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Biodiesel Production From Beef Tallow, Catalyzed by Potasium Hidroxide in Ethanol

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ABSTRACT

A research on conversion of beef tallow into biodiesel using potassium hydroxide (KOH) catalyst has been done. Production of the biodiesel was conducted by esterification process and continued by transesterification process. Esterification process was carried out using 1.25 wt% of 1 M H_2SO_4 as a catalyst with a molar ratio of beef tallow to ethanol of 1:9. After the esterification, oil was separated from ethanol followed by a transesterification step with a molar ratio of 1:12 (tallow to ethanol) using KOH catalyst with varios concentrations; 0.5%, 1.0 % and 1.5% (toward oils and ethanol). The biodiesel produced was characterized by FT-IR, ^{1}HNMR, and Gas Chromatography-Mass Spectrometry (GC-MS). According to ^{1}H-NMR result, biodesel yields is 44.30%, and experimentally yields was 41.06%. Physical characterization was determined by ASTM method and the results obtained were as follows: specific gravity = 0.8641 g/cm^3, kinematic viscosity = 5.156 cSt, flash point = 102.5 °C, pour point = 21 °C, and conradson carbon residue = 0.035%.

Key words: biodiesel, catalyst, ethanol, KOH, beef tallow.

1. INTRODUCTION

Biodiesel has become increasingly important due to the depletion of world petroleum reserves and increased environmental concerns. The main reason causing the fast diminishing of petroleum reserves is due to the rapid population and the global industrialization growth. Based on this phenomenon, the era of cheap crude oil does not longer exist leading to high skyrocketing price of petroleum, bellicose conflicts and increasing the number of undernourished people especially from undeveloped countries [1-4].

Biodiesel is an alternative fuel for diesel engines made from oil/lipid that can be renewed because it can be obtained from vegetable oils or animal fat [5]. In detail, it has several advantages. It is non-toxic, essentially free of sulfur and benzene, can be relatively perfect oxygenated, non-toxic and naturally biodegradable and environmental benign [6-8], and the result of CO_2 can be consumed by plants for photosynthesis (carbon cycle). Biodiesel can significantly reduce environmental pollution, reduce unburned hydrocarbons, polycyclic aromatic hydrocarbons, and acid rain. Furthermore, due to its similar properties with diesel fuel, there is no need to modify the engine when it is fueled with biodiesel or its blends [9-11].

In spite of the many advantages of biodiesel, it is not yet commercialized all over

the world. The major problem is the cost of the raw material. Biodiesel obtained from vegetable oil is costly compared to the petroleum diesel fuel [12]. Beef tallow is a promising alternative resource for biodiesel because it reduces the raw material cost. Animal fats such as beef tallow contain a lot of saturated fatty acids that are not consumed in excess. Although it is not good for human health but it has higher fat content that other animal. Therefore, production of biodiesel from beef tallow is one of the better ways to utilize them efficiently and economically [13].

Most of the biodiesel production was conducted through transesterification reaction using catalysts (generally NaOH or KOH) in methanol. The preparation methods of biodiesel have disadvantages. In the case of methanolisis, the solubility of oil in methanol is less and the reaction is limited mass transfer. On the other hand, methanol makes higher equilibrium conversion due to higher reactive intermediate methoxide [14]. Unlike methanol, ethanol has better solvent properties and can be obtained from renewable resources and esters obtained may act as a good lubricity additive. Another advantage is that it process would be less dependency on the synthetic sources for methanol [12].

The present work deals with optimum condition of biodiesel production of beef tallow using a catalyst of KOH in ethanol. The chemical properties of the biodiesel were characterized by several instruments and physical properties were determined by the ASTM method.

2. MATERIALS AND METHODS

A. Materials

Materials used were beef tallow obtained from Mardika Market located in Ambon City, ethanol, KOH, anhydrous Na_2SO_4, H_2SO_4 (Merck), phenophtalein, distilled water, Whatman-40 filter paper.

B. Preparation of beef tallow and Free Fatty Acid Analysis

The clean beef tallow was heated to a temperature of l20 ^oC to evaporate the water. After that, the liquid fat was decanted to separate the impurities in the solid. In addition, 20 g of the clean liquid fat was put into a 250-ml Erlenmeyer flask, added with 50 mL of ethanol. Furthermore, the sample was heated for 10 minutes in a water bath, cooled and added a few drops of phenophtalein indicator. Finally, the sample was titrated with KOH until a pale pink color appeared.

C. Synthesis of biodiesel through esterification and transesterification reactions

The clean liquid fat was poured into a reflux apparatus, esterified with ethanol (ratio of oil to ethanol was 1: 9) and added 1% w/w of 1 M H_2SO_4. The mixture was refluxed at a temperature of 75 °C for 3 hours. After the esterification process, two layers were formed, ethanol (on the top) and ethyl esters and triglycerides layers (on the bottom). The two layers were separated by a separating funnel, the layer of triglycerides was then transesterified with ethanol (the ratio of oil to ethanol was 1:12) and the basic catalyst of KOH with various concentrations; 0.5%; 1%; and 1.5

%, was added. The mixture was refluxed again at a temperature of 75 °C for 2 hours. The reaction mixture was cooled and two layers were formed; ethyl esters (biodiesel) and glycerol, respectively. The Layers of ethyl ester and glycerol were separated by a separating funnel. Ethyl ester was then evaporated to remove residual ethanol. Ethyl ester was washed with distilled water in a separating funnel to dissolve the left glycerol. The final step was the addition of 1.5 grams of anhydrous Na_2SO_4 to remove the left water then filtered with a Whatman-40 filter paper.

D. Characterization of Ethyl Ester (Biodiesel)

Biodiesel was characterized by GC-MS, FT-IR, and 1H-NMR spectrometers. The physical properties of biodiesel were further tested with the ASTM method. Parameters of biodiesel tested by the ASTM method were specific density of 60/60 ^oF (ASTM D1298), kinematic viscosity 40 ^oC (ASTM D445), pour point (ASTM D97), flash point (ASTM D93), and the residue of Conradson carbon (ASTM D189).

3. RESULTS AND DISCUSSION

A. Free Fatty Acid Analysis

Analysis of free fatty acid was conducted to determine further process of biodiesel production. A process was developed by Canakci and Van Gerpen [15] where the high free fatty acid (FFA) feedstock was initially treated using acidic catalyst to reduce the FFA level below 1%. The pre-treated feedstock with FFA less than 1% was then transesterified with methanol using the basic catalyst. It was observed that two-step acid catalyzed esterification followed by alkaline catalyzed reaction improved the ester yield [16]. The amount of free fatty acid in beef tallow was 7.1%. It showed that production process from beef tallow needed two steps; esterification and transesterification reactions.

B. Synthesis of Biodiesel through esterification and transesterification reactions

The esterification reaction was the initial treatment of beef tallow to reduce the level of free fatty acids. The esterification reaction of beef tallow was done by adding 1.25 w/w % H_2SO_4) and ethanol (ethanol radio 1: 9) at a temperature of 75 °C. The use of the acid catalyst is better than the basic catalyst because it does not produce the soap and can increase the production of biodiesel.

After esterification reaction completed for 3 hours, the reaction followed by transesterification reaction. At this step, triglycerides reacted with ethanol (ethanol ratio 1:12) previously reacted with catalyst 1 M KOH with various composition of 0.5, 1 and 1.5 wt% to oil and ethanol. The mixture was refluxed at temperature of 75 °C for 2 hours. The biodiesel conversion can be seen in Table 1.

Table 1 Result of biodiesel

	The weight of beef tallow and biodisel produced with the conversion percentage		
	0,5% KOH	1% KOH	1.5% KOH
Beef tallow (g)	30	30	30
Biodiesel (g)	12,32	8,69	5,53
% conversion (%)	41,06	28,96	18,43

It is clear that the highest biodiesel conversion (41.06%) is produced at the use of 0.5 wt% KOH, The lowest result (18.43%.) is obtained at 1.5 wt% KOH. This shows that for homogeneous catalysts such as KOH, an excessive amount of catalyst will lead to the formation of soap that can reduce the product of biodiesel [9, 15, 16].

C. Characterization of Biodiesel

GC-MS Analysis

Analysis by GC-MS was used to determine the type of compounds found in biodiesel produced from beef tallow. The GC-MS chromatogram shows 15 peaks detected as fatty acid ethyl esters (Figure 1). The first peak detected is ethyl meristate, the fifth peak is ethyl palmitate, the eight peak is ethyl heptadecanoate, the ninth peak is ethyl oleate, the eleventh peak is ethyl octadec-9-enoate, and the twelfth peak is ethyl stearate. Three peaks with the largest area are generated by ethyl stearate with the amount of 32.77%, a retention time of 24.571 min and the molecular formula of $C_{19}H_{38}O_2$, ethyl oleate as many as 17.13% with a retention time of 23.913 min and the molecular formula of $C_{19}H_{36}O_2$, and ethyl palmitate with the amount of 27.95%, the retention time of 19.738 min and molecular formula of $C_{17}H_{34}O_2$.

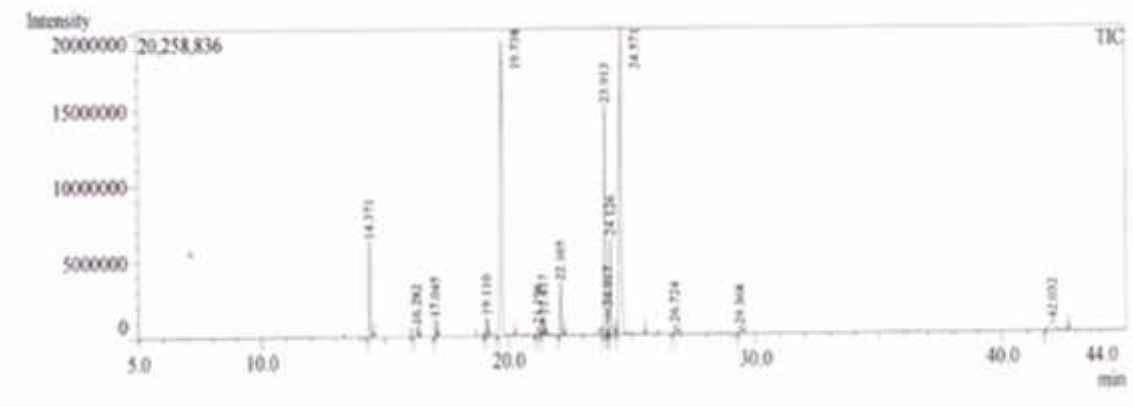

Figure 1 Chromatogram of biodiesel from beef tallow

FT-IR Spectroscopy

Analysis of biodiesel with FT-IR spectrometer was conducted to prove the existence of the transesterification product. The esters can be seen from the characteristic absorption of functional groups; C=O and C-O [2]. The comparison of the functional group obtained from beef tallow and biodiesel produced is given in Table 2.

Table 2. Functional groups found in beef tallow and biodiesel

Group	Wavenumber (cm^{-1}) Beef tallow	Wavenumber (cm^{-1}) Biodiesel
C = O	1743.65	1733.07 – 1738.86
C – O	1172.72	1178.53
C = C	725.23	722.35
C_{sp3} – H	2845.93 – 2924.37	2851.80 – 2954.03
-CH_2-	1442.75	1463.03
-CH_3-	1365.60	1349.23

Table 2 shows the shift in the absorption of carbonyl groups; C = O and C-O. In beef tallow the carbonyl (C = O) group is found with a strong absorption at 1743.65 cm^{-1}. This peak shift to 1733.07 - 1738.86 cm^{-1} in biodiesel (ethyl ester), while for the CO group, the absorption peak shifts from 1172.72 cm^{-1} to 1178.53 cm^{-1}. There is also the small change observed in the sharp absorption from 725.23 cm^{-1} to 722.35 cm^{-1} which is an absorption peak for alkene group (CH = CH) of unsaturated fatty acid chains. The absorption between 2924.09 cm^{-1} and 2851.81 cm^{-1} is the absorption of aliphatic C-H (stretching) supported with the absorption at 1442.75 cm^{-1} to 1463.03 cm^{-1} which is absorption for CH_2 and 1365, 60 cm^{-1} -1349.23 cm^{-1} for CH_3. The peak at 1118.71 cm^{-1} belongs to C-O group adjacent to CH_3 indicating the existance of ethyl ester. This peak shift to 11035.79 cm^{-1} in biodiesel.

^{1}H-NMR Analysis

Biodiesel from beef tallow was analyzed by ^{1}H-NMR to determine the percentage conversion of biodiesel from beef tallow. The determination of the conversion of biodiesel was based on the chemical shifts of 2 to 2.3 ppm that correlated to the α-CH_2 group (C), chemical shifts of 3.9 to 4.3 ppm which is the peak of proton ethyl ester (B), and the chemical shifts of 5.2 to 5.3 ppm for a proton cluster of glycerides (A) [2,17].

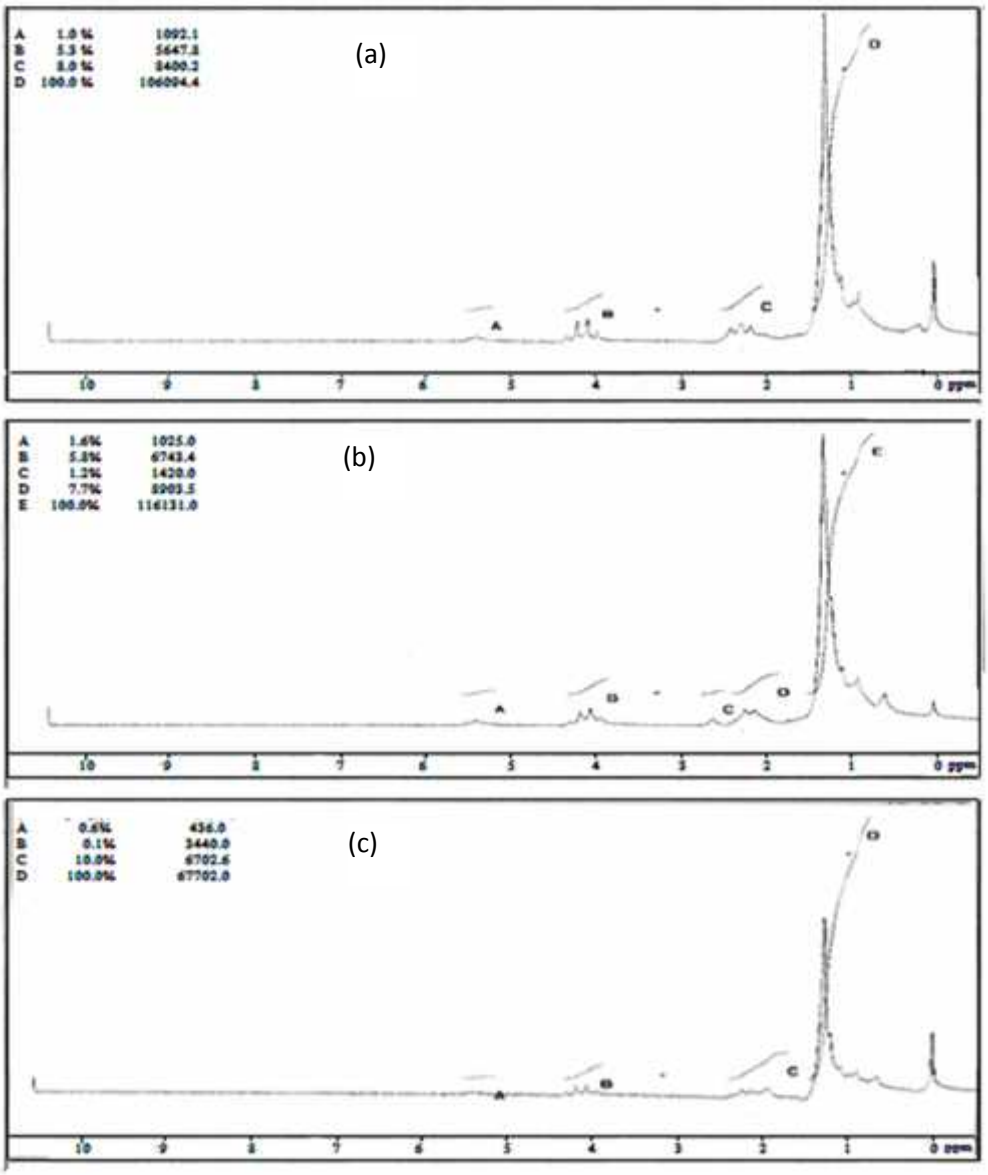

Figure 2 ^{1}H-NMR Spectra of biodiesel using various percentage of KOH (a) 0.5% (b) 1% and (c) 1.5%

Figure 2 (b) and (c) show the peak of glycerol in the region of 5-6 ppm and ethyl ester in the area of 3.9 to 4.3 ppm. The percentage of ethyl ester conversion obtained was 31.43% - 44.30%. Peak at a chemical shift of 3.9 to 4.3 ppm is the proton of ethyl ester (B) and the chemical shifts of 2 to 2.3 ppm of proton results in the CH_2 group adjacent to or part of glycerol ethyl ester (C). The highest conversion of ethyl ester (44.30%) was obtained in the use of 0.5 wt% KOH , which can be seen in Figure 2 (a).

The percentage of ethyl ester conversion at various composition of KOH obtained experimentally is given in Figure 3. It is obvious that the results obtained are not consistent with the theoretical calculation results, this fact can explained due to the loss of ethyl ester during the purification process [3].

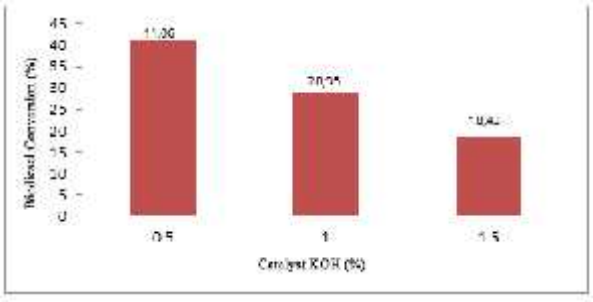

Figure 3 Percent conversion of the beef tallow based experimental

From the [1]HNMR calculations and experimental results, the consistency result that is the highest biodiesel conversion was given at the use of 0.5 wt% KOH. This is due to the fact that the more concentration of catalyst used; the more possibility of saponification reaction to be occurred which can reduce the yield of methyl ester [11, 15].

Physical properties of biodiesel

Characterization of biodiesel with ASTM method (Table 3) was conducted to determine the suitability of the physical character of biodiesel obtained with the physical character of the standard diesel oil. Characteristics of biodiesel should be compared with standard diesel oil specifications, such as ASTM specification for biodiesel [7, 10, 19].

Table 3. Comparison of physical properties of beef tallow biodiesel with petroleum Diesel and biodiesel

Property	Method	Biodiesel of beef tallow	INS Biodiesel	Range petroleum diesel
Density specific (60/60 °F, kg/m^3)	ASTM D 1298	0,8641	0,850-0,890	0,815-0,870
Kinematic Viscosity (40 °C, mm^2/s)	ASTM D 445	5,156	2,3 – 6,0	2,0 – 5,0
Flash point (°C)	ASTM D 93	102,5	min. 100	min. 60
Pour point (°C)	ASTM D 97	21	maks.18	maks.18
Residue Conradson carbon (%wt)	ASTM D 4530	0,035	maks.0,30	maks. 0,30

Based on Table 3, it appears that the specific density of biodiesel produced is in compliance with the standard specifications of diesel oil. Data of the specific density can be used to calculate the heat of combustion. High heat of combustion will make good quality of the biodiesel combustion. The heat of combustion of biodiesel produced meets the standards and specifications for petroleum diesel that is 0.8641 kg /m^3. The kinematic viscosity value generated by beef tallow biodiesel (5.156 mm^2/s) also meets the specifications for diesel fuel. In general it can be said that the value of the viscosity is very dependent on the level of biodiesel conversion percentage. At low conversion rate possible biodiesel still contain glycerides molecules in the form of tri-, di- and mono-glycerides, in which the hydroxide group in the molecule diglycerides and monoglycerides can lead to the

formation of hydrogen bonds so strong that adds density between molecules glycerides. As a result, the formation of intermolecular hydrogen bonds will also increase the viscosity of the compound [20].

A flash point of biodiesel is 102.5 ^{o}C according to the standard specifications of diesel oil. High flash point will facilitate the handling, storage, and transport because it can reduce the risk of ignition. Pour point of biodiesel produced beef tallow at 21 ° C does not meet the specifications for diesel fuel. Pour point is the lowest temperature point which indicates starts the formation of paraffin crystals which can clog fuel lines. Pour point is also related to viscosity, ie the lower the viscosity of biodiesel, the easier biodiesel to flow at certain conditions. Biodiesel from beef tallow classified as having a high pour point. High pour point resulted in a difficult machine is turned on at low temperatures [21].

The test results conradson carbon footprint of beef tallow biodiesel in the amount of 0.035 wt% has met the specifications of diesel oil. Conradson carbon footprint is the carbon value left after evaporation and combustion exhausted. A level of carbon residue depends on the amount of free fatty acids, the amount of triglycerides. Residual value is the lower carbon indicates that the decomposition of triglycerides occurred more nearly perfect and can reduce air pollution [20].

CONCLUSION

Based on the results of study, it can be concluded that the percentage of free fatty acids in beef tallow used as a source of oil was 7.1%. The optimum concentration of KOH as a catalyst for converting beef tallow to biodiesel was 0.5% producing methyl ester by 41.06%. Biodiesel produced from beef tallow has physical charateristics as follows: a specific density = 0.8641 kg /m^3, kinematic viscosity = 5.156 mm^2/s, the flash point = 102.5 °C, and the residu conradson carbon = 0.035 wt%. Meanwhile, pour points not meet the ASTM standard that is equal to 21 °C.

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