthesis methodology.

Thus, superstructure synthesis is generally 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. In particular, 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.

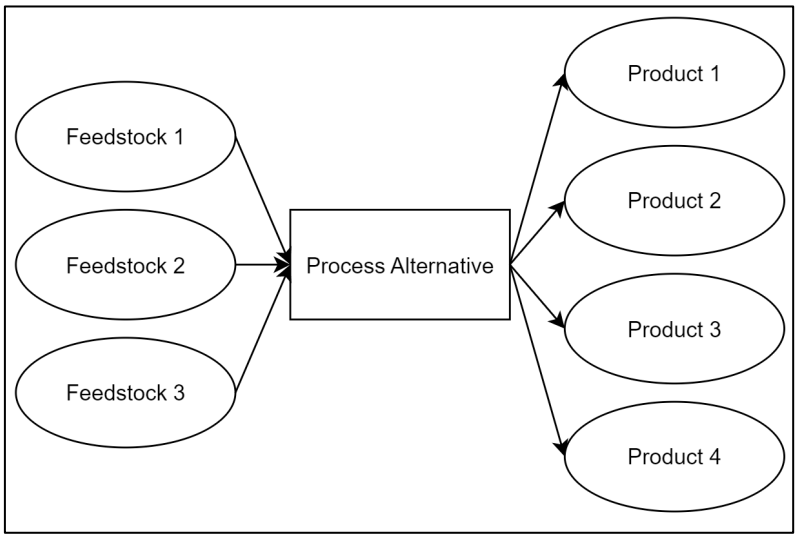


Figure 5. A simplified network of a multi-feedstock multi-product biorefinery.

8.2. Superstructure Formation

Following the sequential problem solving steps outlined in Figure 4, the superstructure is initially constructed after problem identification. The final superstructure includes 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.

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 in 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 are not represented, except non-lipid residues, in Figure 6, 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.

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 products with low process cost requirements [129]. Anaerobic co-digestion of microalgae and solid wastes also showed increased biogas yield as well as digester organic loading rate [130]. 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 produce 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.

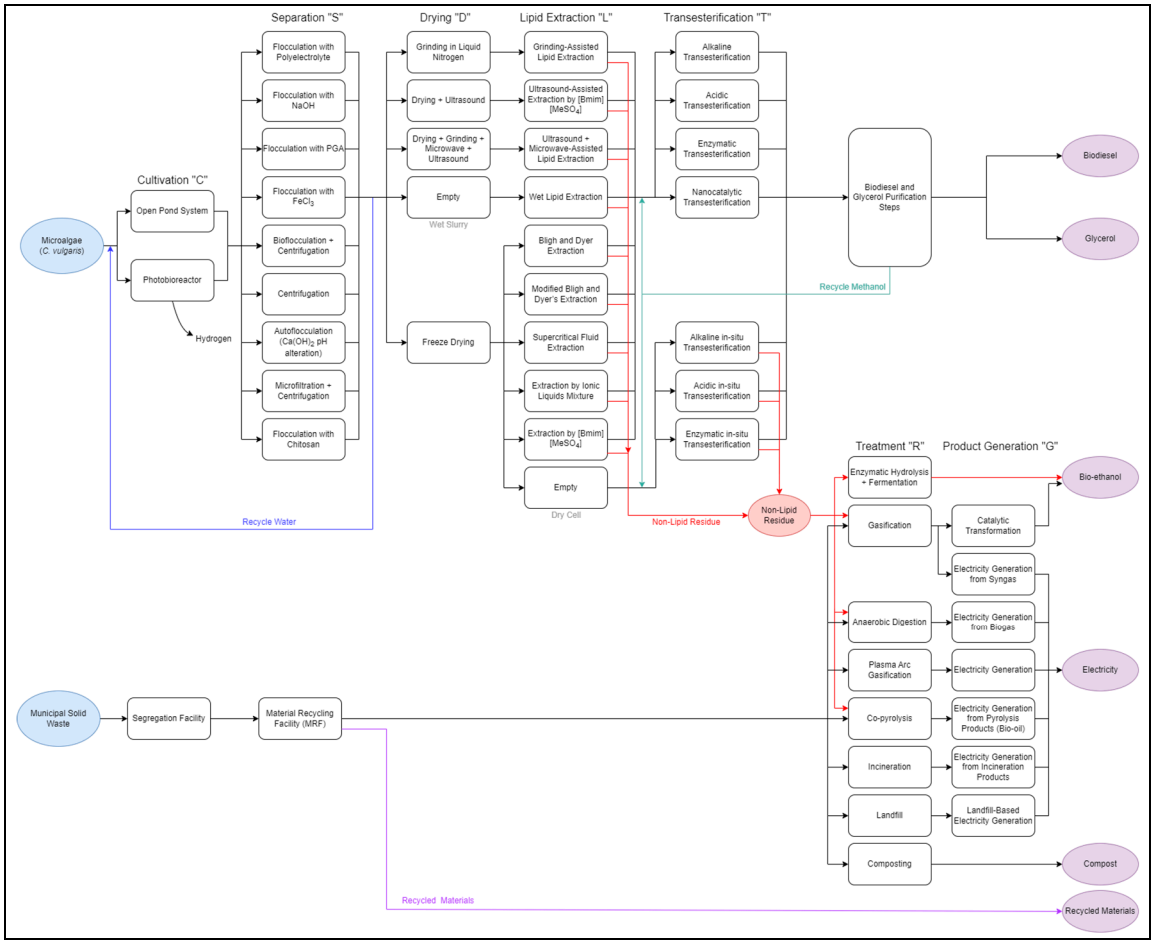


Figure 6. Superstructure of a microalgae and MSW multi-feedstock biorefinery design.

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

Feedstock	Processing stage	Index	Description	Samples of Technical Alternatives
Microalgae (*C. vulgaris*)	Cultivation	c	Growth of Microalgae	Open pond system
	Separation	s	Harvesting of cultivated microalgae biomass	Flocculation with NaOH
	Drying	d	Removal of moisture	Grinding in liquid nitrogen
	Liquid Extraction	l	Extraction of lipid content	
	Transesterification	t	Conversion of lipid into biodiesel	Acidic in-situ
	Biodiesel and Glycerol Purification	p	Post-Treatment	Distillation+ vacuum flash
MSW	Segregation facility	j	Segregation into different categorization	Segregation facility
	Material recycling facility	k	Separation of recyclable materials	MRF
Microalgae (*C. vulgaris*) + MSW	Pre-treatment	r	Pre-treatment of residues of microalgae and MSW	Co-Pyrolysis
	Product generation	g	Generation of value-added products	Catalytic transformation

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

Table 5. Description of color-coded arrows in the superstructure.

Arrow Color	Description
Black	Main processing routes of microalgae and MSW
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

Methanol is another chemical that could be recycled within the process, which is represented as green arrows. The transesterification reaction theoretically requires the molar ratio of methanol to lipid to be 3:1, and in most lab and industrial scale reactions, excess methanol is added to push the reaction equilibrium further to the right and produce as much biodiesel as possible [131]. Therefore, the unreacted methanol could be recovered during the post-transesterification purification stage and recycled.

In addition, there exist "empty" boxes in the superstructure, which represent the entire bypass of certain stages of the process. The purpose of this box is to collect all the intermediate products from the previous stage and send them directly to the following stage for further downstream processing in the mathematical model.

Moreover, regarding the arrows in the microscopic view, the modeling 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 splitting into multiple stages. The following figures are the detailed microscopic view of how individual alternatives are interconnected with subsequent-stage alternatives.

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

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 [132,133]. Instead, the reaction simultaneously extracts lipid content from microalgal biomass and chemically converts it into biodiesel and glycerol products.

Finally, as shown in Figure 9, the 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.

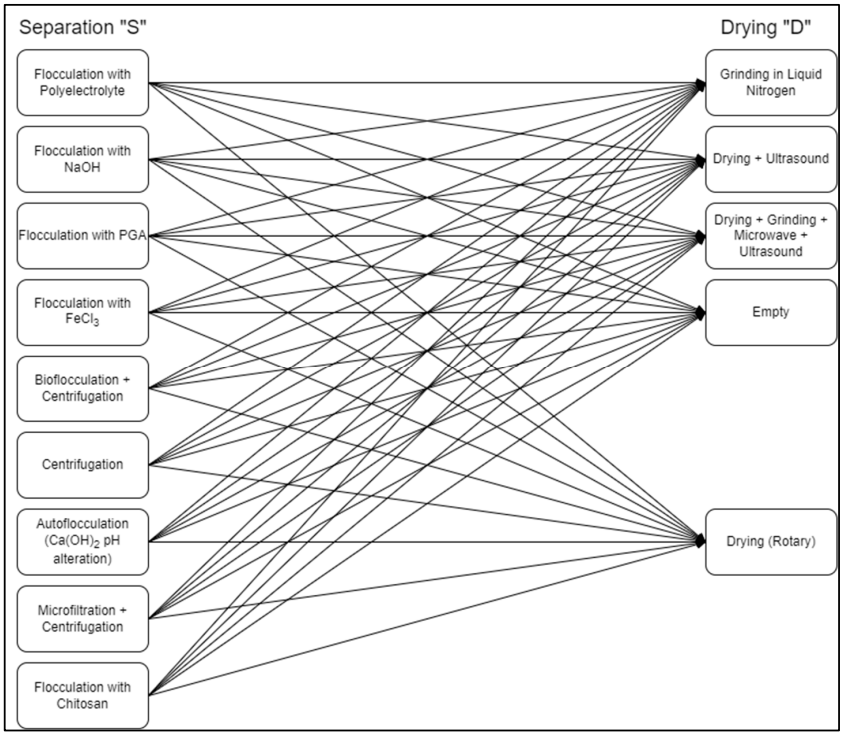


Figure 7. Detailed interconnection representation between separation and drying stages of a biorefinery.

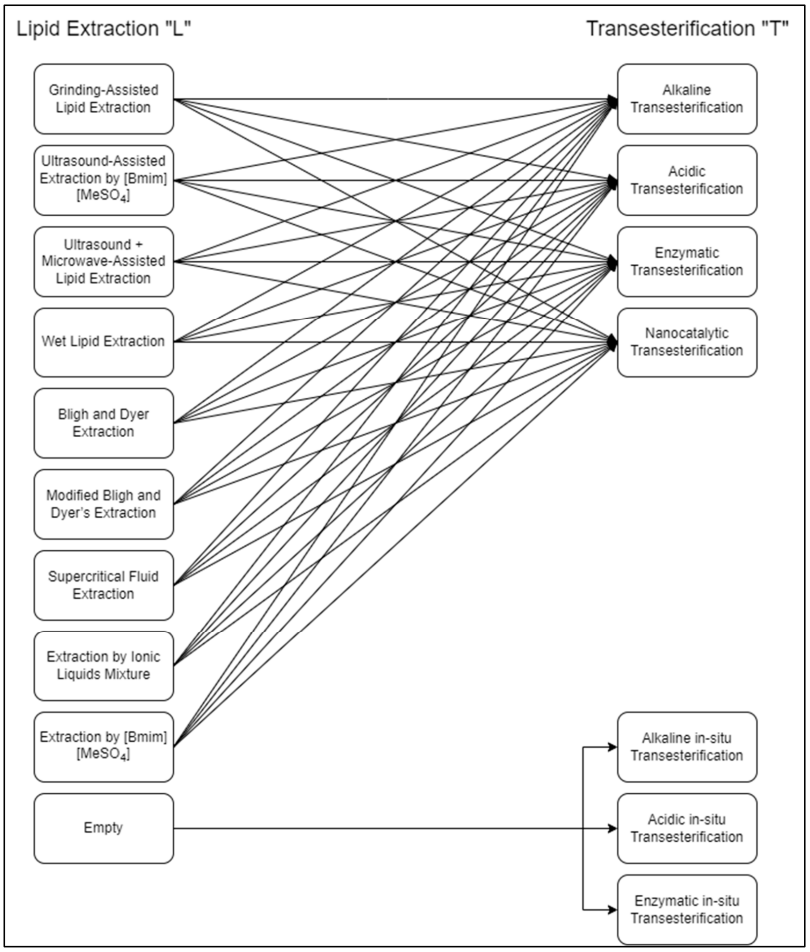


Figure 8. Detailed interconnection representation between lipid extraction and transesterification stages of a biorefinery.

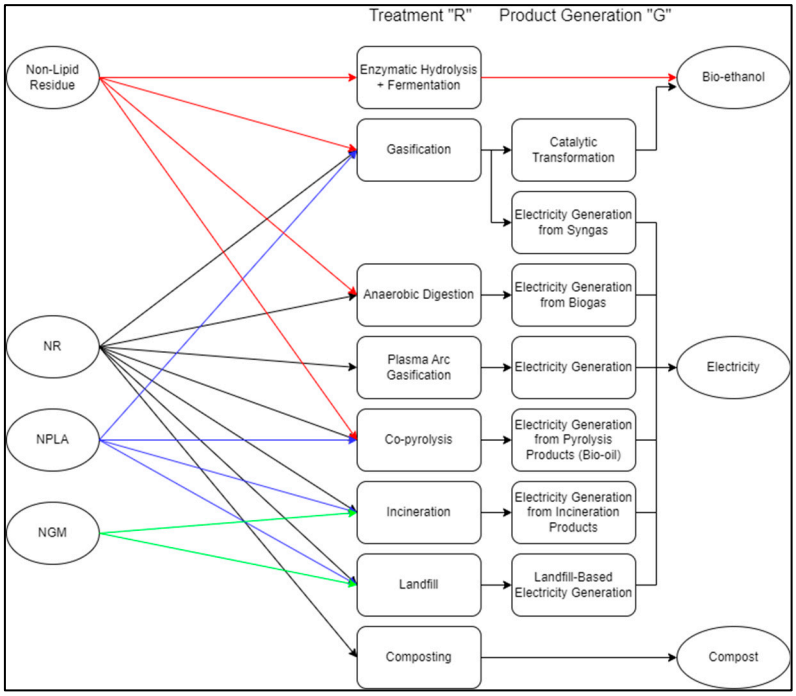


Figure 9. Microscopic interconnection from intermediate products to treatment stage.

9. Conclusions

This paper 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 chains. However, studies in multi-feedstock multi-product biorefinery, only limited to a combination of agricultural and forestry products, strongly suggested the need to integrate other types of biomass feedstocks. Meanwhile, an integrated biorefinery can potentially integrate multiple feedstocks, several potential technologies, and multiple products such as biofuels (biodiesel, bioethanol, bio-oil, biogas, etc.) along with value-added co-products in order to improve the cost-effectiveness of biorefineries in an environmentally sustainable manner. To recap, for this review report, the data from the published literature and other reliable sources were collected to identify all the potential processing pathways for: (1) the production of biofuels and other valuable chemicals from microalgae, and (2) the treatment and processing of MSW into energy and useful materials. The review showed possible crosslinking pathways for microalgae and MSW processing to increase overall product yield, optimize energy consumption, and minimize waste to landfill.

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