Proceedings of
The 5th Sriwijaya International Seminar on Energy and Environmental Science & Technology
Palembang, Indonesia
September 10-11, 2014

Effect of Reaction Temperature and Catalyst Concentration for Producing Biodiesel from Waste Beef Tallow Using Heterogeneous Catalyst CaO from Waste Eggshell

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ABSTRACT

Biodiesel is an alternative fuel for diesel engines consisting of the alkyl monoesters from vegetable oils or animal fats. Beef tallow is the non-edible raw material with low cost production and the availability is huge in the cattle production. 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 eggshells. The waste materials calcined with temperature 900°C and time 2 hours, transformed calcium species in the shells into active CaO catalysts. The oil contained high free fatty acid (FFA) content of 1.86%. The FFA content of the oil was reduced by acid-catalyzed 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 amount of catalyst and temperature were investigated. The biodiesel properties like methyl ester content, density, viscosity, and flash point was evaluated and was found to compare well with Indonesian Standard (SNI). Under the 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 oil at 55°C, for a reaction time 1.5 hours 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

The research on alternate fuels is at a high profile in the world for quite some time now. The increasing energy demands and depleting fossil reserves are the main cause for this [1]. Also the increasing global warming and other environmental hazards force to reduce the energy extraction from fossil fuel. Out of the alternative fuel used as substitution for fossil fuel, biodiesel is an important one [2].

Biodiesel (fatty acid alkyl esters) is a renewable and environmentally friendly energy source. Its properties vary somewhat depending on the oil feedstock and alcohol used but it can always be used as a direct substitute for diesel fuel. It has a higher cetane number than diesel fuel, no aromatics, almost no sulfur, and contains 10% to 11% oxygen by weight. It can be produced from plant oils and animal fats [3-6].

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 [7].

Biodiesel from animal fats is synthesized by the method of transesterification reaction. The reaction requires alcohol in the presence of catalyst to react with triglycerides. Methanol is most commonly used because it is cheap and quickly reacts with triglycerides [8-9]. Many factors affect the biodiesel yield and process economics. The most important factors are alcohol type, alcohol/oil molar ratio, reaction temperature and time, catalyst type and amount, and water content of the reactants [6].

Besides, the free fatty acid (FFA) content of the feedstock is also an important parameter to consider as it could affect the chemical reactions. High FFA in the feedstock would result in soap formation when alkali chemicals are used as catalysts because they react to neutralise the FFA in the oil. The soap formation could decrease the biodiesel yield and complicate the separation and purification of biodiesel product. The saponification can be avoided by pre-treating the oil with an acid catalyst to convert the FFAs into esters before the alkali catalyst is used. However, the acid-catalyzed reaction is much slower than the alkaline-catalyzed reaction [6,10].

The homogeneous catalytic process however, provides some disadvantages, such as, a huge production of wastewater from washing process of catalyst residues and nonreusability of the catalysts. Alternatively, the heterogeneous catalysts have been developed to defeat the problems [11-12]. Meanwhile, they are more easily separated from the liquid products by filtration and can be developed to give higher activity, selectivity and longer catalyst lifetimes. Additionally, a neutralization step producing wastewater would be eliminated [13-15].

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°C, and found that it is active for biodiesel production [12,16].

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 the presence of CaO catalyst. The effects of various reaction variables such as reaction temperature and amount of catalyst on the conversion to methyl esters are investigated.

2. METHODS

2.1 Materials and catalyst preparation

The beef tallow waste used in the biodiesel production was acquired in some slaughterhouses in the area of Petisah, Medan, Indonesia. Compositions of fatty acid in beef tallow oil are given in Table 1. Waste chicken eggshells were collected from local restaurant in Medan, Indonesia. They were transformed to CaO catalyst and were calcined at temperature 900°C and time 2 hours in the muffle furnace [16]. 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 hours. The molar ratio of methanol to oil was 6:1 and the reaction temperature was 60°C which was selected based on the findings from Encinar et al. [17]. At the end of the reaction, the content of each reactor was transferred to a separating funnel to settle for 2 hours. Afterwards clear separation of different layers was noticed. According to Kombe et al. [18], 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.

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°C. A mixture of methanol and catalyst were added to the oil. Then the transesterification reaction was conducted under conditions of various temperature (50, 55, and 60°C) and amount of catalyst CaO (2, 3, and 4 wt%). The molar ratio of methanol to oil was 9:1 and the reaction mixture was stirred by a mechanical stirrer at 600 rpm. The reaction was stopped after 1.5 hours, and the reaction mixture was poured into a separating funnel [16]. 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 °C 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.

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 [19].

3. RESULTS

3.1 Catalyst preparation

Eggshell catalysts sample calcined at 900°C was the most active catalyst. A yield of 82.43% was obtained in the presence of eggshell catalyst calcined at 900°C in 2 hours. 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 [16].

3.2 Esterification reaction

The purpose of this stage was to reduce the FFA content of the beef tallow waste oil to less than 0.5% [10]. The initial percentage of FFA was 1.86%. Experiments were conducted using 6:1 molar ratio of methanol to oil at 60°C, for a reaction time 4 hours in the presence 0.5 wt% of H_2SO_4 catalyst [17]. The FFA content of the product was determined in each case using standard chemical titration procedure [19]. 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 was mixed with methanol and catalyzed by calcium oxide. Such triglyceride was catalyzed to di- and mono-glyceride, subsequently, while biodiesel (or fatty acid methyl ester) was produced

simultaneously during the conversion of triglyceride as well. When the reaction was completed, biodiesel and glycerol co-exist in the process as reaction products. Table 3 summarizes the conditions of transesterification experiments of beef tallow oil with methanol in the presence of CaO catalyst and measured yield.

Table 3. Reaction Conditions and Yield

Temperature (°C)	Catalyst concentration (wt%)	Yield (wt%)
50	2	73,26
50	3	75,81
50	4	71,62
55	2	79,78
55	3	82,43
55	4	77,71
60	2	69,58
60	3	79,39
60	4	74,90

3.3.1 Effect of reaction temperature

Studies were carried out at different temperatures from 50-60°C with different catalyst from 2-4 wt% CaO as a catalyst and molar ratio of methanol to oil was 9:1 in reaction time of 1.5 hours. Figure 1 shows the yield of methyl esters versus temperatures at different catalyst concentrations. It was observed that temperature has positive influence on methanolysis of beef tallow. The reaction rate was slow at low temperature due to the diffusion resistance, as the heterogeneous catalyst forms a three phase system, oil-methanol-catalyst. The reaction temperature at high temperature is avoided since there is chance of methanol loss due to vaporization at high temperatures. The best temperature was 55°C with catalyst concentration 3 wt% of oil. This was in accordance with the result obtained by Omar and Amin [20]. However, they used waste cooking palm oil as feedstock for biodiesel production.

Alcoholysis of beef tallow oil was carried out with CaO as a catalyst at a concentration of 2-4 wt% of oil in reaction time of 1.5 hours with methanol to oil molar ratio of 9:1. Figure 2 shows the yield of methyl esters versus catalyst concentrations at different temperatures. The effect of catalyst concentration on the conversion of oil was negligible when the mass ratio of CaO to oil was increased above 3 wt%. As a result of increasing catalyst concentration, the mixture of catalyst and reactants could become too viscous leading to a mixing problem and a demand of higher power consumption for enough stirring. On the other hand, when the catalyst loading amount was not enough, the maximum production yield could not be reached. The best catalyst concentration was 3 wt% of oil at 55°C. This was in accordance with the result obtained by Lee et al. [21]. However, they used soybean oil as feedstock for biodiesel production.

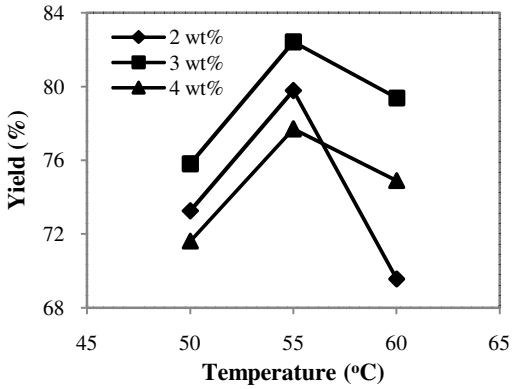

Fig. 1. Effect of Reaction Temperature on Yield at Reaction Time of 1.5 h and Methanol to Oil Molar Ratio of 9:1

3.3.2 Effect of catalyst concentration

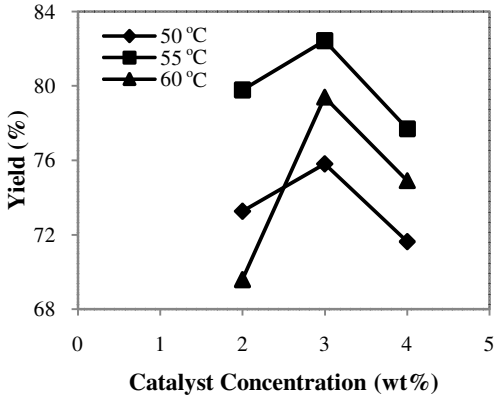

Fig. 2. Effect of Catalyst Concentration on Yield at Reaction Time of 1.5 h and Methanol to Oil Molar Ratio of 9:1

3.4 Properties of beef tallow biodiesel

The important properties of the beef tallow biodiesel like density, kinematic viscosity, conversion, and flash point were determined. The standards specified for biodiesel by SNI and the best condition biodiesel property values are

listed in Table 4. 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 hours 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 (%)	minimum 96.5	97.31
Flash point (°C)	minimum 100	120

3.4.1 Density

Density limits are present in SNI (850-890 kg/m^3 at 40°C), respectively for biodiesel fuels [19]. 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 catalyst concentrations at different temperatures.

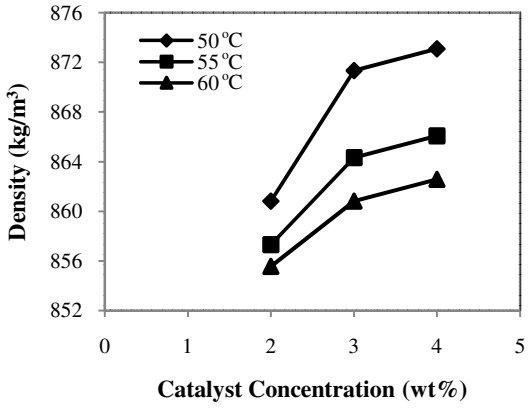

Fig. 3. Effect of Catalyst Concentration on Density at Reaction Time of 1.5 h and Methanol to Oil Molar Ratio of 9:1

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 biofuel. Kinematic viscosity limits are present in SNI (2.3-6.0 mm^2/s at 40°C), respectively for biodiesel fuels [19]. 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 esters versus catalyst concentrations at different temperatures.

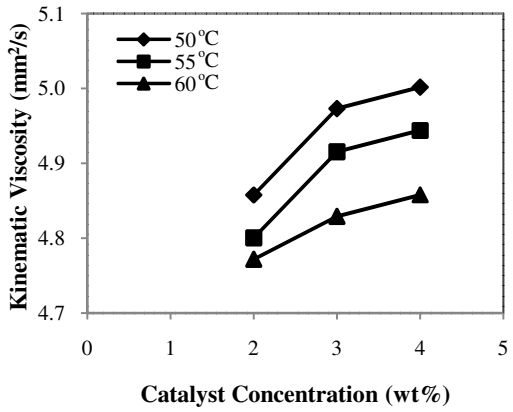

Fig. 4. Effect of Catalyst Concentration on Kinematic Viscosity at Reaction Time of 1.5 h and Methanol to Oil Molar Ratio of 9:1

3.4.3 Conversion

Conversion limits are present in SNI (minimum 96.5%), respectively for biodiesel fuels [19]. The conversion of biodiesel from the best condition was 97.31%. 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 limits are present in SNI (minimum 100°C), respectively for biodiesel fuels [19]. 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 acid-catalyzed esterification with methanol using sulphuric acid as the catalyst. According to the experimental studies, the best condition for alcoholysis of beef tallow waste oil was 3 wt% of CaO catalyst in oil, methanol to oil molar ratio of 9:1, reaction temperature at 55°C for a period of 1.5 hours. The yield of methyl ester was 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 calcium oxide from waste chicken eggshell is also very suitable as low cost and high activity catalyst for biodiesel production.

ACKNOWLEDGMENTS

The authors would like to thank Department of Chemical Engineering, University of Sumatera Utara, and Indonesian Oil Palm Institute (PPKS) Medan for the laboratory facilities.

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