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Biodiesel synthesis from *nannochloropsis oculata* and *chlorella vulgaris* through transesterification process using NaOH/zeolite heterogeneous catalyst

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Abstract. Microalgae are promising sources of biofuel due to its production capacity of lipid that can be utilized as raw material for biodiesel production, especially *Nannochloropsis oculata* and *Chlorella vulgaris*. The lipid produced can be converted into biodiesel through transesterification reaction using homogenous or heterogeneous catalysts. Heterogeneous catalysts are more advantageous than homogeneous catalysts due to its solid form that eases the separation of catalysts from the products. In this research, NaOH/zeolite heterogeneous catalyst is utilized with varying Na loadings in the zeolite to observe its effect towards the *yield* of biodiesel produced from *N. oculata* and *C. vulgaris*. The best result was obtained with Na loading concentration of 20.5%. The biodiesel yields obtained from the lipids are 83.5% from *N. oculata* and 98% from *C. vulgaris*. The biodiesels contain 47.15% of saturated fatty acid methyl esters from *N. oculata* and 56.41% from *C. vulgaris*.

1. Introduction

Microalgae are currently seen as an ideal feedstock for third generation biofuel mainly due to its high growth rate, ability to thrive in non-arable land or saline water, and high lipid productivity [1]. The lipid produced, especially triglycerides, can be utilized as a raw material for biodiesel production. Some of the most potential microalgae to be utilized as feedstock for biodiesel are *Nannochloropsis oculata* which contains 22.7-29.7 wt% lipid and *Chlorella vulgaris* which contains 5-58 wt% [2]. Biodiesel is commonly produced through transesterification process in which triglyceride and methanol react to produce methyl ester and glycerol. The process requires a catalyst otherwise it would require supercritical conditions that are difficult and expensive to achieve [3]. Homogenous base catalysts are commonly used in an industrial scale [4]. However, they are difficult to separate from the products such that biodiesel production processes suffer from environmental concerns [5]. These problems can be alleviated by using basic heterogeneous catalysts which are solid in form and thus easier to separate from the products. It would also be much more beneficial if the selected material for the catalyst is lower in cost, such as using local natural zeolite from Lampung, Indonesia, instead of synthetic zeolite or resin which is more expensive. Aside from reducing costs, using local natural zeolite will also maximize its use as one of the most abundant and highly potential local natural resources. Previous researches suggest that the amount of heterogeneous catalyst loading that is used can significantly affect the yield of the biodiesel produced [6, 7, 8, 9]. Biodiesel production

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from microalgae has been researched for years, but this research aims to provide a basic insight on the potential developments of microalgae in Depok, Indonesia, from which the microalgae were obtained to be cultivated in the Bioprocess Engineering Laboratory, Department of Chemical Engineering, Universitas Indonesia. Depok is a city surrounded by many lakes inhabited by microalgae [10], therefore this research can contribute in the utilization of microalgae in lakes surrounding Depok for a higher economic value. Considering that, this paper intends to find the highest *yield* of biodiesel produced from *N. oculata* and *C. vulgaris* by varying amounts of NaOH/zeolite catalyst loading.

2. Methods

2.1. Microalgae cultivation

Cultivation was conducted at Bioprocess Engineering Laboratory, Department of Chemical Engineering, Universitas Indonesia. *N. oculata* and *C. vulgaris* were cultivated in 6 L photobioreactors using Walne medium. Microalgae growth was measured using BEL UV-M90 Double Beam Spectrophotometer to determine its change in cell density and harvested to be used as feedstock for the transesterification process.

2.2. Lipid extraction

Lipid extraction was conducted at Bioprocess Engineering Laboratory, Department of Chemical Engineering, Universitas Indonesia. Microalgal lipid was extracted using a modified Bligh-Dyer method [11]. The harvested microalgae were centrifuged at 4600 rpm for 15 minutes. The separated biomass was extracted using methanol and chloroform with biomass:methanol:chloroform ratio of 1:4:2 v/v/v. The mixture was then ultrasonicated in Elmasonic S 30 H Ultrasonic Bath for 20 minutes. The mixture was then added with chloroform and water with biomass:chloroform:water ratio of 1:2:2 v/v/v and ultrasonicated again for another 20 minutes. Finally, the mixture was centrifuged again at 4600 rpm for 15 minutes which results in two separate layers. The bottom layer, which was microalgal lipid dissolved in chloroform, was separated from the mixture using a pipette. The chloroform solvent was evaporated in a fume hood such that only the lipid remained.

2.3. Catalyst preparation and characterization

Catalyst preparation was conducted at Bioprocess Engineering Laboratory, Department of Chemical Engineering, Universitas Indonesia. Natural clinoptilolite zeolite from Lampung was immersed in HF 1% solution and stirred for 30 minutes. It was then washed with water and dried in the oven at 120 ^{o}C for two hours. The dried zeolite was then impregnated by immersing it to NaOH solutions with concentrations of 1 M, 1.5 M, and 2 M for 24 hours. The zeolite was then separated and dried again in the oven at 120 ^{o}C for two hours, resulting in NaOH/zeolite. The catalysts were then characterized using X-ray fluorescence (XRF) at PTPSM-BPPT (Pusat Teknologi Pengembangan Sumberdaya Mineral - Badan Pengkajian dan Penerapan Teknologi) to determine the amount of Na that was successfully impregnated into the zeolite.

2.4. Biodiesel synthesis and characterization

Biodiesel synthesis was conducted at Bioprocess Engineering Laboratory, Department of Chemical Engineering, Universitas Indonesia. The process was done with lipid:methanol ratio of 1:50 v/v with 5 wt% of NaOH/zeolite catalyst. The mixture was heated to 60 ^{o}C and stirred at 300 rpm for three hours. The catalyst was then separated by centrifugation at 4600 rpm for 15 minutes. The remaining excess methanol was heated to 65 ^{o}C in a fume hood, leaving biodiesel as the main product. The biodiesel will be calculated for its yield using equation 1.

$$Yield\left(\%\right)=\frac{Mass\ of\ \ Biodiesel}{Mass\ of\ \ Lipid}\left(100\%\right) \tag{1}$$

It was then characterized using gas chromatography - mass spectrometry (GC-MS) at PUSLABFOR MABES POLRI (Pusat Laboratorium Forensik Markas Besar Kepolisian Negara Republik Indonesia) to determine its composition.

3. Results and discussion

3.1. Microalgae growth

The changes in cell density of both *N. oculata* and *C. vulgaris* throughout the cultivation are shown in figure 1 and figure 2. For a cultivation period of 318 hours, the biomass productivity shown is 0.104 g/L/day for *N. oculata* and 0.128 g/L/day for *C. vulgaris*. A previous research stated that the range of biomass productivity for *Nannochloropsis* sp. is 0.17-1.43 g/L/day and 0.02-2.5 g/L/day for *Chlorella* sp. [2]. The biomass productivity obtained from this research is approaching closely to the aforementioned range for *N. oculata* and falls within range for *C. vulgaris*. From their sufficient biomass productivity, both microalgae have shown that they are viable feedstock to be utilized for the process of biodiesel synthesis.

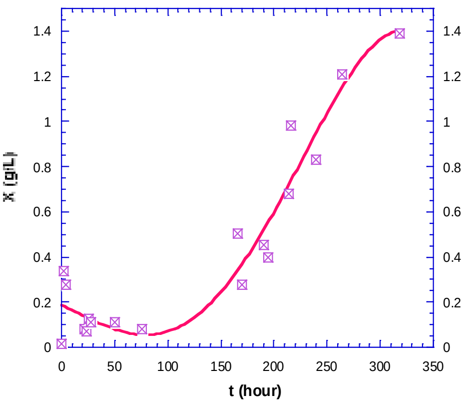

Figure 1. *Nannochloropsis oculata* growth curve in Walne medium.

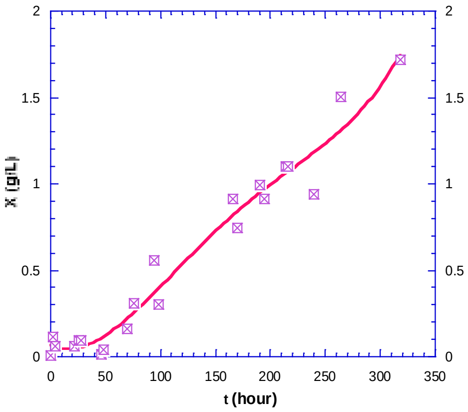

Figure 2. *Chlorella vulgaris* growth curve in Walne medium.

3.2. Catalyst characterization

Catalysts that have been impregnated by NaOH are analyzed using X-ray fluorescence. As shown in table 1, the amount of Na successfully impregnated into the zeolite increases as the concentration of NaOH is increased. A similar trend was also obtained in a previous research that used NaOH concentrations of 1.4, 4, and 10 wt%-eq and resulted in the amount of Na loading of 1.16, 3.09, and 3.64 wt%-eq [12]. The amount of impregnated Na is important since it is the element that reacts with methanol to form an alkoxide as the active species that will catalyze the transesterification process [13, 14].

Table 1. Variations of catalyst loading analyzed at Pusat Teknologi Pengembangan Sumberdaya Mineral - Badan Pengkajian dan Penerapan Teknologi.

Catalyst	Na loading (%)
NaOH/Zeolite (1 M)	15.2
NaOH/Zeolite (1.5 M)	16.4
NaOH/Zeolite (2 M)	20.5

3.3. Biodiesel yield

The resulting biodiesel yield calculated using equation 1 is presented in figure 3. In overall, *C. vulgaris* gave a higher yield of biodiesel in comparison to *N. oculata*. For both *N. oculata* and *C. vulgaris*, the yield obtained increased as the amount of catalyst loading is increased. The highest yield is 83.5% from *N. oculata* and 98% from *C. vulgaris* using 20.5% of catalyst loading. This is most likely due to the higher amount of Na available to catalyze the transesterification process which in turn produces a higher amount of biodiesel. The same increasing trends were also obtained in previous researches in which biodiesel was produced from *N. oculata* and *C. vulgaris* and various amount of loadings were used in heterogeneous catalysts [6, 7, 8, 9].

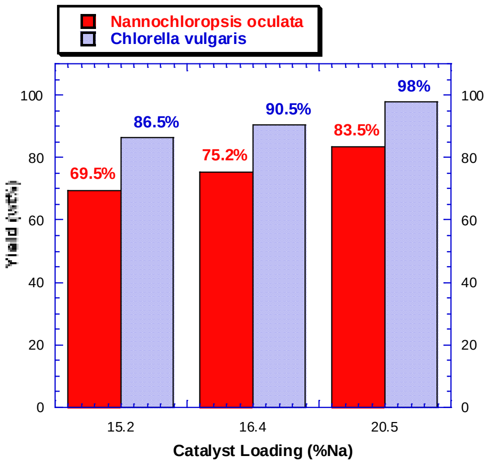

Figure 3. Biodiesel yield from *N. oculata* and *C. vulgaris*.

3.4. Composition of biodiesel

The biodiesel, which is a mixture of various types of fatty acid methyl esters, is analyzed using gas chromatography - mass spectrometry and their composition is presented in table 2. The two types of methyl ester detected in the highest amount from *N. oculata* are methyl linoleate (46.24%) and methyl palmitate (29.45%) while those from *C. vulgaris* are methyl palmitate (56.41%) and methyl linoleate (33.40%). For *N. oculata*, a previous research which analyzed its biodiesel composition stated that the two methyl esters present with the highest amount are methyl oleate (63.8%) and methyl palmitoleate (26.77%) [15]. This difference may be the result of various growth factors such as different nutritional and environmental factors, cultivation conditions, and growth phases which may result in different fatty acid composition produced by microalgae [2] and therefore result in different methyl ester composition. However, for *C. vulgaris*, a previous research which analyzed its biodiesel composition had a more similar result with this research, stating that the two methyl esters present with the highest amount are methyl palmitate (56.34%) and methyl linoleate (25.79%) [16].

The total amount of saturated methyl esters is also calculated which is 47.14% for *N. oculata* and 56.41% for *C. vulgaris*. The amount of saturated methyl ester is a significant aspect since it determines the oxidative stability of biodiesel which is an important property to ensure its acceptability of use especially during a long duration of time in storage [17]. From the results in table 2, biodiesel from *C. vulgaris* has a higher amount of saturated methyl esters compared to *N. oculata*. Unsaturated fatty acid is commonly found to be produced by microalgae [17] which in turn may result in higher amount of unsaturated methyl ester. However, this can be easily reduced by partial catalytic hydrogenation of the fatty acids [17] before biodiesel production. Moreover, this property is not entirely disadvantageous, as a higher amount of unsaturated methyl ester makes it suitable for usage in countries with lower ambient temperature therefore reducing the need for additives [18].

Table 2. Composition of biodiesel (FAME) from *N. oculata* and *C. vulgaris* analyzed at Pusat Laboratorium Forensik Markas Besar Kepolisian Negara Republik Indonesia.

Fatty acid methyl ester (FAME)		Amount (%)	
		N. oculata	***C. vulgaris***
Methyl myristate	C14:0	0.32	-
Methyl palmitate	C16:0	29.45	56.41
Methyl palmitoleate	C16:1	-	3.82
Methyl 7,10-hexadecadienoate	C16:2	5.91	-
Fatty acid methyl ester (FAME)		**Amount (%)**	
		N. oculata	***C. vulgaris***
Methyl stearate	C18:0	15.23	-
Methyl oleate	C18:1	-	6.37
Methyl linoleate	C18:2	46.24	33.40
Methyl 6,9,12-octadecatrienoate	C18:3	0.70	-
Methyl arachidate	C20:0	2.15	-
Total saturated FAME		**47.14**	**56.41**
Total unsaturated FAME		**52.86**	**43.59**

4. Conclusions

N. oculata and *C. vulgaris* are shown to be suitable feedstock for biodiesel production. An increasing amount of NaOH/zeolite catalyst loading (15.2%, 16.4%, and 20.5%) can be achieved by using an increasing concentration of NaOH solution (1 M, 1.5 M, and 2 M). The amount of catalyst loading significantly affects the yield of biodiesel produced. The best yield obtained is 83.5% from *N. oculata* and 98% from *C. vulgaris*, both using 20.5% of catalyst loading. The composition of biodiesel produced from both microalgae contains methyl palmitate and methyl linoleate as the two types of methyl esters present with the highest amount. The amount of unsaturated methyl ester detected in the biodiesel is 47.14% from *N. oculata* and 56.41% from *C. vulgaris*.

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