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THE USE OF ASH OF PALM EMPTY FRUIT BUNCHES AS A SOURCE OF BASE CATALYST FOR SYNTHESIS OF BIODIESEL FROM PALM KERNEL OIL

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ABSTRACT

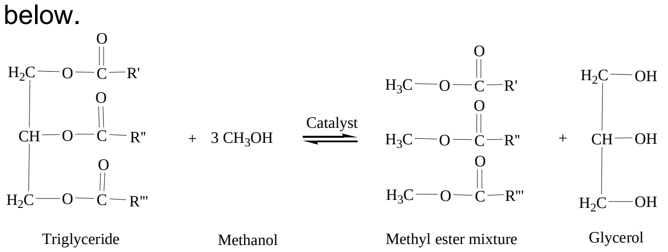
An experiment for the use of ash of palm empty fruit bunches (EFB) as a source of base catalyst for biodiesel synthesis from palm kernel oil has been carried out. The procedure was started with metal content analysis by AAS and carbonate ions content by alkalinity test in the ash. The fatty acid composition of palm kernel oil was analyzed by GC-MS. A certain weight of the ash was immersed in the methanol to form potassium methoxide, and then was used in transesterification of palm kernel oil. With variation of methanol/oil molar ratio, percentage of the biodiesel conversion was determined by ^{1}H NMR spectrometer and physical properties of biodiesel were determined using ASTM standard methods. The results showed that potassium content in the ash of palm EFB was 29.82 % w/w, and the carbonate ion content was 19.63 % w/w, the potassium might be in carbonate form. The biodiesel conversion increased with increasing of methanol/oil molar ratio. The optimum condition was reached at methanol/oil molar ratio = 12:1, that could give biodiesel conversion = 100.00 %, and the results of some physical properties were relatively conformed with biodiesel ASTM D 6751 specification.

Keywords: *Ash of palm empty fruit bunches, palm kernel oil, transesterification, base catalyst, biodiesel.*

INTRODUCTION

There were several research in biodiesel synthesis as an alternative fuel. They have advanced the research to initial stages of commercialization. Nevertheless, various technical and economic aspects require further improvement of these fuels (Knothe, 1997). In ASTM standards, biodiesel was defined as fuel comprised mono alkyl esters of long chain fatty acids derived from renewable resources as vegetable oils and animal fats, for used in compression ignition (diesel) engines (ASTM, 2003[b]). Numerous different vegetable oils have been tested as biodiesel. Indonesia is the second biggest palm oil producer in the world, so there is great opportunity for Indonesia to produce biodiesel from palm oil.

Biodiesel, generally, was synthezised by transesterification with a base catalyst (sodium alkoxides, sodium or potassium hydroxides as well as sodium or potassium carbonates (Pinto *et al.*, 2005)). The transesterification is reversible reaction as illustrated below.



Some factors have affected in the transesterification, i.e. water and free fatty acids, molar ratio, catalyst type and its concentration, temperature, and mixing speed. Graille (in Knothe *et al.*, 1997) reported a synthesis of methyl or ethyl ester study (90 % yield) from palm kernel oil and coconut oil in methanol and ethanol by using ash from their waste as a base catalyst.

In a ton of fresh empty fruit bunches, there were 230-250 kg of empty fruit bunches (EFB) (Kittikun *et al.*, 2000). The EFB were used as substrate in mushroom cultivation, boiler fuel (Kittikun *et al.*, 2000), and incinerated to give their ash (Saletes *et al.*, 2004). The ash of EFB were used as fertilizer substituent. (Saletes *et al.*, 2004). Alkali solution from the ash also used in pulping process for paper production (Darnoko *et al.*, 1995)), and soap production (Onyegbado *et al.*, 2002). The ash of EFB have high potassium content (45-50 %) (Kittikun *et al.*, 2000). Untill this time, there were no publication in biodiesel synthesis from palm kernel oil with the ash of EFB palm tree as a base catalyst.

There were several methods to determine the degree of methyl ester conversion in biodiesel synthesis, and proton nuclear magnetic resonance (^{1}H NMR) spectrometry was one of them. By ^{1}H NMR spectrometer, metoxy spectra from methyl ester would appear at 3,7 ppm (singlet), spectra at 4,2 ppm (*doublet of doublet*) was glyceridic proton. (Knothe, 2000). The spectrum could be used as reference to

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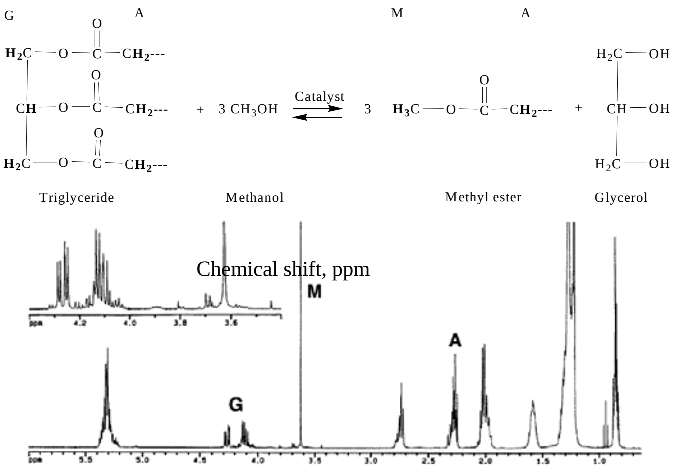

Fig. 1. ^{1}H nuclear magnetic resonance (NMR) spectrum of a progressing transesterification reaction (spectrum recorded after 5 min reaction time at 45°C). The letters **A**, **G**, and **M** denote the a-CH2, glyceridic, and methyl ester protons, respectively

determine the degree of biodiesel conversion, because spectra at chemical shift 4.2 ppm was characteristic for triglyceride that methyl ester did not have it. Whereas, spectra at chemical shift 3.7 ppm was characteristic for methyl ester that triglyceride did not have it. The extent of both spectrum indicated for incompletness in biodiesel synthesis. Fig. 1 showed the ^{1}H NMR spektrum in transesterification process after 5 minutes (at 45°C)

Methyl ester conversion (in %) was calculated by equation (1). The percentage of TG remain in product could be determine by equation (2). The percentage of TG remain in product (% b/b) was calculated by equation (3).

$$C_{ME}, \% = 100 \text{ X } \frac{5\ I_{ME}}{5\ I_{ME} + 9\ I_{TG}} \quad (1)$$

$$C_{TG}, \% = 100 - C_{ME} \quad (2)$$

$$\text{TG, \% b/b} = \frac{C_{TG} \times MW_{TG} \times d_{TG}}{(C_{TG} \times MW_{TG} \times d_{TG}) + (C_{ME} \times MW_{ME} \times d_{ME})} \quad (3)$$

where C_{ME} = conversion of methyl ester, %; I_{TG} = spectra integration of triglyceride, %; C_{TG} = unconverted triglyceride, %; MW_{TG} = molecular weight of triglyceride, g. mol^{-1}; MW_{ME} = molecular weight of methyl ester, g. mol^{-1}; d_{TG} = density of triglyceride, kg. m^{-3}; and d_{ME} = density of methyl ester, kg. m^{-3}.

With abundant palm oil production in Indonesia, it make a sense that Indonesia has a great opportunity to produce biodiesel from palm oil. The ash of EFB, as waste of palm oil industries, have high potassium content and it could be use as a source of base. In this research, biodiesel had been synthezised from palm kernel oil in methanol medium and the ash of EFB were used as a source of base catalyst. The aim of this research were explore the potential of the ash of EFB (usually being treated as waste) as a source of base catalyst in biodiesel synthesis, and effect of methanol/oil molar ratio in the effectivity of transesterification of palm kernel oil.

RESEARCH METHODS

Reagens

Ash of EFB (palm oil plant-Palembang), palm kernel oil, methanol (Bratachem), Merck chemical reagens were: cesium nitrat p.a, potassium chloride p.a., lantanum oxide p.a., hydrochloric acid (37 %) p.a., nitric acid (65 %) p.a., fluoride acid (40 %) p.a., and anhydrous sodium sulfate p.a.

Apparatus

A unit of laboratory glassware (three neck round bottom flask 500 mL cap., thermometers, magnetic stirrer, hot plate, condenser), stopwatch, analytical balance, AAS (SpectrAA, Varian), ASTM D 1298, ASTM D 445 (Pusdiklat Migas-Cepu), filter 100 mesh, mortar and porcelain cup, oven, GC-MS (Shimadzu QP-5000), ^{1}H NMR (JEOL JNM-MY60) spectrometer (Organic Chemistry Laboratory, Mathematic and Natural Sciences Faculty, GMU).

Procedure

The ash of EFB were heated to remove any water, crushed with mortar and filtered through 100 mesh filter. The filterred ash then dried in oven at 110°C for 2 hours. Metal contents were determined by dissolved 0.5 g the ash in 2-3 mL aquaregia and 3-5 drop of fluoric acid, then stirred with little heated untill completly dissolved. The solution was diluted with double deionized (DDI) water to 100 mL in volumetric flask. The series of standard solutions according to metal being analysed were prepared. The standard solutions, blank and sample solutions were analyzed by AAS. The carbonate ions in the ash of EFB were determined by alkalinity test. Ten grams of the ash of EFB were immersed in 100 mL DDI water, and stirred for 1 hour. The extracts were filterred and alkalinity content was tested by acidimetry titration method.

The palm oil stocks were analyzed with ^{1}H NMR spectrometer. The physical properties of the palm oil stocks were analyzed with kinematic vicosity at 40 °C (ASTM D 445), and density at 15 °C (ASTM D 1298).

Palm Kernel Oil Transesterification

Palm kernel oil transesterifications were done with percentage of weight of ash to oil = 6 % m/m. Fifthteen grams of the ash EFB were immersed in 75 Ml methanol (MR = 32,04 g. mol^{-1}, density at 15 °C = 0,7907 kg. L^{-1}) for 48 hours at ambient temperature. After filterred, the extract was diluted to the weight desired to obtained the weight of methanol solution correspond to methanol/oil molar ratio desired, then used it in transesterification of 250 g of palm kernel oil

(BM = 704 g. mol^{-1} (Lele, 2005)). The amount of potassium that could be extracted from the ash was determined by AAS.

Transesterification have been done in three neck round bottom flask, 500 mL cap., equipped with magnetic stirrer, hot plate, thermometer, and condenser. The palm kernel oil was poured in three neck flask and weighted so the weight of palm kernel oil was 250 g, and then assembled with condenser system. The mathanol solution was poured into the three neck flask, and magnetic stirred was turned on. Time was recorded as the magnetic stirrer was turned on. After 2 hours, stirring was stopped. The mixture poured into separating funnel, and settled for 2 hours untill separation occured at ambient temperature. The glycerine layer was drawn off, and the methyl ester layer was collected in distilling flask and distilled to remove the methanol remained. The remained catalyst in methyl ester layer were removed by washing gently with DDI water several times, untill clear methyl ester observed. The methyl ester was dried by anhydrous Na_2SO_4. This procedure was proceed with variation made in methanol/oil molar ratio, i.e 3:1, 6:1, 9:1, and 12:1 at 6 % m/m of the ash to oil.

Analytical Methods

Methyl ester composition were analyzed by GC-MS Electron Impact Ionization (column type: CP Sils CB, column lenght: 25 m, column diameter: 0.25 mm, helium gas pressure, 12 kPa, split ratio: 49.00, injector temperature: 300°C, detector temperature: 300°C, temperature programming: rate 10 °C/minute up to 280 °C for 60 minutes. The percentage of methyl ester conversion was analyzed by ^{1}H NMR spectrometer (60 MHz, $CDCl_3$ solvent). The methyl esters conversion (as methyl esters concentration) were determined by equation (1). The percentage of triglycerides remained were determined by (2). The triglycerdes remained in unit weight percent were determined by equation (3). Palm kernel oil density, kg. L^{-1}, = 0.9180 and the density of biodiesel produced = 0.880. Relative molecular weight of palm kernel oil (TG) = 704 g. mol^{-1} (Lele, 2005), and relative molecular weight of three methyl ester produced = 708 g. mol^{-1}.

RESULTS AND DISCUSSION

The metal contents and alkalinity of the ash of EFB were showed in Table 1. In Table 1 showed that potassium content in the ash of EFB were relative high (29.82 % m/m). The alkalinity test showed that carbonate ions in the ash of EFB were relative high (19.63 % m/m). Therefore, probably, potassium in the ash of EFB were in the carbonate form. Solubility of potassium carbonate in methanol was 16,500 ppm (Anonim, 2006).

Table 1. Chemical composition of the ash of EFB

Parameter	*Results*
K (% m/m)	29.82
Si (% m/m)	14.24
Ca (% m/m)	6.72
Mg (% m/m)	4.34
Na (% m/m)	2.37
Fe (% m/m)	0.31
Mn (% m/m)	0.17
Cu (% m/m)	0.02
Alkalinity,	
- $CO_3^{=}$ (% m/m)	19.63
- HCO_3^{-} (% m/m)	3.21

Feedstock Analysis

The chemical composition of palm kernel oil was determined by analysed the methyl ester resulted from transesterification of the palm kernel oil in methanol medium by GC-MS method. Characteristic fragment for methyl ester was $[M-31]^+$ ion that indicated bond breaking of methoxy groups and this fragments could give confirmation that methyl ester were exist.. The $[M-43]^+$ ion indicated bond breaking involved 3 carbon atoms, i.e carbon no. 2-4. The relative abundance of m/z = 74, were ions resulted in Mc. Lafferty arrangement. Homolog series of ion with m/z = 87, 101, 115, 129, 143, 157, 199, etc. indicated $[CH_3OCO(CH_2)_n]^+$ ions that could be used as indicator that there were no another groups in methyl esters. The chemical compositions of palm kernel oil were showed in Table 2.

Table 2. The chemical composition of fatty acids in palm kernel oil

Trivial (systematic) name; acronim	Fatty acids in palm	
	Feedstock	Kurata
Capric acid (decanoic acid); C10:0	6.34	11.7
Lauric acid (dodecanoic acid); C12:0	72.11	69.3
Miristic acid (tetradecanoic acid); C14:0	12.16	9.7
Palmitic acid (hexadecanoic acid); C16:0	1.35	2.3
Stearic acid (octadecanoic acid); C18:0	-	0.3
Oleic acid (9*Z*-octadecanoic acid); 18:1	-	2.2
Linoleic acid (9*Z*,12*Z*-octadecanoic acid); C18:2	-	0.4
Others:		4.1
Caprilic acid (octanoic acid); C8:0	8.03	

Table 3. The percentage of biodiesel conversion resulted from palm kernel oil transesterification at 6 % m/m of ash to feedstock and ambient temperature in different methanol/oil molar ratio

Code	Methanol/oil molar ratio	Conversion, %
6/3:1	3:1	42.94
6/6:1	6:1	69.67
6/9:1	9:1	77.43
6/12:1	12:1	100.00

Table 4. The percentage of biodiesel conversion resulted from palm kernel oil transesterification at 6 % m/m of ash to feedstock and ambient temperature in different methanol/oil molar ratio

Code	Methanol/oil molar ratio	Coversion, %
6/3:1	3:1	42.94
6/6:1	6:1	69.67
6/9:1	9:1	77.43
6/12:1	12:1	100.00

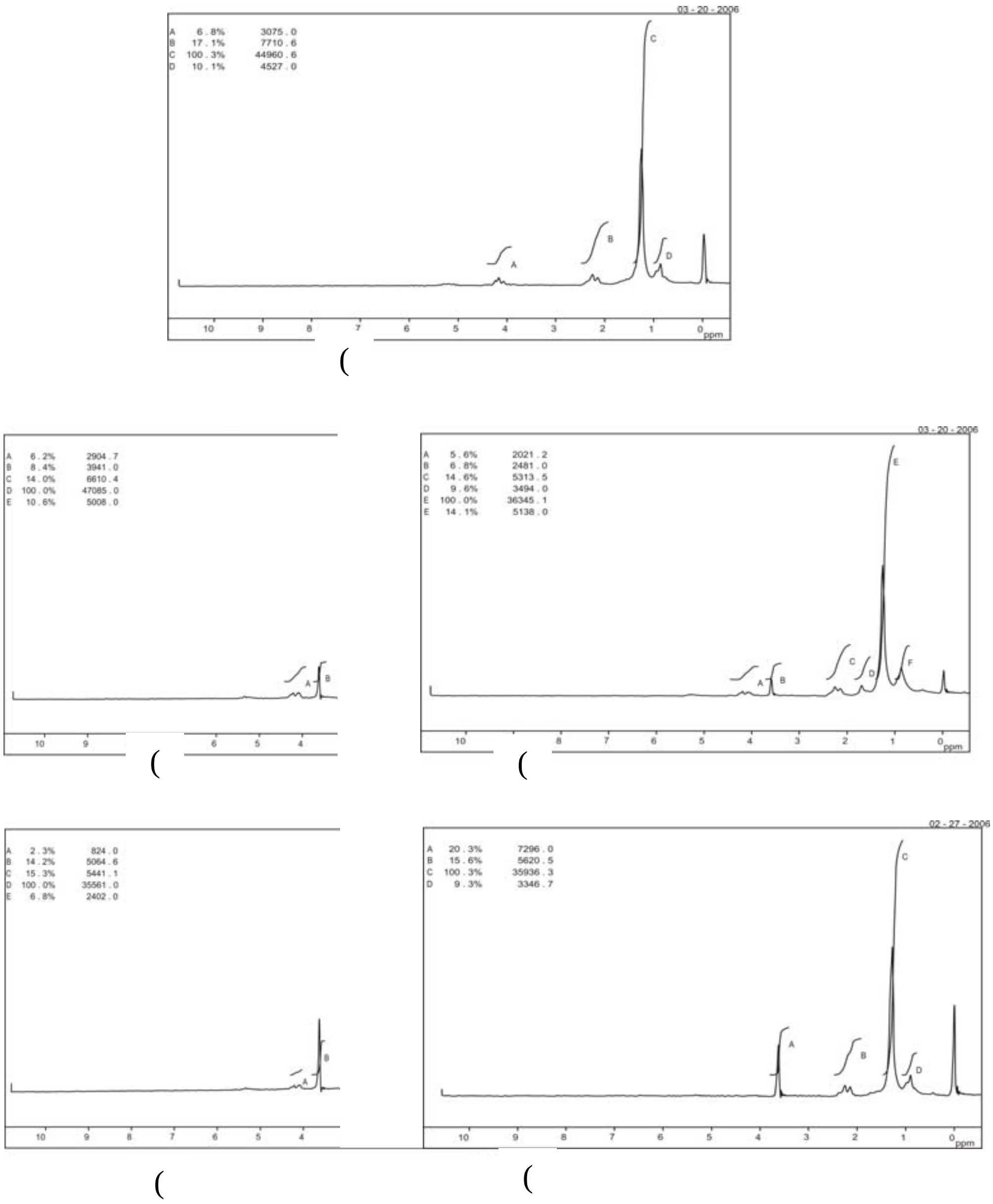

Fig 2. ^{1}H NMR spectrums: (a). Palm kernel oil; (b), (c), (d), and (e) Products from palm kernel oil transesterification with 6 % m/m ash to feedstock, in methanol/oil molar ratio ratio 3:1, 6:1, 9:1, and 12:1 (2 hours, ambient temperature)

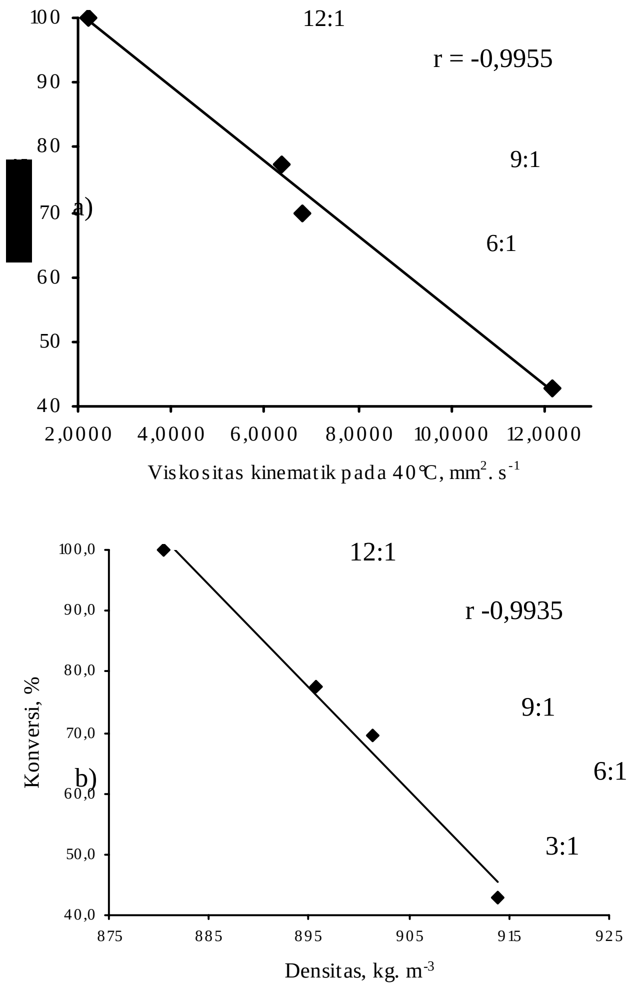

Fig. 3. The correlation of percentage of biodiesel conversion with physical properties: a) Kinematics viscosity at 40 °C; b). Density at 15°C biodiesel, in different methanol/oil molar ratio

Transesterification in methanol with K_2CO_3 p.a. 1 % m/m to feedstock as a base catalyst, in 6:1 methanol/oil molar ratio, and at ambient temperature has been done. The methyl esters were analysed by ^1H NMR spectrometer. By using equation (1), the methyl esters conversion were = 94,23 %. It gave indicator K_2CO_3 could be used as a base catalyst in biodiesel synthesis.

The effect of methanol/oil molar ratio to the percentage of biodiesel conversion

^1H NMR analysis of biodiesel resulted from palm kernel oil transesterification in methanol with variation in methanol/oil molar ratio as follow: 3:1, 6:1, 9:1, and 12:1 with 6 % m/m of ash to feedstock. The biodiesel conversions by different in methanol/oil molar ratio were showed in Table 3.

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From Table 4, there were appeared that the percentage of biodiesel conversion incresead when methanol/oil molar ratio were increased. Biodiesel conversion of 100 % could be resulted by methanol/oil molar ratio 12:1 (with respect to equipment detection limit). 1H NMR spectrum were showed in Fig.2. Transesterification stoichiometry showed that 1 mol of oil reacted with 3 mol of methanol in reversible reaction. Maximum product would achieved if used methanol in exess, so reaction tends to shift to the right dirrection. Methanol/oil molar ratio affected glycerols separation and recovery, and catalyst distribution between methyl ester layer and gycerol layer (Encinar *et al.* 2002). Junek and Mittel in Encinar *et al.* (2002), stated that in 3:1 methanol/oil molar ratio, catalyst tends to shifted in glycerol layer, but with methanol in excess, catalyst would distribute uniformly in both layers. Although methanol in excess were used to increased product, in other side methanol in excess affected gycerol recovery diffucuties. (Schuchardt *et al.*, 1998).

The results from Kinematic viscosity and density could give good correlation with biodiesel conversion, as showed in Fig. 3. These were advantage for routine analysis, i.e. from Kinematic viscosity or density data of the transesterification products could give estimation of the completeness of biodiesel synthesis from certain vegetable oil/animal lipid.

CONCLUSION

In the ash of EFB, potassium metal was the mayor component (29.82 % m/m), and might be in carbonate form. The potassium carbonate was a base species, thus the ash of EFB had potential to be used as a source of a base catalyst in biodiesel synthesis.

Biodiesel conversion increased with methanol/oil molar ratio increasing. Biodiesel reached 100 % conversion in methanol/oil molar ratio 12:1 (at 6 % m/m and ambient temperature).

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