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Synthesis of biodiesel from palm oil with dimethyl carbonate and methanol as reagent variation using KOH and enzyme catalyst

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Abstract. Biodiesel is a methyl ester transesterification process from the result of triglyceride with a methyl reagent source using a catalyst. One of novel reagent used is Dimethyl Carbonate (DMC) which can eliminate the formation of glycerol as the byproduct through the reaction resulting a compound of glycerol dicarbonate. The advantage of this compound has the same physical properties and to be a mixture in one phase liquid product with methyl ester. Lipase is a hydrolase enzyme that can catalyze the formation of fatty acid molecule from the triglyceride containing oil in the reaction of transesterification. The purpose of this research is to produce biodiesel product by observing the formation of one phase mixture of biodiesel product from the palm oilusing methanol and DMC as the reagent, KOH and lipase catalyst andthe variation of molar ratio of the oil. To obtain the best biodiesel quality examined by four characteristics: methyl ester (FAME) content, density, viscosity, and cloud point. The result of this research is that biodiesel can be produced by both reagent, and for biodiesel by DMC there was only one-phase biodiesel formed without impurities shown visually. For catalyst variation, the best biodiesel produced by methanol is biodiesel with KOH catalyst and has 98.2% ester content, 0.858 g/ml density, and 4.58 cSt viscosity. The best biodiesel produced by dimethyl carbonate is biodiesel with KOH catalyst and has 89.0% ester content, 0.883 g/ml density, and 4.91 cSt viscosity.

1. Introduction

Biodiesel is one of the most potential renewable fuel and has already been developed in this decade. It can be produced from Jatropha or palm oil that can be found easily in Indonesia because they were spread in many areas in this country. In a few years, biodiesel will be primary choice of fuel in Indonesia. To maintain the eco-friendly factor of biodiesel, in some research there were found a new type of catalyst used in the synthesis process called Lipase enzyme. Lipase could bring the reaction specifically towards the product without any disadvantageous side reaction. Lipase is a heterogen catalyst with the result that it required an easy separation treatment after being used**[1]**.

In the process of biodiesel synthesis, there are some drawbacks that need to be considered, for example the formation of by-product, glycerol. Glycerol is a side product of biodiesel production that formed by tryglyceride and alcohol reaction, while methyl ester is the main product. At the end of biodiesel production process, glycerol must be separated because it is an impurity that will decrease the biodiesel quality **[2]**. For this reason, researchers start to develop novel reagent called Dimethyl Carbonate (DMC) as alkyl reagent. This compound is known as *green reagent* and useful to eliminate glycerol as impurity in the biodiesel product**[2]**. And in this research, a new alternative of biodiesel production will be proposed. The material used will be palm oil, with novel reagent dimethyl carbonate as alcohol substitute and lipase enzyme as catalyst alternative in transesterification reaction.

2. Material and Methods

2.1. Palm Oil

Among the vegetable oils, palm oil is the most used oil especially in Indonesia. Palm oil contained triglyceride, a carboxylic acid with number of carbon from 6 to 30. Triglyceride is the largest component in palm oil, besides monoglyceride and diglyceride. Other advantage of palm oil is the content of saturated fatty acid, which is higher than other plant oil. Palmitic acid, one of the saturated fatty acid, has 47% content in the palm oil. And if the saturated fatty acid number is high, it will affect on cetane number [1].

Table 1. Fatty Acid Composition Comparison

Fatty Acid	Soybean Oil	Sunflower Oil	Corn Oil	Canola Oil	Coconut Oil	Palm Oil
C8					7	
C10					7	
C12					47	
C14					18	1
C16	11	6	11	4	9	45
C18	4	5	2	2	3	4
C20						
C22		1				
C16:1						
C18:1	23	29	28	61	6	39
C18:2	54	58	58	22	2	11

2.2. Dimethyl Carbonate

Dimethyl carbonate (DMC) is an organic compound, and categorized as carbonate esther $OC(OCH_3)_2$.DMC has liquid phase and colourless. DMC can be used as methylation agent, and can be used as solvent in biofuel production.In a normal biodiesel production with alcohol, there will be a glycerol as side product formed. Glycerol is an impurity for biodiesel and need to be separated with several processes[3]. This can be eliminated by DMC usage as solvent. Despite of producing glycerol, DMC reaction with triglyceride will form a compound called glycerol decarbonate. Glycerol decarbonate is a side product that has the same physical appearance as methyl ester, and biodiesel will visually seen as only one phase product[4].

2.3. Lipase Enzyme

Lipase enzyme (Triacylglycerol acylhydrolase) is one of the novel catalyst used in transesterification process [5]. Lipase is part of hydrolase enzyme that works in carboxylic esther bond. Lipase can be found inside animal, fungi, or in bactery. The general function of lipase is to hydrolize triglyceride and

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form diglyceride, monoglyceride, glycerol, and fatty acid. Because of this reason, lipase can be used in transesterification process[6].

2.4. Biodiesel Synthesis

2.4.1. Biodiesel with Methanol. For biodiesel synthesis with methanol as alkyl source, two types of catalyst were used as variation (KOH and Lipase). Mole ratio methanol/oil given is 1:6 and 1:12. For the synthesis with KOH catalyst, the first procedure was to heat up the oil until 80°C to vaporize water content, and then cool it down until 40°C. Then, the oil and methanol (which already dissolve the KOH about 0.8% oil mass) were mixed up in a beaker glass with magnetic stirrer for about 180 minutes at 60°C. After the product was formed, the methyl ester phase then separated from the glycerol by decantation and then washed by de-ionized water. Biodiesel was then heated up until 90°C to vaporize the water content inside it. For biodiesel reaction with lipase enzyme, the similar procedure were performed, but the difference step was only the lipase mass (5% oil mass) and the reaction time is about 300 minutes[1].

2.4.2. Biodiesel with DMC. For biodiesel with DMC as alkyl source, two types of catalyst will be used as variation (KOH and Lipase). Molar ratio between oil and DMC given is 1:6 and 1:12. The first procedure is to heat up the oil until 80°C to vaporize water content, and then cool it down until 40°C. Then, the oil and DMC (which already dissolve the KOH about 0.8% oil mass) were mixed up in a beaker glass with magnetic stirrer for about 180 minutes at 90°C.Biodiesel then heated up until 150°C to vaporize the water content and glycerol dicarbonate inside it.For biodiesel reaction with lipase, almost all the procedures are the same, the difference only the lipase mass (5% oil mass) and the reaction time is about 300 minutes at 70°C[3].

2.5. Methyl Ester Content

Biodiesel sample was analyzed using GC-FAME (*Gas Chromatography – Fatty Acid Methyl Ester*) CLARUS 680 and FTIR. This instrument analysis was used to determine the content of methyl ester in the product, and to analyze the fatty acid compounds in the biodiesel product. Like all other chromatographic techniques, a mobile and a stationary phase are required for this technique. The mobile phase is comprised of an inert gas. The stationary phase consists of a packed column in which the packing or solid support itself acts as stationary phase, or is coated with the liquid stationary phase.

2.6. Density Measurement

Density was measured using *automatic densitymeter*. Digital density meters based on the oscillating U-tube technique: The sample to be measured is filled into a U-shaped tube which is induced to vibrate. The eigenfrequency of the oscillation of the U-tube is influenced by the mass and therefore by the density of the sample. Biodiesel sample used in this test was about 20 ml. The densitymeter needs to be prepared until the operation temperature stabilized at 40°C. Sample of biodiesel was injected to the instrument apparatus for about three injections and the density can be obtained directly from the screen monitor.

2.7. *Viscosity Measurement*

The Viscosity of biodiesel was measured using Otswald Viscometer. Biodiesel was aspirated with a volumetric pipe until the first sign, and then the time for biodiesel to reach the second sign was measured using stopwatch[7]. Then, the viscosity can be determined using equation 2.1.

$$\mu = K \times t \qquad \text{.........(2.1)}$$

where:

μ = Kinematic Viscosity (centi stokes or cSt)
K = Oswald Viscometer Constant
t = Fluid Flow Time inside the Viscometer (s)

3. Result and discussion

3.1. Biodiesel with Methanol

After several steps of biodiesel synthesis with KOH catalyst, the product could be found in the form of two-phase liquid. The first phase layer visually appeared in lighter colour and expected to be methyl ester (biodiesel) and the second phase layer (below the first phase layer) seems to be product glycerol with more viscous. The existence of glycerol formation, it showed that the biodiesel synthesis through the transesterification reaction was proceeded smoothly according to its reaction theory.

In this reaction, methanol as the alkyl source along with KOH should break the binding chain between C-H and the esters, and then the C-H bond will connected to esters group from triglyceride compound. At the beginning, triglyceride will be converted into diglyceride and then methanol will start to attack the bond, and diglyceride will converted to monoglyceride. At last, methyl ester compound will be formed and hydroxy group from methanol will react with monoglyceride to form a glycerol [8].

A difference reaction mechanism is happening when lipase catalyst is used. Enzyme works with binding the carbon substance in triglyceride. This carbon substance then was binded by oxygen that exists on the active side of the enzyme. Later on, an Enzyme Substrate Complex (ES) will be formed.To form a methyl ester compound, methanol as methyl source will form a methoxy group by releasing hydrogen substance to active side of the enzyme and make a new group (N-H). The metoxy (CH_3O) will react with the Enzyme Substrate Complex and form Enzyme Alcohol Complex (E-AcA). At last, N-H group on enzyme active side will bind with oxygen and CH_2 compound in the E-AcA, and those bond will be released from the E-AcA so that enzyme structure will be shown the same asin the first form, and E-AcA will be a new compound called Fatty Acid Methyl Ester (FAME)[8].

(a)
(b)
(c)

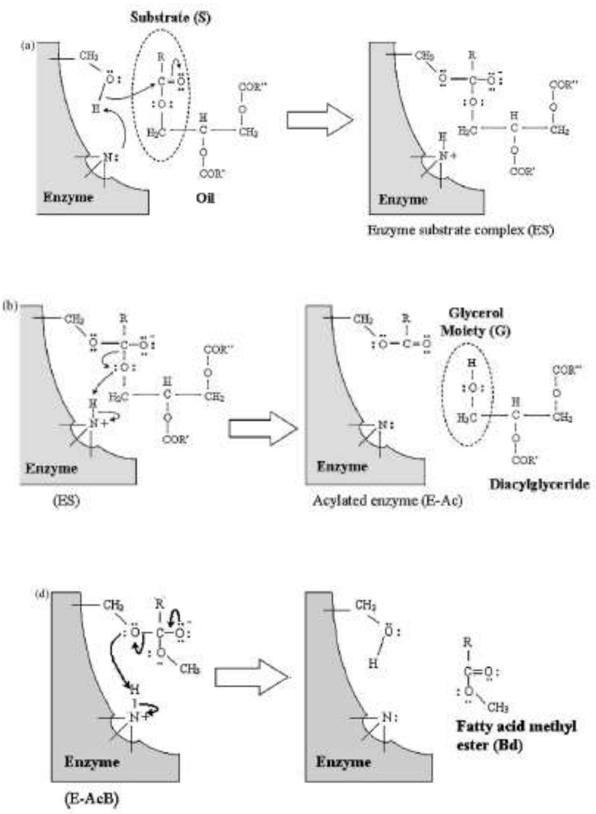

Figure 1. (a) Triglyceride Reaction with Enzyme; (b) Diglyceride and Monoglyceride Formation Mechanism; (c) FAME Formation by Enzyme from E-AcA

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3.2. Biodiesel with Dimethyl Carbonate

In the experiment of biodiesel synthesis with DMC, it was visually found to be one phase product. There was no separated layer, unlike the product resulting from the trans-esterification using methanol. Almost all reaction mechanisms are the same, but this can be happened because of the C-H group from triglyceride will bind with ester group from DMC and will form glycerol di-carbonate compound [9]. Because both FAME and glycerol di-carbonate are having ester group inside their compound, then physically FAME and glycerol di-carbonate will not show any difference visually, and seems to be one-phase mixture. Glycerol is not formed in this reaction, on the other hand glycerol di-carbonate is found in the product. This can be proven by FTIR analyzer (Fig.2).

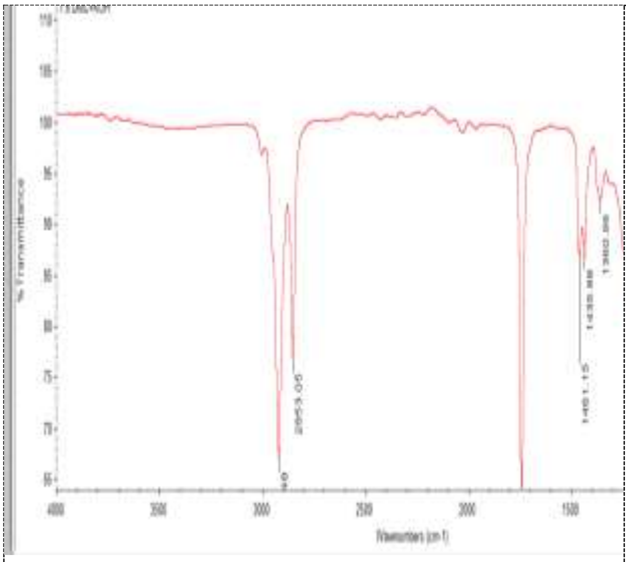

Figure 2. The Spectrum FTIR Analyzer Result shown a Compound with wavenumber 1790.1 cm^{-1}

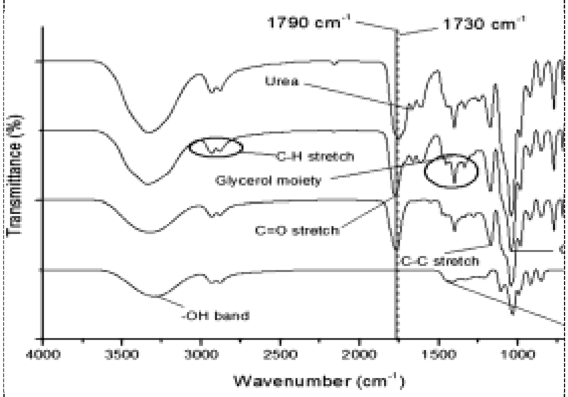

Figure 3. The Standard of FTIR Result of for of Glycerol Dicarbonate [10]

From this FTIR spectra, it can be concluded that a new compound is formed by reaction between triglyceride and DMC. The wavenumber was detected in 1790.15 cm^{-1} and based on former research, it was glycerol dicarbonate.

3.3. Biodiesel Characteristics

Based on these results on the data of density and viscosity characteristics, most of the biodiesel sample meet the requirement of standard biodiesel in Indonesia (SNI). But for methyl ester content (table 2), only enzyme biodiesel with molar ratio of 1:12 that seems to has a methyl ester compound. It happened for several reasons. Molar ratio 1:12 is the biggest molar ratio to be given in this research, so that the the number of oil and alkyl source are also in high value. Because of this reason, the reaction will occur better than the lower molar ratio. On the other hand, the number of enzyme given is getting higher while the reactant number is increased. Enzyme and substrate concentration are two important factors, that make the reaction become optimum. So in sample 1:12, the reaction is better than the other enzyme biodiesel sample.

Table 2. Characterization Result of Biodiesel Samples

Biodiesel Sample		Methyl Ester Content	Density	Viscosity
Methanol + KOH	1:6	97.5%	0.858	4.47
	1:12	98.2%	0.859	4.58
Methanol + Enzim	1:6	0.0%	0.887	5.75
	1:12	58.0%	0.858	4.48
DMC + KOH	1:6	89.7%	0.883	4.91
	1:12	81.8%	0.852	5.25
DMC + Enzim	1:6	0.0%	0.899	6.28

4. Conclusion
From this research, it can be concluded that transesterification reaction with methanol reagent could produce the compound of methyl ester and glycerol as side product. While the transesterification using dimethyl carbonate and KOH catalyst could resulted in glycerol dicarbonate compound as side product. The advantage of this compound is able to mix and dissolve each other with methyl esters product and so that the product would look in one-phase only. The characterization analysis shows that the transesterification with methanol, KOH catalyst and molar ratio 1:12 is the best biodiesel product achieved 98.2% methyl esther content, 0.858 g/ml density, and 4.58 cSt viscosity. For DMC biodiesel, the one with KOH catalyst and molar ratio 1:6 is the best biodiesel sample with 89.0% methyl esther content, 0.883 g/ml density, and 4.91 cSt viscosity.

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