Biorefinery Approach for Biodiesel Production from Microalgae

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Abstract. As the availability of fossil fuel resources is decreasing and leads to energy crisis all around the world, the researchers now are looking for potential renewable sources that can be transformed into energy and replace fossil fuel resources. One of the most potential resources for fuels with many applications is microalgae. As a highly populated country with 264 million, the development of microalgae for biodiesel in Indonesia is needed to fulfill the high energy demand. With wide territorial waters and a tropical climate in Indonesia, microalgae cultivation can be conducted massively. There is no need for land to cultivate microalgae. It is only required water, CO$_2$, and sunlight. The biorefinery approach can be used to produce biodiesel from microalgae and keep the greenhouse gases (GHG) near to negligible. The wastewater generated from the process can be used again as the input of the pond for cultivation. Therefore, this biorefinery approach is promising to enhance national energy and income by optimizing the microalgae development in Indonesia.

1. Introduction
Fossil fuel production and consumption keep increasing with a 30% increase in the world’s population. In a highly populated country, like Indonesia, with 264 million, the primary energy consumption is increasing in the past five years. However, the availability of fossil fuel keeps depleting due to the fact that they are nonrenewable resources. As the world is facing an energy crisis and environmental damages because of the emission from GHGs formed by the combustion of fossil fuel, a potential renewable resource is needed to tackle this problem.

Microalgae have become the most promising feedstock to produce biodiesel in these past few years. Microalgae is a unicellular photosynthetic organism that has the potential for chemicals, food additives, bio-sorption metals, and bio-fixation of CO$_2$ [1]. Most microalgae can grow optimally at a neutral pH of 7.0-7.6 at temperatures of 15-40°C, depending on the strain [2]. The lipid content of certain microalgae biomass species can reach more than 50% [3] and their growth also tends to be exponential, which within 3.5 hours it can increase twice of initial biomass. Microalgae can produce 50 times more biomass compared to other higher plants [4]. Oil content in microalgae usually in the form of glycerol and fatty acids with a chain length of C14 to C22. Oil accumulation in microalgae tends to increase if the organism is under pressure. Besides, the oil content varies depending on environmental conditions where the growth of microalgae [5].

The productivity of microalgae biomass is much faster than oil palm, which takes around three months to 5 years to be harvested. Also, microalgae do not need land, but they only need CO2 and water to produce CH$_2$O and O$_2$ by utilizing sunlight. This is undoubtedly beneficial from an environmental perspective because microalgae can reduce the effect of GHG compared to oil palm, which requires land so that it increases GHG emissions due to land use [6] threatens food supply, and increasing forest destruction and biodiversity [7]. Microalgae also have the ability to remediate the...
wastewater to tackle pollution. In Indonesia, several microalgae are quite abundant. The magnitude potency of territorial water in Indonesia, which is around 70% of the total area, and also the tropical climate conditions with the sun shining throughout the year, is very suitable for microalgae life.

Although some types of microalgae have been developed for cosmetic raw materials and pharmaceutical needs, their applications as biofuel are still rare and under development. For example, Nanocloropsis oculata, a marine microalgae, which has a high oil content of 31-68% and widely spread throughout the seas in Indonesia, has not been optimally developed as the source of biodiesel [8]. With proper utilization and process technique, microalgae can provide the right amount of sustainable fuel and also are environment-friendly.

2. Biodiesel Production

Biodiesel production from microalgae can be developed at three major phases, which are the production of microalgae biomass, followed by the creation of microalgae oil, and the last is the production of biodiesel. In Figure 1, there is a block diagram of biodiesel production from the microalgae biomass, extraction of microalgae oil, up to the production of biodiesel itself.

2.1. Microalgae Biomass Production

In the production of microalgae biomass, some input materials are needed, such as water as the growing medium, fertilizer or nutrient, CO2 gas, and electrical energy input to drive the pedal wheel to mix microalgae inhomogeneous state. Then, these microalgae biomass can be harvested, and the oil can be extracted at the algal oil production stage. There are two types of microalgae cultivation technologies. The first and the simplest one is open pond systems, and the second is photobioreactors. In this phase, some factors affect the growth rate and biomass production of microalgae, such as temperature, pH, salinity, O2, CO2, light, nutrient stress, toxic chemicals, pathogens, dilution rate, depth, harvesting frequency, and addition of bicarbonate [9]. The following is a description of the two microalgae cultivation systems.

2.1.1. Open Pond Systems

Open pond system is the most straightforward system that is commonly used to produce microalgae in large scale. This system is also the conventional type because it requires an open lake, pond, or lagoon to grow the microalgae and paddlewheels mix to prevent sedimentation. Because of its open system, it allows contact between the pond and the air, which results in contamination by predator organisms and high rate of evaporation [10]. Controlling the growth condition for microalgae is also difficult that might limits the extraction of microalgae's oil. To deal with those conditions, it is required to create the water medium that can survive in a harsh environment or is called extremophiles conditions [11]. More than that, this system requires low energy input and there is no need to do the maintenance [12] regularly. So, it is cheaper than the photobioreactor system.

2.1.2. Photobioreactors

PBR provides better control on microalgae growth conditions and parameters rather than open pond system. PBR is operated in a closed system to reduce evaporation and produce more productive and useful species. Because of that, the more high-value products can be produced by this system [13]. However, the cost of using PBR is higher than open pond system because PBR requires higher energy input. Due to that, the implementation of PBR is only to produce microalgae in small scale.
Figure 1. Block diagram of biodiesel production from microalgae.
2.2. Microalgae Oil Production

In the final stage, namely biodiesel production, raw materials will be given solvents (generally methanol), catalysts (generally NaOH and HCl), water, and electricity to produce products in the form of biodiesel, fuel oil, and glycerol. Considerations needed in the selection of the biodiesel production process are microalgae species, extraction methods, transesterification systems [14]. Microalgae species that are required have specific characteristics, such as high-value side products in cells, oil productivity, growth rate, optimal growth conditions, and potential for development [15]. After producing the microalgae biomass, the oil is about to be extracted from the microalgae cells. The oil extraction process also produces wastewater and residual biomass in the form of fiber. Wastewater can be reused as a growth medium, while fiber waste can be burned and fermented to obtain CH4 gas.

Generally, the process of oil extraction is to break the cell wall, which is called sonication. Sonication methods is using ultrasonic waves with the help of organic solvents have also been carried out, such as using ethanol or n-hexane [16]. This method uses dangerous organic solvents in a relatively large number, making it less environmentally friendly and expensive. The cells are separated from water and prepared for downstream processing. In this downstream process, the microalgae biomass is harvested and dried. Biomass harvesting and drying process may constitute significant energy consumption in microalgae biofuel production.

In the method of extracting microalgae oil, several factors must be considered, such as the length of time needed during the process, the energy efficiency used, cost, toxicity, and ease of handling. There are several methods for oil extraction from microalgae biomass, such as press, microwave-assisted extraction (MAE), soxhlet method, supercritical fluid extraction (SCFE), pressurized solvent extraction (PSE), ultrasonic extraction, and osmotic shock. The technology for harvesting and drying of microalgae biomass is costly and requires much energy. That's why the development of a biorefinery or co-product strategy must be optimized.

2.2.1. Press

Press is the simplest method because it only requires a press device. This method is very suitable for small scale production and laboratory scale. This process has a very low efficiency because, in order to get oil, microalgae must be pressed until it breaks. This method can only extract oil up to 70% from the amount of microalgae oil content, while the rest is still mixed with the rest of the extraction in the form of carbohydrates [17].

2.2.2. Microwave-Assisted Extraction (MAE)

MAE is a technique for extracting dissolved materials in plant material with the help of microwave energy. The technology is suitable for taking compounds that are thermolabile because they have control over temperature, and it is better than the conventional heating process. MAE also has several other advantages, including shorter extraction times, less energy and solvent consumption, higher accuracy and precision, and equipment settings that combine soxhlet features and the advantages of microwaves [18]. This method depends on the dielectric constant of the solvent used. Dielectric constants are electrical insulators that are equal to the ratio of the capacitance of the filled capacitor with the material given to the capacitance of identical capacitors in vacuum space without dielectric material.

2.2.3. Soxhlet Method

This method is classified as a conventional extraction method. Soxhlet is a device used to extract an ingredient by repetitive dissolution with an appropriate solvent. The sample to be extracted is placed in a lead, which is permeable to the solvent, and placed on a distillation tube. Condensate will fall into the lead, immerse the sample, and accumulate around the lead. After a certain extent, the solvent will automatically reenter the distillation tube. This process repeats itself in tools, especially in Soxhlet equipment used for oil extraction. The principle of the Soxhlet method is extraction, always using new solvents, which generally results in continuous extraction with a constant amount of solvent in the presence of reverse cooling.

2.2.4. Supercritical Fluid Extraction (SCFE)

SCFE is the oil extraction method that utilizes the properties of the fluid under supercritical conditions to extract organic material from solid samples.
Supercritical fluid is a state when the fluid is at supercritical temperature and pressure, and in this state, the cell wall will be damaged and cause the oil to come out. However, this method requires a special tool for holding pressure and requires supercritical or CO2 extraction fluid. CO2 is liquefied under pressure and heated until it reaches a point between liquid and gas. Sometimes, CO2 is modified by co-solvents, such as ethanol or methanol. Extraction conditions for supercritical CO2 are above the critical temperature of 31°C and the critical pressure of 74 bar.

2.2.5. Pressurized Solvent Extraction (PSE) PSE is a method to extract the essential oil from plant materials where the solvents are near their supercritical region with high temperatures and high diffusion rates of solutes in the solvent. This condition leads to high penetration of the solvent in the sample. Several extraction parameters should be optimized within this method, including the polarity and volume of extracting solvent, sample size, temperature, pressure, and extraction cycle. The choice of extraction solvent is important not only for the efficient extraction of analytes from solid matrices, but also to consider this method as environmentally friendly. The most common solvent that is used in this method and safe for the environment are ethanol, ethyl lactate, and d-limonene.

2.2.6. Ultrasonic Extraction This method is known as sonication, which is the utilization of the effects of ultrasonic waves to influence changes that occur in the process. The main advantages of ultrasonic wave extraction compared to conventional extraction using soxhlet method are greater efficiency and shorter operating time. The ultrasonic method uses an ultrasonic reactor to produce ultrasonic waves that can be used to make cavitation bubbles in the solvent. When bubbles burst near the cell wall, it creates a tidal wave and causes the cell wall to rupture and thereby releasing the oil [19].

2.2.7. Osmotic Shock This osmotic shock method performs a sudden decrease in osmotic pressure on a microorganism that will cause rapid change of water movement across its cell membrane and, as the result, damage the cells. This method can be used to release cellulite components such as oil. However, this method is not commercially viable methods due to high operation costs.

2.3. Biodiesel Production
The process of turning microalgae oil into biodiesel includes several steps. Biodiesel is a clean energy with sulfur content (SOx and SO2) nearly negligible, only less than 15 ppm. To produce biodiesel, transesterification is done because the product from transesterification can be used directly in engines and no need for further modification. The process of transesterification needs acid, methanol, or alkali catalysts for the reaction to occur. The products are glycerol, excess acid/alkali/methanol, lipid contamination that did not experience conversion during transesterification process, and residual catalyst [20]. The catalyst needed for the transesterification process has to be very active and soluble because of the difficulty to purify the glycerol and the fact that glycerol is classified as dangerous waste. The important part of this process is cleaning the ester because this step produces lots of waste water. The combination of lipid extraction and transesterification in one step is called direct transesterification. Supercritical methanol is required in this process.

3. Biorefinery Approach
Although the present cost for biodiesel production from microalgae is higher than palm oil, research is still carried out to lower the cost. For microalgae cultivation, flue gas and wastewater offer are promising cheap nutrient sources that can save fresh water needs. Finding and manipulating the best conditions for cultivation process might be the challenge. Once it’s done, the amount of lipids in microalgae cells can increase.

Biorefinery concept is a good approach that should be integrated in biodiesel production from microalgae to recycle the CO2 produced as the feed for microalgae cultivation. Therefore, the process is more economics and produce zero GHG emissions [21]. It allows additional income from the coproducts. It also optimizes the process conditions and steps for biodiesel production which are environmentally friendly and economically feasible [22].
4. Conclusion
The depleted fossil fuel resources require alternative energy to deal with the increasing demand and environmental damages caused by the processing and usage of fossil fuels. Microalgae offer promising feedstock for biodiesel with several advantageous. Biodiesel production from microalgae consists of three main processes, such as production of microalgae biomass, microalgae oil, and biodiesel itself. Although the cost of biodiesel production is still high, with biorefinery approach, the cost can be reduced while maintaining zero GHG emissions. Indonesia is a high potential country with wide territorial waters along with abundant numbers of microalgae. Therefore, this biorefinery approach will optimize the microalgae development to enhance national energy and economy.

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