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REVIEW ARTICLE

Sustainable Production of Biofuels from Microalgae (*Chlorella vulgaris*) Using Irradiation Microwave as Future Green Energy; a Review

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Abstract

Biodiesel is a solution to the problem of depleting fossil fuel sources in Indonesia. Biodiesel can be derived from vegetable and animal fats. On the other hand, microalgae cultivation areas are spread across 26 provinces in Indonesia with a production potential of 462,400 tonnes/year. Microalgae with lipid content ranging from 38% - 60% can be converted into crude biodiesel as much as 35%. Irradiation microwave is the simplest and most effective technology with a constructive method for extracting oil from animal and vegetable fats, and biomass, and can be scaled easily. Using irradiation microwave, oil will be extracted from microalgae using hexane: methanol solvent for 60 minutes with a microwave power of 600 watts. Microalgae extraction with the help of irradiation microwave can produce more lipids compared to conventional lipid extraction which is 31% and 26% higher. Microalgae that go through a treatment process using irradiation microwave is more efficient because the average cost is two-thirds less compared to conventional heating, its lower energy consumption, lower costs, a more effective heating process, can increase production, and have a big impact on increasing biofuel yields.

Keywords: Biodiesel, Energy, Irradiation, Microalgae, Microwave

Introduction

Indonesia is an archipelago country that stretches from Sabang to Merauke with the fourth largest population in the world [1]. Indonesia's population has increased so that in 2022 it will reach 275,773.8 thousand people [2]. Population density has a positive impact on industry to help economic growth by expanding the market for goods or services [3]. In supporting the industrial economy, the population mobilizes to carry out various economic activities. With this large population, the mobilization of the community is getting bigger. The large population mobility requires oil-fueled transportation as a means of supporting the community to move to other places. The amount of consumer biodiesel in Indonesia is almost 90.000 thousands of barrels for industrial accommodation [4]. This amount has an influence on the existence of the number of fossils as the main ingredient for making transportation fuel oil which will decrease along with the high consumption of fuel oil [5]. This triggers the number of fossils whose existence is undeniably depleted in the future. Therefore, it is necessary to have environmentally friendly transportation by empowering alternative energy as a solution to replace fossil fuels that make up oil.

Replacing fossil fuels with biofuels is a solution to the problem of depleting fossil fuel sources in Indonesia. The alternative energy that can be developed is biodiesel. Biodiesel is a mono-alkyl ester fuel derived from fatty acids, which is used as a substitute for diesel [6]. Biodiesel has good potential to replace fossil fuels whose availability is dwindling. Another advantage of biodiesel besides having renewable raw materials, biodiesel is also more environmentally friendly and does not increase CO levels in the environment [7]. Biodiesel is one of the alkyl esters derived from long chains of fatty acids derived from vegetable and animal fats [8]. This shows that plants and animals with high lipid levels are suitable as biodiesel feedstock. Biodiesel can be produced using a transesterification process where triglycerides will react with alcohol and produce Fatty Acid Methyl Ester (FAME) and glycerin [9]. Based on a literature study of previous research by Mirzayanti et al. (2020) stated that microalgae with lipid content ranging from 38% - 60% can be converted into crude biodiesel as much as 35% [10].

The development of microalgae *(Chlorella vulgaris)* into biofuels can be one of the renewable energy solutions in Indonesia. Microalgae are the fastest-growing organisms and do not require large areas of land to grow [11]. Apart from consuming CO_2 compounds and N elements, microalgae are also one of the most important oxygen producers on Earth [12]. Microalgae have a CO_2 fixation efficiency of 10-50 times better than other plants [13]. Moreover, microalgae generally contain important components such as protein (6 – 52%), carbohydrates (5 – 23%), and lipids (7 – 23%) [12]. Generally, the oil content of microalgae ranges from 31-68% per dry weight and the lipid content is 39.6% [14]. From a geographical perspective, microalgae cultivation areas are spread across 26 provinces in Indonesia, such as Bali, Riau, South Sulawesi, Southeast Sulawesi, North Sulawesi, and Maluku. The potential for microalgae in Indonesia covers an area of 26,700 Ha with a production potential of 462,400 tonnes/year [15]. Referring to the content and benefits of microalgae, it can be concluded that microalgae have a high potential to become a renewable fuel in the future. Research by [16] it was said that microalgae are a renewable fuel source that is able to meet global demand and has the potential to replace the full use of fossil fuels.

The main challenge in the production of biofuels from microalgae is the high cost involved in extracting lipids from microalgae before they are converted into biofuels [17]. Based on research conducted in [18] shows that 90% of the energy consumed for the conversion of biodiesel from microalgae biomass is in the lipid extraction process, so this has an impact on production costs. One of the technologies commonly used in the process of converting microalgae into biofuels is lipid extraction technology using sound waves (ultrasonic) that propagate into a liquid medium produced in alternating cycles [19]. The extraction method using this technology requires a long extraction time, a large volume of solvent, and high costs [17].

One of the alternative technologies being considered for biofuel production from the conversion of microalgae lipids is irradiation microwave [20]. Irradiation microwave is the simplest and most effective technology with a constructive method for extracting oil from animal and vegetable fats, and biomass, and can be scaled easily [21]. Irradiation microwave can be used to overcome the large energy consumption of wet microalgae drying for biofuel production [22]. Microalgae that go through a treatment process using irradiation microwave have higher bio-oil yields [23]. The advantage of using irradiation microwave is that it is more efficient because the average cost is two-thirds less compared to conventional heating, its lower energy consumption, lower costs, a more effective heating process, can increase production, and have a big impact on increasing biofuel yields [24].

In this reviewed paper, the availability of raw material from microalgae and the processing method into biodiesel using an irradiation microwave to optimize bioethanol production in Indonesia. This article has also reviewed lipid extraction of microalgae methods. The system investigated in this study is expected to contribute to optimizing the potential of microalgae into products with a higher selling value in the case of Indonesia.

Materials and methods

2. 1 Material

2. 1. 1 Microalgae

Microalgae are a renewable fuel source that is able to meet global demand and has the potential to replace the full use of fossil fuels [16]. The potential for microalgae in Indonesia covers an area of 26,700 Ha with a production potential of 462,400 tonnes/year [15]. One type of microalgae that can be used is *Chlorella sp.* which has thick cell walls [25]. *Chlorella sp.* is a group of green algae that is most abundant among other green algae, namely 90% in fresh water and 10% in seawater. *Chlorella sp.* contains quite high lipids in the range of 28-32% dry weight so it has the potential to be used as biodiesel feedstock [10]. The vegetable oil used in producing biodiesel must have C16 and C18 fatty acids [26]. The fatty acid composition in *Chlorella sp.* is shown in Table 1.

Table 1. Composition of fatty acids in *Chlorella sp* [26]

No	Fatty Acids	%Total
1	Saturated Fatty Acid (SFA)	0,61 ± 0,13
	C12:0 Dodecanoic (Lauric Acid)	0,61 ± 0,13
	C14:0 Tetradecanoic (Myristic Acid)	8,62 ± 0,78
	C16:0 Palmitic Acid	30,99 ± 2,55
	C18:0 Stearic Acid	9,00 ± 0,50
	C20:0 Eicosanoic (Arachidic)	17,85± 1,12
	C22:0 Docosanoic (Behenic acid)	0,10 ± 0,03
	C24:0 Tetracosanoic (Lignoceric)	0,23 ± 0,02
	Total SFA	67,4 ± 0,06
2	Mono Unsaturated Fatty Acid (MUFA)	
	C16:1 Palmitolic Acid	25,68 ± 2,58
	Oleic Acid	0,37 ± 0,02
	Total MUFA	26,05 ± 2,59
3	Poly Unsaturated Fatty Acid (PUFA)	
	C18:2 Linoleic Acid	0,96 ± 0,01
	C18:3 Linolenic Acid	0,05 ± 0,01
	C18:4 Octadecatetraenoic	-
	C20:5ωt Eicosapentaenoic Acid (EPA)	0,17 ± 0,01
	C22:6 Docosapentaenoic Acid	0,01 ± 0,01
	Total PUFA	1,19 ± 0,03

2. 1. 2 Hexane

Hexane is a hydrocarbon compound included in the alkane group with the formula C_6H_{14}. This compound is included in nonpolar solvent compounds that are volatile [27]. This solvent is often used to obtain the yield of extraction by separating the residue. This is because hexane is included in nonpolar compounds so that it can extract nonpolar compounds such as oil with the same polarity [28]. In other words, hexane becomes a compound that can bind lipid compounds in the extraction process [29].

2.1.3 Methanol

Methanol or methyl alcohol is a derivative compound in the form of a clear liquid with the formula CH_3OH. This compound can be easily dissolved in water so that it has polar compound properties [30]. Its polarity has a lower value than water with a polarity rating of 33, so methanol can dissolve polar and semipolar substances [31]. This methanol solvent is used to bind non-lipid compounds produced in the extraction process [29].

2.1.4 Aquadest

Aquades is a pure clear solvent with properties that have no smell and taste [32]. Aquades solvents are included in solvents obtained from distillation or distillation so that they have a better level of purity than other types of solvents [33]. Aquades solvents are included in polar compounds with a fairly high polarity value [34]. The use of aquades is used to wash the extraction results that have previously been dissolved with hexane and methanol solvents [35].

2.2 Methods

2. 2 Lipid Extraction of Microalgae

The first process is oil extraction from microalgae using hexane: methanol solvent. A total of 10 grams of Chlorella sp. was extracted using a microwave with 50 ml of hexane: methanol solvent (3:2 v/v) for 60 minutes with a microwave power of 600 watts. After the extraction process was done using a microwave, the extract results were filtered with a vacuum filtrate to separate the residue (sediment) and the filtrate. The residue was then washed with 30 ml of hexane: methanol (1:1 v/v) solvent three times with the aim that the remaining residual oil could be recovered. Furthermore, the filtrate is washed with distilled water to bind the salts. The washed filtrate is then distilled to separate the solvent and microalgae oil. Next, a calculation of the % yield obtained is carried out and an analysis of biodiesel is carried out [36].

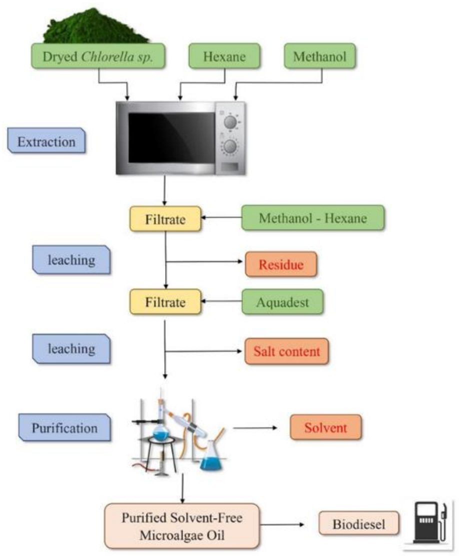

Figure 1. Production of biodiesel from microalgae using irradiation microwave

Results and discussion

4.1 Biodiesel Yield Improvement using Irradiation Microwave

Biodiesel from microalgae can make a significant contribution to sustainable energy security. Microalgae with 30% and 70% oil can produce biodiesel products of 51.927% kg/year and 121.104 kg/year [37].

Table 2. Characteristics of Biodiesel from Microalgae using Microwave Irradiation [38].

Parameter	**Microalgae Biodiesel**	**American Standard Testing Materials (ASTM)**
Density (kg/L)	0.864	0.86-0.90
Viscosity (mm^2/s, cSt in 40°C)	5.2	3.5-5.0
Boiling Point (°C)	115	Min 100
Freezing Point (°C)	-12	-
Acid Value (mg KOH/g)	0.374	Max 0.5
Combustion Value (MJ/kg)	41	-
H/C Ratio	1.81	-

Microalgae extraction with the help of irradiation microwave can produce more lipids compared to conventional lipid extraction. Heating using irradiation microwave is said to have an effect on this increase so that it can cause more lipids to be extracted [17]. The yield of lipids obtained during extraction also influences the high yield of biodiesel produced [39]. The high temperature and pressure on the microalgae cell walls due to irradiation microwave causes the cells to efficiently release large amounts of lipids which are then converted to biodiesel in less than 5 minutes. Whereas in conventional heating, heat energy is transferred to the reaction mixture through convention and conduction from the surface reactor which requires a longer time and a large amount of energy [17].

Based on research by Cheng et al (2013) bio-oil and biodiesel yield using irradiation microwave is 31% and 26% higher than conventional heating. Irradiation microwave has a thermodynamics efficiency about 1.3 times higher if compared with conventional heating, so irradiation microwave has a higher conversion efficiency for converting oil into biodiesel than conventional heating, which is 94% [24].

Table 3. Yield Biodiesel from Microalgae using Conventional Heating Methods and Irradiation Microwave (temperature 60°C) [24].

Parameter	Conventional Method (%)	Irradiation Microwave Method (%)
Yield of Bio-oil (% of dry biomass)	14.52 ± 0.53	19.03 ± 0.64
Yield of biodiesel (% of dry biomass)	8.34 ± 0.23	10.51 ± 1.37

4.2 Effect of Biodiesel to Methanol Ratio on Yield of Crude Biodiesel

Microalgae biodiesel to methanol ratio has a significant effect using irradiation microwave [40]. Methanol has a function as a solvent for the extraction of microalgae lipids or oils and as a reactant during the irradiation microwave process [41]. Due to the need to shift the equilibrium, excess alcohol is required to shift the reaction to the right, resulting in an early high ratio of microalgae biodiesel to methanol [42]. Higher amounts of methanol facilitates maximum contact between methanol and microalgae, resulting in higher yields. Using excess methanol increases the material's ability to absorb microwaves, enhances the excitation of molecules within the material, and causes an increase in temperature [41].

4.3 Influence of Temperature on Biodiesel Yields

The results showed that temperature had a significant impact on the conversion of microalgae biomass into biodiesel [43]. The temperature due to microwave irradiation causes the microalgae cell wall to efficiently release large amounts of lipids which are then converted to biodiesel in less than 5 minutes [44]. At low temperatures, molecular diffusion is slow and there are no active molecules that encourage the lipid extraction process so that the yield produced by biodiesel will decrease [45]. The biodiesel yield increases significantly to 10.51% - 19.01% when the temperature is 60°C. However, the yield of biodiesel does not increase significantly if temperature is more than 60°C. This is happen because the methanol's boiling point is 64.8°C [46]. It can be concluded that high temperature has no impact on high biodiesel yield [47]. So, 65°C is the optimal temperature that can be used for the synthesis of biodiesel from microalgae using microwave irradiation [48].

4.4 Influence of Reaction Time Biodiesel Yields

By using the extraction and transesterification methods simultaneously, the reaction time is about 30 minutes with an increase in bio-oil yield of 1.95% - 3.54% dry biomass. This is in accordance with the results of Purnomo et al. (2020) [49] which showed that the yield of biodiesel from wet biomass that went through a microwave irradiation process increased which required more reaction time. Rate of formation of biodiesel at reaction time of 2 to 10 and 30 minutes, biodiesel yield increased from 4.94% (dry biomass) to 8.16% (dry biomass) and 10.51% (dry biomass). These results indicate that the biodiesel generation rate is lower than the bio-oil extraction rate [50]. This is in accordance with Vardon's research, 2013 [51] which showed that lipids would be released more quickly when the breakdown of algae cells occurred, but the reaction time required was longer to release lipids to be converted into biodiesel. The two-step method of extraction and transesterification takes 30 minutes each to produce 8.47% biodiesel (dry biomass) in 1 hour. Yield biodiesel produced is higher by using microwave irradiation [52]. This is due to greater efficiency and shorter operating time [53]. In research using this method, the proportion conversion becomes 8.16% within 10 minutes. Thus, the one-step method using microwave irradiation is more efficient than the two-step method because it has been proven to have a rate conversion 6 times faster [54]. This finding is in line with previous research by Harinda et al. in 2019 [55], who reported that the kinetic conversion of castor oil into biodiesel using micro-wave irradiation is more efficient with a speed ratio of 3 times better than conventional methods, so this is in line with existing results.

4.5 Lipid Loose Rate and Efficiency of Cell Severance and under Irradiation Microwave

Through an extraction process based on a diffusion process will produce cells that are damaged and still intact [56]. Destruction of the microalgae cell wall is necessary because the hard texture of the microalgae cell wall can inhibit oil production in it [57]. The diffusion process is divided into unhindered diffusion for the release of damaged lipids and hindered diffusion for the extraction of undamaged lipids [58]. Oil extraction rates and yields have various variations in the amount of methanol which can be calculated with the assumption that all algal cells have the same amount of lipids.

Percentage of disrupted cells (%) = $\frac{ed_2}{(ed_2+ed_1)}$

Through this formula, damaged cells account for 77.5% of the total cells. In the use of microwave irradiation, it takes 30 minutes to damage the cells at 60ºC without sulfuric acid and extraction agents and 2 minutes if using sulfuric acid and extraction agents. This is because sulfuric acid is very tolerant of microalgae with high lipid content so that it can accelerate cell damage [59].

The use of microwave irradiation can accelerate heating up to 100 times faster because there is no pretreatment process [60]. The wave used at 2.45 GHz heats the water in the cell to form a high temperature and pressure which will damage the cell wall and release lipids with an R value of 286.06%/min which is the initial rate of extraction. The elevated temperature and pressure that ensue will lead to a small-scale explosion, causing a significant release of lipids [61]. The first minute, the lipid extraction rate is reduced by 0.48%/min because the lipids are released by unhindered diffusion. Lipids released by diffusion are inhibited, indicated by 10 minutes which decreases to 0.01% / minute.

Conclusions

As an alternative energy, biodiesel can be developed independently in Indonesian with various evaluations. This review study studied the possibility of producing biodiesel using microalga (Chlorella vulgaris) as raw material. The potential of obtaining raw materials is high because microalgae cultivation areas are spread across 26 provinces in Indonesia with a production potential of 462,400 tones/year. Irradiation microwave is the simplest and most effective technology with a constructive method for extracting oil from microalgae. Microalgae that go through a treatment process using irradiation microwave is more efficient because the average cost is two-thirds less compared to conventional heating, its lower energy consumption, lower costs, a more effective heating process, can increase production, and have a big impact on increasing biofuel yields. In addition, the separating solvent can be used to produce biodiesel are hexane and methanol. This is because hexane is included in nonpolar compounds so that it can extract nonpolar compounds such as oil with the same polarity. Also, methanol can be easily dissolved in water so that it has polar compound properties. This study is expected to help advance biodiesel using irradiation microwave with microalgae as raw materials in Indonesia.

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