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The Influence Of Alcohol Compound On Biodiesel Production Through Esterification Reaction: A Mini Review

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Abstract – Biodiesel is a renewable alternative energy that has been developed replacing conventional fuel material. Biodiesel can be produced from estereification reaction. Alcohol compound is a substantial reactant for producing biodiesel. The alcohol will donate)-acyl group to yield biodiesel. Several best alcohol compounds that yield the highest conversion is methanol with FFA conversion achieved 96 – 99,1 %. Methanol yield the highest conversion because it has low steric hindrance so the thermodynamically of esterification reaction getting fast and the FFA conversion becoming high. In the meantime, butanol gives the lowest, i.e. 87 – 94%. Butanol has high steric hindrance resulting low FFA conversion. Biodiesel with low FFA conversion is difficult to be used as fuel material, This type of biodiesel may damage injection channel for fuel material and with high acid number may cause engine corrosion.

Keywords – alcohol, biodiesel, free fatty acid.

I. Introduction

Population growth in the world during several decades has caused increasing global energy consumption resulting limited availability of energy supply [1]. This is a serious problem as continually occurred that may influence human life. Biodiesel is a renewable energy, which is sulphur free and biodegradable [2]. Besides, it is potential in reducing carbon dioxide emission that may diminish global warming problem. This matter is related to CO2 removal during burning process of plant biomass as vegetable oil that is balanced with CO2 capture by plants during photosynthetic process. As a result, the carbon monoxides in atmosphere has not increased. Therefore, biodiesel can be used as an alternative energy. Biodiesel is a compatible product with environment and can be produce from renewable natural source such as non-edible oil, fat and animal lard, recycled oil or wastes from vegetable oil distillation such as oleic acid [3], babassu oil [4] , PFAD [5], and jatropha curcas oil [6].

There are two kinds of reaction to produce biodiesel, i.e. esterification and transesterification reactions. Both reactions have been carried out adjusted with composition in the raw material used for biodiesel synthesis. In addition, both reactions need a catalyst to increase reaction rate and to reduce activation energy. The transesterification reaction is a reaction between triglycerides applying base catalyst [7]. While esterification reaction is a reaction of FFA (>2% FFA) using acid catalyst. Important factors in esterification reaction to yield biodiesel should be noted, i.e. free fatty acid in raw material, alcohol, catalyst, glycerine free, and low sulphur [8]. Alcohol has significant role in both reactions because alcohol will react with the raw material to undergo conversion to form fatty acid alkyl ester or biodiesel. Alcohol selection in esterification reaction is significant in order to convert FFA to form biodiesel. Alcohol with long chain may reduce FFA conversion due to steric hindrance of alcohol structure [9]. Several alcohols were reported as reactants for biodiesel production, i.e. methanol, ethanol, propanol, and butanol. Generally, methanol and ethanol are often used due to many available.

II. DISCUSSION

A. Esterification reaction applying methanol

Methanol is a primary alcohol with chemical formula as CH_3OH. Its trivial name is methyl alcohol. Methanol is coming from fossil fuel material, having reactivity, and separating easily [10]. Methanol is a polar solvent that is often used in esterification reaction due to its low boiling point so easily evaporated . Besides, methanol is often to be advantaged as solvent for extraction of secondary metabolite in plant. Several reports applying methanol for esterification reaction are show in Table 1:

Table 1. Esterification of methanol and several FFA sources.

Feedstock Source	Temperature; Time; Molar ratio	Catalyst Loading	%Conversion	Reference
Babassu Oil	90^{o}C ; 4,5 h; 1:2	10% wt p-toluenesulfonic acid (PTSA)	97,1%	[4]
Oleic Acid	90^{o}C ; 6 h; 1:12	9% wt sulfonated magnetic solid acid catalyst (ZrFe-SA-SO_3H)	96,9%	[11]
Oleic acid	75^{o}C; 10 h; 1:12	10% wt *S150-4*	98,06%	[12]
Palm Fatty Acid Destilate (PFAD)	90^{o}C ; 1 h; 1:18	5% wt solid acid catalyst derived glycerol	97,8%	[13]
Palm Fatty Acid Destilate (PFAD)	170; 3 h; 1:2	1,5% wt CrWO2	86%	[14]
Palm Fatty Acid Destilate (PFAD)	90^{O}C; 1 h; 1:18	4% wt of SCD-(10) catalyst	96.5%	[15]
Waste vegetable oil	240^{O}C ; 20 menit; 1:24	0.1 g ccarbon material from pyrolysis process of rubber fibers	96%	[16]
Jatropha oils	90^{O}C; 2 h; 1:20	5% wt Zr- SO3H@CMC catalyst	99.1%	[17]

Based on the table above, each catalyst and feedstock has different parameters in order to get the highest number of biodiesel production. it can be deduced that the highest conversion, i.e. 99.1 % is the FFA from Jatropha Oil and the esterification reaction applied carbon base solid acid catalyst from glycerol derivate with mole ratio of 1:20 at 90^{o}C for 2h.

B. Esterification reaction applying ethanol

Ethanol is a primary alcohol with 2 carbon atoms. The chemical formula of ethanol is written as C_2H_5OH with its trivial name called as ethyl alcohol. Ethanol has been many used as solvent because it has some benefits including low boiling point, non toxic, perfectly dissolved in water, and recoverable [6]. Ethanol is assumed as the best organic solvent based on alcohol that is able to break intra-molecule in biomass [7]. The following table (Table 2) lists several reports using ethanol for biodiesel production.

Table 2 Esterification reaction between ethanol and several sources containing FFA

Feedstock Source	Temperature; Time; Molar ratio	Catalyst Loading	%Conversion	Reference
Babassu Oil	90^{o}C ; 4,5 h; 1 : 2	10% wt p-toluenesulfonic acid (PTSA)	93,5%	[4]
Oleic Acid	130^{o}C ; 2 h; 1 : 60	5% wt MF9S4	62,5%	[18]
Palm Fatty Acid Destilate (PFAD)	45^{o}C ; 8 h; 1: 2	5% wt Novozym 435	92%	[19]
Oleic Acid	85^{o}C; 3 h; 1:7	12% wt Ph-SO_3H	96%	[20]
Oleic acid	75^{o}C ;10 h; 1:1	0,2 g of catalyst PC200S-SO_3H	94%	[21]
FOG (Fat, Oil and Grease)	75^{o}C; 3 h; 1:6	3% wt H_2SO_4	98%	[22]

On the basis of the above table, the conclusion is that the highest conversion using ethanol as reactant may achieve 98%. The FOG (Fat, Oil and Grease) source is using 3% wt H_2SO_4 as catalyst with molar ratio of 1:6 at 75^{o}C for 3h.

C. Esterification reaction applying propanol

Propanol has its chemical formula written as C_3H_7OH, and the trivial name is propyl alcohol. Propanol has 3 carbon atoms in its structure and can be obtained through fermentation. The following table (Table 3) lists several reports using propanol for biodiesel synthesis.

Table 3 Esterification reaction between propanol and several sources containing FFA.

Feedstock Source	Temperature; Time; ratio molar	Catalyst loading	%Conversion	Reference
Babassu Oil	90^{o}C; 4,5 h; 1 : 2	10% wt p-toluenesulfonic acid (PTSA)	92,7%	[4]
Oleic Acid	60^{o}C; 5 h; 1 : 3	5% wt H_2SO_4	92%	[23]
Acetic Acid	383 K; 1 h; 1 : 1	0,5 g Hβ catalyst	94%	[24]
acetic acid	150^{o}C; 10 h; 1:2	0,1 g Al-MCM-41	86,31%	[25]
Palm Fatty Acid Destilate (PFAD)	42^{o}C ; 12 h; 1:25	12% wt Oxone® salt	85,7%	[26]

Based on the data above in the table 3, a conclusion can be drawn that the highest conversion (94%) with propanol was achieved by applying acetic acid at 383 K for 1h using 0.5 g Hβ catalyst with molar ratio 1:1.

D. Esterification reaction applying butanol

Butanol is an alcohol obtained from biomass. Butanol with its chemical formula as C_4H_9OH and its trivial name called as butyl alcohol. Butanol has low reactivity compared to that of methanol, ethanol, and propanil. Several reports using butanol to yield biodiesel are listed in Table 4 as follow:

Table 4 Esterification reaction between butanol and sources containing FFA

Feedstock Source	Temperature; Time; Molar ratio	Catalyst Loading	%Conversion	Reference
Acetic acid	200°C ; 9 h; 1:2	0,1 g Al-MCM-41	88,7%	[27]
Oleic Acid	60°C ; 5 h; 1 : 3	5% wt H_2SO_4	87%	[23]
Palm Fatty Acid Destilate (PFAD)	42°C ; 12 h; 1:25	0,5 g Hβ catalyst	90%	[16]
Palm Fatty Acid Destilate (PFAD)	42°C ; 12 h; 1:25	12% wt Oxone® salt	90%	[26]
Oleic acid	120°C ; 4 h; 1:1,2	7% wt ZS catalyst	94,98%	[28]

Based on the data above, it can be concluded that the highest conversion (94,98%) achieved by using butanol reacted with oleic acid at 120°C for 4h applying 7% wt ZS catalyst with molar ratio 1:1,2.

E. PFAD esterification with varied alcohol compounds

Palm fatty Acid Distillate (PFAD) is a non-edible oil and containing high FFA [14]. The compositions of PFAD include ±90%, 10% triglycerides, diglycerides, monoglycerides, and small amount of other impurities [15]. The usage of PFAD as raw material for biodiesel synthesis can reduce production cost because PFAD is a by-product from palm oil distillation. The acid compound in PFAD contains 15 – 18 carbon atoms including lauric acid, myristat acid, palmitic acid, stearic acid, oleic acid, and linoleic acid [16]. Table 5 presents several reports using PFAD as FFA source applying several alcohol compounds for biodiesel synthesis.

Table 5 Esterification reaction of PFAD and varied alcohol compounds

Variasi Alkohol	PFAD				
	Temperature dan time	Catalyst loading	Ratio Molar	%Conversion	Reference
Metanol	90°C ; 1 h	5% wt Sulfonated cow dung-derived carbon	1:18	97,8%	[15]
Etanol	45°C ; 8 h	5% wt Novozym 435	1:2	92%	[19]
Propanol	42°C ; 12 h	12% wt Oxone® salt	1:25	85,7%	[26]
Butanol	42°C ; 12 h	12% wt Oxone® salt	1:25	90%	[26]

Based on the reviews mentioned above, it is apparent that methanol possessed the best conversion, i.e. 97.8%, while the lowest conversion was found to be 85.7% (using propanol) with PFAD as the source for FFA.

F. Characterization of PFAD and Biodiesel

1. FTIR

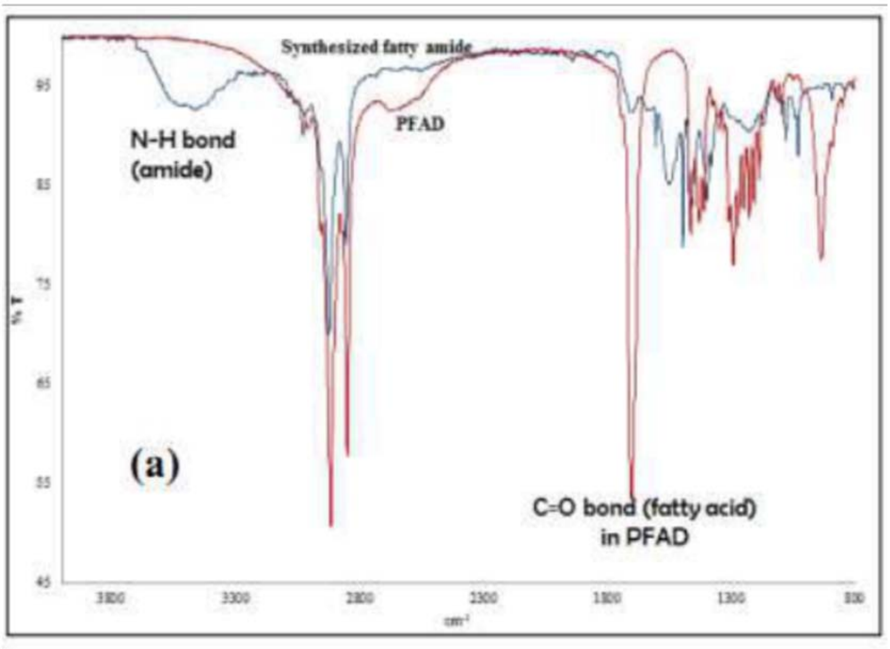

Fig.1 FTIR Spectrum of PFAD [29].

FTIR spectra of PFAD and the generated biodiesel are show at Fig.1. Spectra of PFAD were observed at 1702 and 2916 cm^{-1} shows a functional group of C=O from carboxylic acid and C-H of molecules respectively [29]. Ferreira et al [19] reported FTIR characterization of biodiesel in order to identify functional groups in biodiesel. Fig.1 shows two absorption peaks at 1434 cm-1 and 1741 cm-1 attributed to carbonyl functional group (C=O), while absorption peak at 1100 cm-1 related to asymmetric and symmetric stretching. Stretching vibration of CH_3, CH_2 and CH appeared at 2853 cm^{-1}, 2928 cm^{-1} and 3008 cm^{-1}, respectively. Absorption band at 722 cm-1 shows a stretching from olefin carbon (-C=CH_2).

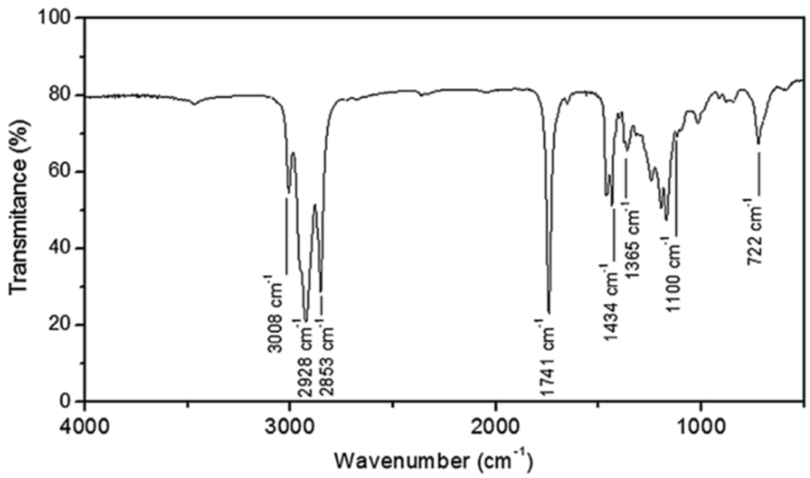

Fig.2 FTIR spectrum of Biodiesel [30]

2. GC-MS

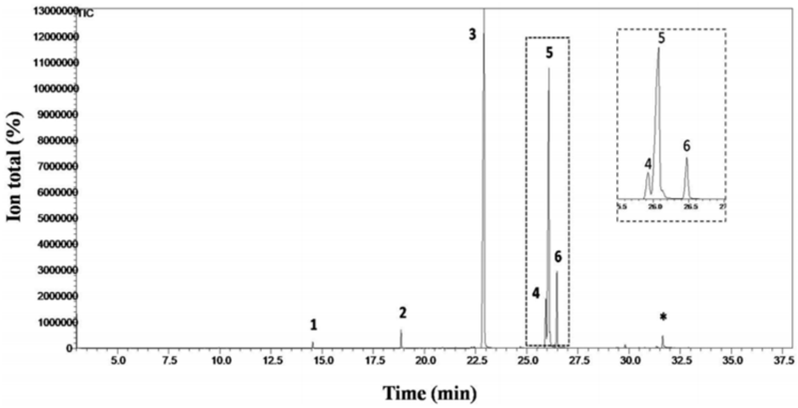

Fig.2 Chromatogram of PFAD [26]

Lopes at al. [26] carried out analysis of components presence in PFAD applying GC-MS. The GC-MS is an equipment used for determination of composition of components in a sample. The parameters used for analysis by GC-MS are as follows: split ratio 1:15, helium carrier gas, injection volume 1.0 ml, temperature of injector 250°C, temperature of detector 270°C, column initial temperature 100°C for 2 min. with increasing heating rate 5°C/min. until achieved 260°C for 4 min. The time is totally 38 min. Fatty acid ethyl ester will be examined based on its fragmentation spectrum using MS database, NIST 5.0 software.

The chemical composition in the PFAD was identified applying gas chromatograph coupled with mass spectrometer (Table 6 and Fig.2). The findings showed that FFA in PFAD consisted of 62.3% saturated fatty acid containing palmitic acid (54.3%), which is relevant for biodiesel characterization including stability and volatility. The 33.4% unsaturated fatty acid was dominated by oleic acid (33.4%). Thus, the sample contained saturated and unsaturated fatty acid in balance level that can yield biodiesel.

Table 6 The components in PFAD analyzed by GC-MS [26].

Fatty Acid[a]	Peak	Relative Concentration (%)[b]
Lauric (C12:0)	1	0.5
Myristic (C14:0)	2	1.3
Palmitic (C16:0)	3	54.3
Linoleic (C18:2, υ-6)	4	4.3
Oleic (C18:1, υ-9)	5	33.4
Stearic (C18:0)	6	6.2
Total Saturated	-	62.3
Total Monounsaturated	-	33.4
Total Polyunsaturated	-	4.3

[a]% FAEE corresponding to fatty acid

[b]MS database (NIST 5.0)

III. Conclusion

1. Alcohol plays important role for conversion of free fatty acid to produce fatty acid alkyl ester. As the alcohol chain getting longer the FFA conversion getting reduced due to stearic hindrance of alcohol structure. Alcohols with branched chain will increase FFA conversion.

2. Methanol is the alcohol shows the highest conversion (96 – 97%). On the other hand, butanol is the alcohol shows the lowest conversion, i.e. 87 – 90%.

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