Effect of Reaction Time and Molar Ratio of Alcohol to Beef Tallow for Producing Biodiesel from Waste Beef Tallow Using Heterogeneous Catalyst CaO from Waste Eggshell

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ABSTRACT

Biodiesel is defined as renewable fuel for diesel engines, derived from vegetable oil or animal fats. Beef tallow is one residual material from slaughterhouses which main destination is the soap industry. The objective of the study was to utilize waste animal fat (beef) for biodiesel production using solid oxide catalyst. The solid oxide catalyst derived from the industrial waste shells of egg. The waste materials calcined in air with temperature 900 ^oC and time 2 hours, transformed calcium species in the shells into active CaO catalysts. The oil contains high free fatty acid (FFA) content of 1.85%. The acid value of the oil was reduced by acid esterification. The product from this stage was subjected to transesterification to produce biodiesel. Transesterification process produces methyl ester and glycerol. The produced methyl ester on the upper layer was separated from the glycerol and then washed. Effect of various process variables such as reaction time and molar ratio of alcohol to beef tallow were investigated. The biodiesel properties like methyl ester content, density, and viscosity was evaluated and was found to compare well with Indonesian Standard (SNI). Under best condition, the maximum yield of 82,43% beef tallow methyl ester was obtained by using 9:1 molar ratio of methanol to beef tallow at 55 ^oC, for a reaction time 90 minutes in the presence 3 wt% of CaO catalyst. The results of this work showed that the use of beef tallow is very suitable as low cost feedstock for biodiesel production.

Keywords: biodiesel, beef tallow, calcium oxide, esterification, transesterification

1. INTRODUCTION

Energy demand of fuel for the transportation and industrial sectors in Indonesia increased due to enhancement of human population. However, it is derived from a non-renewable, non-sustainable resource [1]. The World Energy Forum reveals that the fossil-based oil, coal and gas reserves are predicted to be exhausted in less than another ten decades [2].

Biodiesel is a renewable energy for diesel engines that is biodegradable, non-toxic and has low emission profiles as compared to petroleum diesel [3]. The common way to produce biodiesel is to transesterify triacylglycerols in vegetable oil or animal fats with an alcohol in presence of an alkali or acid catalyst[4].

The raw material of biodiesel was a reject of any other industrial or agricultural activity, an important environmental aspect is added. Beef tallow is one residual material from slaughterhouses which main destination is the soap industry, but when this market is overloaded, the fats are usually incinerated or disposed in a sanitary landfill. In both cases there is a pollutant impact. Thus the integrated use of industrial residues generated in slaughterhouses can avoid such problems, allowing new alternative jobs and minimizing the environmental impact of the accumulation of these residues [5].

The conventional process of biodiesel production proceeds in transesterification of oils or fats using homogeneous catalysts. However, the use of homogeneous catalysts have the disadvantage of separating the catalyst from the products is quite complex. The heterogeneous catalytic process overcomes the homogeneous one since the solid catalysts can be easily recovered and therefore potentially be reusable [6,7].

In fact, a number of heterogeneous catalysts, for example, CaO, MgO, SrO, Zeolite, Al_2O_3, ZnO, TiO_2, ZrO, and hydrotalcites have been employed in the transesterification process. Among these catalysts, the alkaline earth metal oxides (e.g. MgO, CaO, and SrO) have the high activity for using in the typical process (at low temperature and under atmospheric pressure condition). Among the alkaline earth metal oxides, CaO is close on the environmental material. Generally, $Ca(NO_3)_2$, $CaCO_3$, or $Ca(OH)_2$ is the raw material to produce CaO catalysts. As alternative way to synthesize CaO catalyst, there are several natural calcium sources from wastes, such as eggshell, mollusk shell, and bone. Not only eliminating a waste management cost, but also the catalysts with high cost effectiveness can be simultaneously achieved for biodiesel industry. Recently, Jazie et al. examined transesterification of rapeseed oil catalyzed by combusted chicken eggshell at 900 ^oC, and found that it is active for biodiesel production [8].

The objectives of this study are to develop a simple and effective method to produce biodiesel from beef tallow waste using heterogeneous catalyst CaO from waste chicken eggshell and to develop the best condition of transesterification reaction for maximum FAME (fatty acid methyl ester) yield in presence of calcium oxide (CaO) catalyst. The effects of various reaction variables such as reaction time and molar ratio of alcohol to beef tallow on the conversion to methyl esters are investigated.

2. METHODS

2.1 Materials and catalyst preparation

The beef tallow used in the biodiesel production was acquired in some slaughterhouses in the area of Petisah, Medan, North Sumatera, Indonesia. Compositions of fatty acid in beef tallow oil are given in Table 1. Waste chicken egg shells were collected from local restaurant in Medan, North Sumatera, Indonesia. They were transformed to CaO catalyst by thermal synthesis. They were calcined at designated temperature 900 ^oC and time 2 h in the muffle furnace. The crystalline phases of calcined samples were analyzed by AAS (*Atomic Absorption Spectrophotometry*). Compositions of chicken eggshell are given in Table 2. All catalysts were kept in the close vessel to avoid the reaction with CO_2 and humidity in air before used. All other chemicals used were analytical reagents.

Table 1. Fatty Acid Compositions of Beef Tallow Oil

Fatty acid	Composition (wt%)
Lauric (C12:0)	0.24
Miristic (C14:0)	5.07
Palmitic (C16:0)	24.03
Palmitoleic (C16:1)	0.88
Heptadecanoic (C17:0)	3.81
Stearic (C18:0)	27.26
Oleic (C18:1)	34.55
Linoleic (C18:2)	2.57
Linolenic (C18:3)	0.68
Arachidic (C20:0)	0.34
Eicosenoic (C20:1)	0.57

Table 2. Compositions of Chicken Eggshell

Property	Composition (wt%)	Analysis method
CaO	66.16	AAS
Water	0.12	Oven

2.2 Esterification reaction

The main objective of acid-catalyzed esterification was to reduce the FFA content of the oil. The FFA content of the oil should be less than 0.5% so as to facilitate transesterification reaction. The esterification reaction was carried out in a batch reactor. The oil (100 g) was poured into the flask and heated. To this, the acid catalyst (0.5 wt%) H_2SO_4 was added, followed by methanol and the reaction was carried out for 4 h. The molar ratio of methanol to oil was 6:1 and the reaction temperature was 60 ^oC which was selected based on the findings from Encinar et al. [9]. The progress of the reaction was monitored by measuring the FFA content of the oil. At the end of the reaction, the content of each reactor was transferred to a separating funnel to settle for 2 h. Afterwards clear separation of different layers was noticed. According to Kombe et al. [10], the upper layer contained unreacted methanol, the middle layer contained fatty acid methyl ester (small amount obtained by conversion of free fatty acids to esters) and esterified oil, and the lower layer contained mainly water, acid, and other impurities. The esterified oil was used in the transesterification step. The yield of this step was calculated as the weight of pre-treated esterified oil divided by the weight of raw oil used.

2.3 Transesterification reaction

The transesterification reaction was carried out in a batch reactor. The pre-treated esterified oil (100 g) in a 500 cm^3 round bottom flask equipped with a reflux condenser was stirred at 60 ^oC. A mixture of methanol and catalyst were added to the oil. Then the transesterification reaction was conducted under conditions of various time (60, 90, and 120 minute) and molar ratio of alcohol to beef tallow (6:1; 9:1; and 12:1). The reaction temperature was 55^oC using amount of catalyst was 3%(w/w). The reaction mixture was stirred by a mechanical stirrer at 600 rpm. The reaction mixture was poured into a separating funnel [8]. The reaction mixture was allowed to cool down and equilibrate which resulted in separation of three layers. The upper layer was unreacted methanol, methyl esters and unreacted triglycerides, the middle layer was glycerol, and the lower layer was a mixture of solid CaO and a small amount of glycerol. After separation of the three layers by sedimentation, the upper layer was washed with distilled water three times. The washing step removes residual methanol. Then the washed methyl esters were heated at 105 ^oC for 10 min to remove residual water. The product before and after drying was weighed to calculate the methyl ester yield by dividing the final weight of methyl ester by the initial weight of the oil. The compositions of methyl ester were determined by a gas chromatograph. The methyl ester content was represented in term of %FAME as a function of time.

2.4 Fatty acid methyl ester (FAME) analysis

The compositions of each methyl ester were determined in duplicate using a gas chromatographer equipped with a flame ionisation detector and an auto injector.

2.5 Other analysis

The density, kinematic viscosity, and flash point of each methyl ester were determined in duplicate according to the procedure of SNI [12].

3. RESULTS

3.1 Catalyst preparation

Eggshell catalysts sample calcined at 900 ^oC was the most active catalyst. A yield of 82.43% was obtained in the presence of eggshell catalyst calcined at 900 ^oC in 2 h. The calcination at higher temperatures led to desorption of carbon dioxide from the eggshell catalysts, producing basic sites that catalyzed transesterification of animal fat with methanol [8].

3.2 Esterification reaction

The purpose of this stage is to reduce the FFA content of the beef tallow waste oil to less than 0.5% [11]. The initial percentage of FFA was 1.86%. Experiments are conducted using 6:1 molar ratio of methanol to oil at 60 ^oC, for a reaction time 4 h in the presence 0.5 wt% of H_2SO_4 catalyst [10]. The FFA content of the product is determined in each case using standard chemical titration procedure [13]. The reaction progressed rapidly and showed more reduction in the FFA content of the oil. The percentage of FFA after reaction was 0.35%.

3.3 Transesterification reaction

By the transesterification in heterogeneous process, the beef tallow oil or triglyceride is mixed with methanol and catalyzed by alkaline earth oxide; CaO in this case. Such triglyceride is catalyzed to di- and mono-glyceride, subsequently, while biodiesel (or fatty acid methyl ester) is produced simultaneously during the conversion of triglyceride as well. When the reaction is completed, biodiesel and glycerol co-exist in the process as reaction products.

Table 3. Reaction Condition and Yield

Molar Ratio of Oil to Beef Tallow	Time (minute)	Yield (wt%)
6:1	60	67,63
6:1	90	70,57
6:1	120	68,97
9:1	60	69,47
9:1	90	82,43
9:1	120	73,93
12:1	60	70,93
12:1	90	73,23
12:1	120	70,04

Table 3 summarizes the conditions of transesterification experiments of beef tallow oil with methanol in the presence of CaO catalyst and measured yield.

3.3.1 Effect of reaction time

Studies were carried out at different times from 60-120 minute with different molar ratio of alcohol to beef tallow from 6:1-12:1 in reaction temperature of 55°C and amount of catalyst 3%(w/w). Figure 1 shows the yield of methyl esters versus time at different molar ratio of alcohol to beef tallow. It was observed the increase in fatty acid esters conversion when there is an increase in reaction time. Besides, longer reaction time does not increase the yield of product (biodiesel). The less time make fatty acid esters conversion was not maximal [13]. The best time was 90 minute with molar ratio of alcohol to beef tallow 9:1. This was in accordance with the result obtained by Padil et al. [14]. However, they used coconut oil as feedstock for biodiesel production.

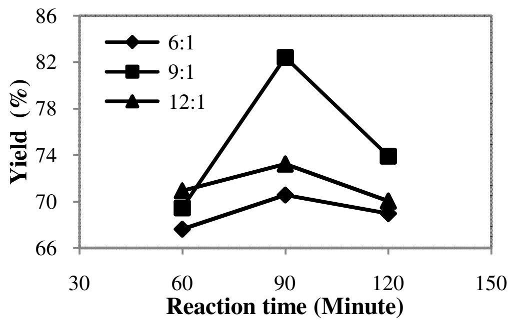

Fig. 1. Effect of Reaction Time on Yield at Reaction Temperature of 55°C and Amount of Catalysts of 3%.

3.3.2 Effect of molar ratio of alcohol to beef tallow

Alcoholysis of beef tallow oil was carried out with different molar ratio of alcohol to beef tallow from 6:1-12:1 with different times from 60-120 minute in reaction temperature of 55°C and amount of catalyst 3%(w/w). Figure 2 shows the yield of methyl esters versus molar ratio of alcohol to beef tallow at different times. When the methanol concentration increased above or reduced below the optimal concentration, did not increase in the production of biodiesel, but an more or less of methanol concentration will lead to increased formation of glycerol and emulsion [15]. The best time was 90 minute with molar ratio of alcohol to beef tallow 9:1. This was in accordance with the result obtained by Jazie et al. [8]. However, they used rapeseed oil as feedstock for biodiesel production.

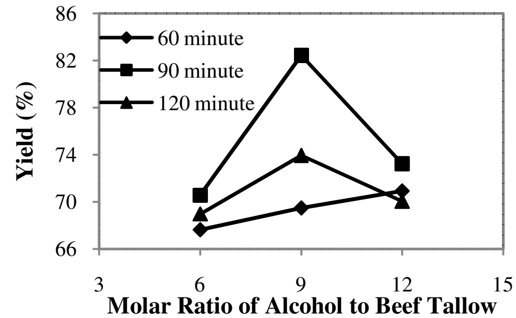

Fig. 2. Effect of Molar Ratio of Alcohol to Beef Tallow on Yield at Reaction Temperature of 55°C and Amount of Catalysts of 3%

3.4 Properties of beef tallow biodiesel

The important properties of the beef tallow biodiesel like density, kinematic viscosity, conversion, and flash point are determined. The standards specified for biodiesel by SNI and the best condition biodiesel property values are listed in Table 3. Under the best condition, the maximum yield of 82.43 was obtained using 9:1 molar ratio of methanol to oil at 55 °C, for a reaction time 1.5 h in the presence 3 wt% of CaO catalyst.

Table 4. Properties of The Best Beef Tallow Biodiesel in Comparison with Biodiesel Standard SNI

Property	Biodiesel standard SNI	Beef tallow biodiesel
Density at 40 °C (kg/m^3)	850-890	864.31
Kinematic viscosity at 40 °C (mm^2/s)	2.3-6.0	4.92
Conversion (wt%)	minimum 96.5	97.31
Flash point (°C)	minimum 100 °C	120

3.4.1 Density

Density limits are present in SNI (850-890 kg/m^3 at 40 °C), respectively for biodiesel fuels [12]. The density of biodiesel from the best condition was 864.31 kg/m^3. Biodiesel density fall within the scope of the SNI biodiesel specification ranges. Figure 3 shows the density of methyl esters versus reaction time at different molar ratio of alcohol to beef tallow.

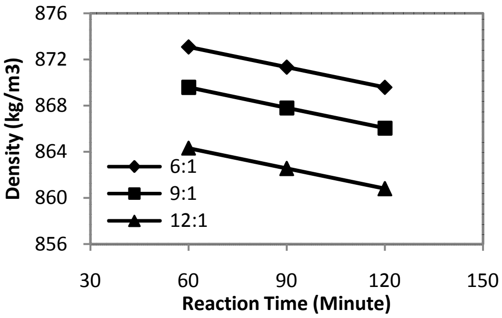

Fig. 3. Effect of Reaction Time on Density at Reaction Temperature of 55°C and Amount of Catalysts of 3%

3.4.2 Kinematic viscosity

The kinematic viscosity is the measure of the resistance to flow of the fuel and can also be used to select the profile of fatty acids in the raw material used for the production of the bio-fuel. Kinematic viscosity limits are present in SNI (2.3-6.0 mm^2/s at 40 °C), respectively for biodiesel fuels [12]. Viscosity is a key fuel property because it persuades the atomization of a fuel upon injection into the diesel engine ignition chamber and ultimately, the formation of engine deposits. The kinematic viscosity of biodiesel from the best condition was 4.92 mm^2/s. Biodiesel kinematic viscosity fall within the scope of the SNI biodiesel specification ranges. Figure 4 shows the kinematic viscosity of methyl ester versus reaction time at different molar ratio of alcohol to beef tallow.

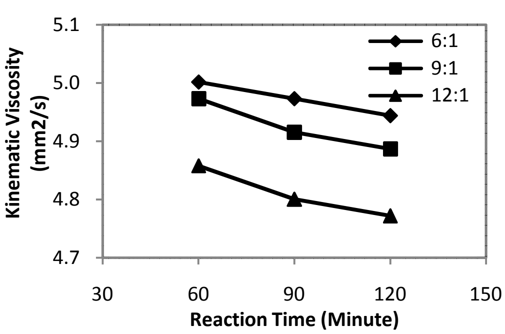

Fig. 4. Effect of Reaction Time on Kinematic Viscosity at Reaction Temperature of 55°C and Amount of Catalysts of 3%

3.4.3 Conversion

Conversion limit is present in SNI (minimum 96.5 wt%), respectively for biodiesel fuels [12]. The conversion of biodiesel from the best condition was 97.31 kg/m^3. Biodiesel conversion fall within the scope of the SNI biodiesel specification ranges.

3.4.4 Flash point

This property is as indicative of the precautions that must be taken during the handling, transport and storage of the fuel. With regard to the biodiesel, the specification of the flash point has as objective to limit the amount of alcohol in this biofuel. Flash point limit is present in SNI (minimum 100 °C), respectively for biodiesel fuels [12]. The flash point of biodiesel from the best condition was 120 °C.

Biodiesel flash point fall within the scope of the SNI biodiesel specification ranges.

4. CONCLUSION

The present work developed a two stage procedure to produce biodiesel from beef tallow waste oil. Free fatty acids (FFA) in beef tallow waste oil can be effectively removed by esterification with methanol using sulphuric acid as the catalyst. According to the experimental studies, the best conditions for alcoholysis of beef tallow waste oil is 3% of catalyst in oil, methanol to oil molar ratio 9:1, reaction temperature 55 °C for a period of 1.5 h. The yield of methyl ester is 82.43%. The biodiesel properties like methyl ester content, density, kinematic viscosity and flash point was evaluated and fallen within the scope of the SNI biodiesel specification ranges.The results of this work showed that the use of beef tallow is very suitable as low cost feedstock and the calcium oxide from waste eggshell is also suitable as low cost catalyst for biodiesel production.

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REFERENCES

[1] Roliadi, Han., Sudradjat, R. and Anggraini, Arum., "Kemungkinan Penggunaan Antioksidan Guna Mempertinggi Ketahanan Oksidasi Biodiesel dari Minyak Biji Tanaman Jarak Pagar (Jatropha curcas L.)", *Jurnal Penelitian Hasil Hutan,* 30(1), pp. 69-86, 2012.

[2] Liew, Weng Hui, "Case Study of Neural Network Modeling on Catalyzed and Enzymatic Transesterification Process for Biodiesel Production", *Journal of Applied Sciences Research*, 8(3),pp. 1673-1681, 2012.

[3] Watcharathamrongkul, Kornkanok., Jongsomjit, Bunjerd dan Phisalaphong, Muenduen, "Calcium Oxide Based Catalysts for Ethanolisis of Soybean Oil", *Songklanakarin J. Sci. Technology,* 32 (6), pp. 627-634, 2010.

[4] Zhang, Y, M.A Dube, D.D Mclean, dan M. Kates, "Biodiesel Production From Waste Cooking Oil: 2 Economic Assessment and Sensitivity Analysis", *Bioresource Technology,* 90, pp. 229-240, 2003.

[5] Da Cunha, M.E., Krause, L.C., Moraes, M.S.A., Faccini, C.S., Jacques, R.A., Almeida, S.R., Rodrigues, M.R.A., Caramao, E.B., "Beef Tallow Biodiesel Produced in A Pilot Scale", *Fuel Processing Technology*, 90, pp. 570-575, 2009.

[6] Empikul, N. Viriya., Krasae, P., Nualpaeng, W., Yoosuk, B., Faungnawakij, K., "Biodiesel Production Over Ca Based Solid Catalysts Derived from Industrial Wastes", *Fuel*, 92, pp. 239-244, 2011.

[7] Zahrina, Ida and Herman, Syamsu., "Kinetika Reaksi Metanolisis Minyak Sawit Menggunakan Katalis Heterogen", *Jurnal Sains dan Teknologi*, 5 (2), pp. 38-41, 2006.

[8] Jazie, Ali A., Pramanik, H. dan Sinha, A. S. K., "Egg Shell As Eco-Friendly Catalyst for Transesterification of Rapeseed Oil : Optimization for Biodiesel Production", *Special Issue of International Journal of Suistanable Development and Green Economics (IJSDGE)*, Vol. 2, No.1, 2013.

[9] Encinar, J.M., Sanchez, N., Martinez, G., Garcia L., "Study of Biodiesel Production from Animal Fats with High Free fatty Acid Content", *Bioresource Technology*, Vol. 102, No. 23, pp. 10907-10914, 2011.

[10] Kombe, G.G., Temu, A.K., Rajabu, H.M., Mrema, G.D., "High Free Fatty Acid (FFA) Feedstock Pre-Treatment Method for Biodiesel Production", *Second International Conference on Advance in Engineering and Technology*, pp. 176-182, 2011.

[11] Marchetti, J.M., Miguel, V.U., Errazu, A.F., "Heterogeneous Esterification of Oil With High Amount of Free Fatty Acids", *Fuel*, 86, pp. 906-910, 2006.

[12] Badan Standarisasi Nasional, "*Standar Nasional Indonesia*", www.bsn.com, SNI : 7182:2012, 2012.

[13] Mathiyazhagan, M and A. Ganapathi., "Factors Affecting Biodiesel Production", *Research in Plant Biology*, 1(2), pp. 1-5,

[14] Padil., Wahyuningsih, Slamet and Awaluddin, Amir., "Pembuatan Biodiesel dari Minyak Kelapa melalui Reaksi Metanolisis Menggunakan Katalis $CaCO_3$ yang Dipijarkan", *Jurnal Natur Indonesia,* 13 (1), pp. 27-32, 2010.

[15] Awaluddin, Amir, Saryono, Sri Nelvia, dan Wahyuni, Effect Production of Crude Palm Oil Biodiesel Using Solid Catalysts Calcination of Calcium Carbonate, *Journal Natur of Indonesia*, 11(2), pp. 129-134, 2008.