

Effect of Reaction Temperature on Biodiesel Production from *Chlorella vulgaris* using CuO/Zeolite as Heterogeneous Catalyst

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Abstract. Human needs for fossil energy increase every year. Biodiesel is the main way to resolve this world problem. Biodiesel produces from vegetable oil. But then, the alternative way came from the uses of microalgae in *Chlorella vulgaris* type causes by its simplicity of growing. In the other hand, this microalgae known for its high lipid content by considering several parameter such as light intensity, medium nutrition, pH and also salinity. Lipid content will be extracted by using Bligh-Dryer method which will be reacted with methanol along transesterification. Beside, there come another matter which is the utilization of homogeny catalyst. The difficulty of separation is the main matter so then biodiesel need to be washed in case normalizing the pH and this process will decrease the quality of biodiesel. To resolve this problem, we'll be using a heterogeneous catalyst, zeolite, with ability to catalyst the process. Zeolite is easier to separate from the biodiesel so there will not be needed washing process. Heterogeneous catalyst work as well as homogeneous. Variation implemented on transesterification included reaction temperature of 40°C, 60°C, and 80°C. Reaction time, catalyst percentage and the solvent amount remain steady on 4 hours, 3% and 1:400. Complete best result obtained at 60°C with the yield of 36,78%. Through this, heterogeneous catalyst CuO/Zeolite proved to have a capability for replacing homogeneous catalyst and simplify the production of biodiesel particularly in separation step.

Keywords : Biodiesel, *Chlorella vulgaris*, CuO, Zeolite, Temperature

1. Introduction

Declining of world's crude oil reserve and increasing of green fuel needs led to the developing of renewable fuel production [1]. The movement of world economy requires development of technology as well as energy section. Green diesel demand predicted to reach 900 million tons in 2020 [2]. Green fuel demand was not balanced by the supply, managing the fossil fuel for being the main fuel sources.

Greater amount of green fuel production will maintain the situation and replaced the fossil fuel production. Green fuel as well as green diesel and biodiesel produced mostly from plant oil which needs time to grow and grant the oil ready. The alternative sources would better be the microalgae. Essential composition of microalgae will be the positive value rather than its oil. Lipid's content of microalgae reaches the percentage of 34% w/w, which on the other side, palm oil only reach 17-23,8% [3]. Moreover, photosynthesis efficiency of microalgae (6-8%) way higher than the other usual plant with 1,2-2,2% [4].



Microalga will be used as the sources for biodiesel by the research using the transesterification process. *Chlorella vulgaris* would be the microalgae species used because of its high lipid content [5]. The catalyst which dominate the reaction of transesterification is the homogeny catalyst such as KOH and NaOH because of its solubility with methanol and helping the reaction to reach methyl ester [6]. The disadvantage of using the homogeny catalyst would be the needed of biodiesel washing to neutralize the pH which cause the adding of water in system. Water need to be dried and it cost one more process. Also, homogeny catalyst could not be recovered, recycle nor reuse from the system. However, heterogeneous catalyst has the advantage of replacing the disadvantage from the homogeny catalyst.

Heterogeneous catalyst that could be used for the transesterification process will be zeolite. Zeolite which impregnated with metal oxide will result a high yield of biodiesel. This statement supported by result obtained by Sani in 2013 whose Hierarchical H-Beta Zeolite uses as a catalyst for algae's oil transesterification with the conversion of 99%. The effect of big pore structure ($729 \text{ m}^2/\text{g}$) led to the diffusion of microalgae's oil to the active site of catalyst. On the other side, BET surface area should be greater too, which cause the amount of acid site to increase. Si/Al ratio will effect on acidity surface [7]. Heterogeneous catalyst for transesterification process usually needs the temperature up until $>350^\circ\text{C}$ [8], but the zeolite uses decrease the temperature process because of its channels and greater pore [7].

In this paper, zeolite will be used as heterogeneous catalyst. To improve the capability of conversion, metal oxide should be inserted in between zeolite, which in this case CuO will be used. Jack Vincent and Dheeban Chakravarthi on 2009 shows that transesterification process using heterogeneous CuO might reach 90%. In this research, CuO/Zeolite will be used as a catalyst in transesterification process, and temperature will be the variation to acknowledge the ideal condition needed to reach highest biodiesel conversion.

2. Experimental Method

2.1 Pre-Treatment of Zeolite

First, zeolite washed by the water. Right after, washed zeolite immersed in HF 1% for about 30 minutes. Make sure that all the zeolite being gently mixed to enhanced the purification from polluter. Dry zeolite about 2 hours in 110°C microwave, then immersed again in the 1M of NaOH for 24 hours and dry zeolite for 2 hours in 110°C .

2.2 Zeolite Impregnation

Mix zeolite in 0,001M $\text{Cu}(\text{NO}_3)_2$ for 4 hours. Right after, do the decantation for a day and separate the zeolite (at the bottom) with the residue. Mix impregnated zeolite with NaOH solution (pH of 8) for 4 hours. Do the decantation for a day and separate it as mentioned before. Dry zeolite in 110°C for 2 hours and then do the calcination occur in 350°C for 2 hours.

2.3 Lipid Extraction

1ml of cake (biomass) being centrifuge for 10minutes (4500 rpm). Every 1 ml of cake react with 2ml of methanol and 1ml of chloroform using sonicator for 5 minutes. Right after, add up 1 ml chloroform and 1 ml of demin water. React using sonicator for 10 minutes. Centrifuge the tube for around 5 minutes to distinguish the phase. Throw the upper part (methanol, water and biomass) and uses the bottom part (lipid and chloroform).

2.4 Transesterification

Extracted lipid react with methanol and zeolite catalyst in three neck flash and condenser system. Ratio of lipid : methanol uses is 1:400 and catalyst uses is 3% of w/w. Do the reaction in 4 hours with the variation of temperature (40°C , 60°C , and 80°C). Biodiesel purification using decantation need in total of 24 hours and then purification between biodiesel and glycerol could be done manually. Biodiesel

phase then being mixed with boiled water up until water phase being clear. Right after, biodiesel phase then being heated until 100°C to evaporate water. Biodiesel percentage calculated using equation below.

$$Y_{px} / Y_{bx} = \frac{m_{biodiesel}}{m_{sel}} \times 100\% \dots (1)$$

$$Y_{ps} / Y_{bs} = \frac{m_{biodiesel}}{m_{lipid}} \times 100\% \dots (2)$$

where,

Y_{px} or Y_{bx} = Yield of Biodiesel per Biomass Weight (g.g⁻¹)

Y_{ps} atau Y_{bs} = Yield of Biodiesel per Lipid Weight (g.g⁻¹)

$m_{biodiesel}$ = Biodiesel Weight (gr)

m_{cell} = Biomass Weight (gr)

m_{lipid} = Microalgae's Lipid Weight (gr)

2.5 GC-MS Analysis

Sample which being analyzed is the most optimum biodiesel obtained. This analysis is done to figure the methyl ester existence. Composition of methyl ester obtained analyze using Gas Chromatography and Mass Spectrophotometry (GCMS) in Pusat Laboratorium Forensik, Markas Besar Polisi Republik Indonesia.

3. Result and Discussion

3.1 Reaction Temperature Variation

Based on research done by Kim in 2014, effect of reaction temperature in transesterification reach the number of 47%, which beat the other factor such as solvent amount, reaction time and catalyst percentage (each of it has the percentage of 26,7%, 17,5% and 8,3%). To observe the effect of the variation, the other parameter remained consistent in 4 hours and 3% w/w of catalyst with the variation of 40°C, 60°C, and 80°C. Following figure shows the result of the reaction variation.

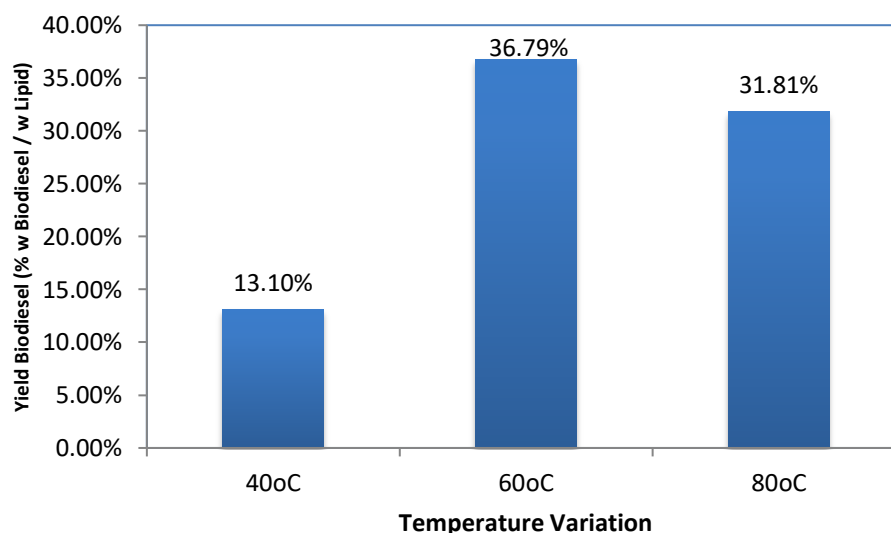


Fig1. Reaction Temperature Variation for Transesterification Process

Consecutively, conversion obtained is 23,91%, 28,66% and 23,97% (Y_{ps}), and on the other side it result an amount of 2,28%, 6,41% and 5,54% for Y_{xs} (from biomass to biodiesel percentage) and 13,1%, 36,79%, and 31,81% for Y_{ps} (from lipid to biodiesel percentage). Effect for the reaction

temperature more likely gave a big effect for the yield produced. Biodiesel produced gain the highest point at 60°C, while at 80°C it decreased. The 80°C for the system temperature excess the boiling point of the methanol (64,7°C). Methanol easily evaporate into gases for they are a volatile compound and produced the bubble in a great amount. The gases conduce a three-phase reaction system inside the three neck flash [8]. The bubble will prevent the contact of each reactant [9]. Higher temperature should be effective to escalate the catalyst activity, accelerate movement of molecule so that the frequency of collision from one and another molecule is bigger and reaction will go even faster [10]. On the other hand, 60oC reach the maximum point for producing biodiesel because there is a limitation of methanol boiling point. It reduces the amount of methanol so that the methanol become insufficient [11].

Teo et.al. in 2014 reacted the *Nanochloropsis sp.* oil with heterogeneous base catalyst such as CaMgO and CaMgO/Al₂O₃ in variant reaction temperature. It shows that in 60°C, it reach the maximum yield while reaction temperature up until 100°C shows the decrease level of biodiesel produced cause by the methanol loss (evaporated). However, in 40°C, catalyst is not yet activated. Reaction rate of the molecule and frequency of the collision reduce so that reaction itself became slow. Reaction constant in low temperature show a small level [12]. N the other hand, low reaction temperature result the small amount of copper methoxide form. Copper methoxide is a mid reactant whose function as a bond breaker of triglyceride. In low temperature, this process will took a lot more time.

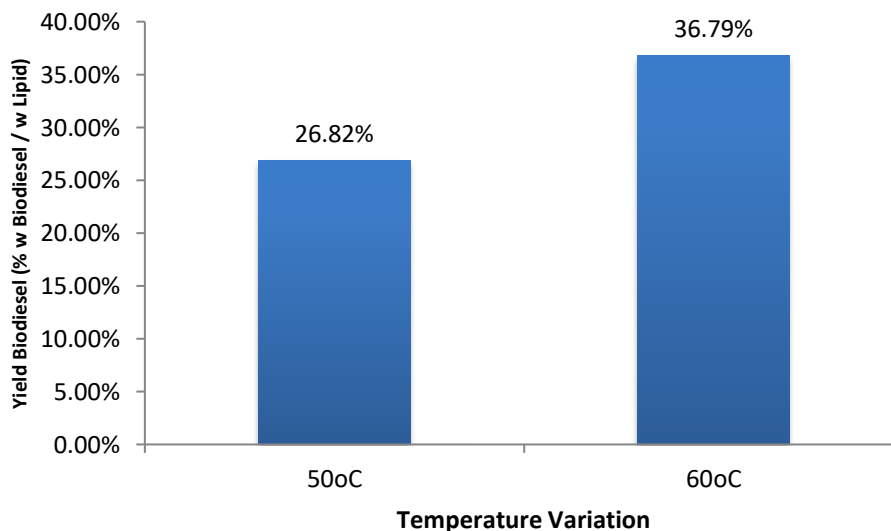


Fig2. Reaction Temperature Variation for Transesterification Process (50°C and 60°C)

Optimum variation temperature checked by further research operate in 50°C condition. New variation (50°C) produce only 4,61% of Y_{ps} , as well as the Y_{ps} of 26,82%, smaller than the 60°C reaction. according to research by Teo in 2014, this variation seems to have a parallel result where the maximum point reached on 60°C. This maximum yield do not exceed the boiling point of methanol. apart from Teo, Kumar in 2015 and Kim in 2014 also prove that the best reaction temperature is 60oC.

3.2. GC-MS Analysis

Methyl ester obtained by the reaction of microalgae lipid and methanol catalyzed by CuO/Zeolite being analyzed using GC-MS. This result is being compared with methyl ester obtained by lipid tranesterification catalyzed by homogeneous catalyst such as KOH and NaOH.

Compared to other kind of oil or lipid, microalgae lipid is kind of different. It does not rich of polyunsaturated fatty acid with four or more double bond. Eicosapentaenoic acid (EPA, C20:5n-3) and docosahexaenoic acid (CHA, C22:6n-3) is one of the most common composition of microalga oil. Fatty acid and FAME with 4 or more double bonded will easily being oxidize within storage phase and will decreasing the ability of commercialization. Generally, biodiesel produced by *C. vulgaris* will produce

more unsaturated methyl ester. On the other hand, more saturated FAME will cause higher melting point, better oxidative stabilization, and lower NO_x emission [14]. Greater unsaturated FAME in microalgae oil lead to a lower melting point of biodiesel, therefore it suits more to country with lower ambient temperature and need more additive.

Table1. FAME analyzed by GC-MS compared to Previous Research

Fatty Acid Methyl Ester (FAME)		Comparison		
		CuO/Zeolit <i>C. vulgaris</i>	KOH <i>C. vulgaris</i> (Anggraini, 2013)	KOH <i>C. vulgaris</i> (Religia, 2014)
Methyl Myristate	C14:0	Nd	4,48	Nd
Methyl Palmitate	C16:0	58,42	28,3	31,22
Methyl Palmitoleate	C16:1	Nd	11,1	4,45
Methyl 7,10- hexadekdienoate	C16:2	Nd	Nd	2,39
Methyl 7,10,13- heksadektrienoat	C16:3	Nd	Nd	5,52
Methyl Stearate	C18:0	Nd	17,1	11,55
Methyl Oleate	C18:1	41,58	39,1	30,83
Methyl Linoleate	C18:2	Nd	Nd	14,05
Total of Saturated FAME		49,88	42,77	58,42
Total of Unsaturated FAME		50,12	57,23	41,58

GC-MS analysis in Table1. shows the methyl ester variant produced. Similar research done by Anggraini and Pijar in 2013 and 2014 using homogeneous catalyst which show that Methyl Palmitate and Methyl Oleate commonly and mostly produced by *C. vulgaris* rather than other methyl ester. On the other hand, in consecutive 4 years, it also show that ratio of saturated methyl ester and unsaturated methyl ester is more than 1.

Transesterification process with CuO/Zeolite as the catalyst only result Palmitate and Oleate as its methyl ester. This outcome lead to 2 main reasons. First reason is because of the newly come strain of *Chlorella vulgaris*, and second reason is because of the pH from the catalyst. pH from homogeneous catalyst will lead to a higher pH in reaction (between 10-12) and heterogeneous catalyst will only result a lower pH (between 8-9). The pH itself could result the minimum amount of methyl ester produced by the reaction. From GC-MS analysis on Table2., it can be seen that there are several adverse reaction. Most adverse reaction produce siloxane with amount of 17,66% (*tetrasiloxane*, *cyclotetrasiloxane*, *cyclohexasiloxane*, *cycloheptasiloxane*, *cyclooctasiloxane*, serta *cyclononasiloxane*). Siloxane is an organosilicon compound which has Si-O-Si chain. Siloxane lead to a Si-O bond with organic compound, which in this research, the organic compound assumed as methanol or the other fatty acid. Si-O which being trapped inside zeolite after activation process react with methanol excess in system. Si-O itself is a destructed framework from HF cleaning phase.

CuO as a catalyst still need to compete with free Si-O chain inside system. Siloxane in system will lead to “shine” on biodiesel. On the other hand, Ala-beta-ala trimethylsilyl ester (4,95%) is a methyl ester compound whose structure being distracted by siloxane. It explain why methyl ester produce being decreased even more. Siloxane and nitrogen mostly attack unsaturated methyl ester, forming ala-beta-ala trimethylsilyl ester, and decrease the amount of unsaturated methyl ester.

Reverse reaction produced the product written in Table2. Recombination between ester group in methyl ester form another ester compound such as 1-Alanine, N-valeryl -, hecdecyl ester. On the other hand, alcohol group formed by the hydroxyl (OH⁻) which react with another component. Hydroxyl itself constructed by reaction of methanol and base catalyst (CuO/Zeolite) and it recombine with another compound so the alcohol group compound formed. Aldehyde and ketone group form by dehydration and further oxidation reaction from alcohol group. Eicosane is the rest free fatty acid which not reacted with methanol. (C:16).

Table2. GC-MS Analysis for Transesterification Product

No	Component	Percentage
1	FAME	33,7%
2	Siloxane	17,66%
3	14-BETA-H-PREGNA	9,94%
4	Ala-beta-ala trimethylsilyl ester	4,95%
5	Estra-1,3,5(10)-trien-17.beta.-ol	4,77%
6	4-and 5-(1,1,3-Trimethyl-2-butenyl)-2-cyclopenten-1-ol (isomer a)	3,63%
7	Cyclohexyl 2-Methylenebutanyl Ketone	3,17%
8	(tetrahydroxycyclopentadienone)tri carbonyliron	2,99%
9	1H-Pyrrole-2,5-dione, 1-(hydroxymethyl)	2,28%
10	l-Alanine, N-valeryl-, hexadecyl ester	2,25%
11	Eicosane	2,18%
12	Benzil Alkohol	1,90%
13	Benzenemethanol	1,30%
14	(trans)-1,2-Dihydroxy-1,2-dihydro- acronycine	1,28%
15	N-methyl-N-n-propylamine	0,36%

4. Summary

Best variation reaction shown in 60°C reaction condition with Y_{ps} of 36,79% and Y_{px} of 6,41%. Further temperature will cause an evaporated methanol to form and inhibit the reaction, on the other hand, reaction temperature below 60°C will cause the slower reaction rate and production.

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