

BIODIESEL PRODUCTION FROM WASTE COOKING OIL USING HYDRODYNAMIC CAVITATION

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Abstract

The aim of this research was to study biodiesel production from low cost feedstock of waste cooking oil (WCO) using hydrodynamic cavitation apparatus. A two-step processes esterification process and transesterification process using hydrodynamic cavitation for the production of biodiesel from WCO is presented. The first step is acid-catalyzed esterification process for reducing free fatty acid (FFA) content of WCO and followed by base-catalyzed transesterification process for converting WCO to biodiesel as the second step. The result of esterification process with methanol to oil molar ratio of 5 and temperature of 60 °C showed that the initial acid value of WCO of 3.9 mg KOH/g can be decreased to 1.81 mg KOH/g in 120 minutes. The highest yield of biodiesel in transesterification process of 89.4% obtained at reaction time of 150 minutes with methanol to oil molar ratio of 6. The biodiesel produced in the experiment was analyzed by gas chromatography-mass spectrometry (GC-MS), which showed that it mainly contained five fatty acid methyl esters. In addition, the properties of biodiesel showed that all of the fuel properties met the Indonesian National Standard (INS) No. 04-7182-2006 for biodiesel.

Abstrak

Produksi Biodiesel dari Minyak Goreng Bekas Menggunakan Kavitas Hidrodinamik. Penelitian ini bertujuan untuk mempelajari proses produksi biodiesel dari minyak goreng bekas menggunakan peralatan kavitas hidrodinamik. Proses produksi biodiesel dilakukan dalam 2 (dua) tahap. Tahap pertama adalah proses esterifikasi menggunakan katalis asam yang bertujuan untuk menurunkan kandungan asam lemak bebas dalam minyak goreng bekas. Pada tahap kedua dilakukan proses transesterifikasi menggunakan katalis basa untuk mengkonversi minyak menjadi biodiesel. Hasil penelitian proses esterifikasi dengan perbandingan molar metanol terhadap minyak 5:1 dan temperatur 60 °C menunjukkan bilangan asam awal minyak goreng bekas sebesar 3,9 mg KOH/g dapat diturunkan menjadi 1,81 mg KOH/g dalam waktu 120 menit. Pada proses transesterifikasi, rendemen biodiesel tertinggi sebesar 89,4% diperoleh pada waktu reaksi 150 menit dengan rasio molar metanol terhadap minyak 6:1. Analisis komponen biodiesel menggunakan kromatografi gas-spektrometer massa (GC-MS) menunjukkan biodiesel terdiri dari 5 (lima) metil ester asam lemak dominan yaitu metil oleat, metil palmitat, metil linoleat, metil stearat dan metil miristat. Selain itu, beberapa parameter biodiesel yang diuji telah memenuhi persyaratan SNI No. 04-7182-2006.

Keywords: biodiesel, hydrodynamic cavitation, transesterification, wasted cooking oil

1. Introduction

Developing alternative energy source to replace traditional fossil fuels has recently become more and more attractive due to the high energy demand, the limited resource of fossil fuel and environmental concerns [1]. Biodiesel fuel derived from vegetable oils or animal fats is one of the promising possible sources to

be substituted for conventional diesel fuel and produces favorable effects on the environment [2]. There are several ways to make biodiesel, and the most common way is transesterification of oils with short chain alcohols or by the esterification of fatty acids, as the biodiesel can be used directly or as blends with diesel fuel in diesel engine [3-4].

There are several technical challenges that need to be addressed to make biodiesel profitable. The high cost of virgin vegetable oil as the source of triglycerides plays a large role in process profitability. In order to reduce production costs and make it competitive with petroleum diesel, low cost feedstock of waste cooking oil (WCO) could be used as raw materials [3,5-6]. However, the relatively higher amounts of free fatty acids (FFA) and water in WCO results in the production of soap in the presence of alkali catalyst [7-8]. Thus, additional steps are required in order to remove any water and either the free fatty acids or soap from the reaction mixture. According to several researchers, the oil or fat used in alkaline transesterification reaction should contain no more than 1% FFA, which is equivalent to 2 mg KOH/g triglyceride [9-10]. If the FFA level exceeds this threshold, saponification hinders separation of the ester from glycerine and reduces the yield and formation rate of fatty acid methyl ester (FAME). Canakci and Van Gerpen [11] reduced the recommended acidity to below 1 mg KOH/g triglyceride.

The transesterification reaction involves two immiscible phases. The less-dense phase has the catalyst dissolved in the alcohol, whereas the other contains the oil or fat. The reaction between these species can occur only in the interfacial region between the liquids. Presently, mixing and heating are the commonly adopted processes to increase the area of contact between the two immiscible phases. Considering these limitations, currently, there is a strong quest to develop an efficient, time-saving, economically functional and environmental friendly biodiesel production process at laboratory and industrial scale having superiority over the classical procedure. Keeping this aspect into consideration, some of the recently developed biodiesel production technologies are power ultrasound [12-16], hydrodynamic cavitation [12-14] and supercritical methanol processes [17-18].

Among recently developed techniques, hydrodynamic cavitation is a potential method for biodiesel production at industrial scale due to its easy scale-up property. The cavitating conditions identical to acoustic cavitation could be generated in hydrodynamic cavitation, which even had a better effect on mixing immiscible liquids [14]. Furthermore, scale-up of hydrodynamic cavitation to meet industrial-scale operations had better opportunities than the ultrasonic reactor by reason of its easier generating and less sensitivity to the geometric details of the reactor. Hydrodynamic cavitation is a cheaper alternative and requires approximately a half of the energy that is consumed by the conventional mechanical stirring method. In hydrodynamic cavitation method, mixing of two phases of reaction is carried out by cavitation conditions. The cavitation condition is

produced by pressure variation, which in turn obtained by using the geometry of system to create velocity variation. Cavitation is generated by the flow of liquid under controlled conditions through simple geometries such as venturi tubes and orifice plates. When the pressure at the throat falls below the vapour pressure of liquid, the liquid flashes, generating a large number of cavities which subsequently oscillate. This phenomena give rise to pressure and temperature pulses. These pulses cause the better mixing of immiscible liquids and enhanced transesterification process [19].

In the present study, the use of two-step of esterification process and transesterification process using hydrodynamic cavitation for the production of biodiesel from WCO is presented. The first step is acid-catalyzed esterification process for reducing FFA content of WCO and followed by base-catalyzed transesterification process using hydrodynamic cavitation for converting WCO to biodiesel as the second step.

2. Experiment

Samples of WCO were collected from restaurant around the city of Banda Aceh. The chemicals used in experimental including methanol, sulfuric acid (H_2SO_4), phosphat acid (H_3PO_4) and kalium hydroxide (KOH) were purchased from Merck Chemical Company (Germany). The acid value of WCO used in this study was about 3.95 mg KOH/g, i.e. acid value of 2%, which is above the limit for satisfactory transesterification reaction using alkaline catalyst. The acid value was determined by a standard titrimetry method.

First, WCO was screened to remove food residues and solid precipitate. Then, WCO was dried by heating to 110 °C during 10 min for water removal. In addition, degumming process was performed to remove gumming in WCO such as phospholipids. In degumming process, the mixture of H_3PO_4 of 0.6% by weight of distilled water, and WCO was stirred at a speed of 400 rpm for 15 minutes. The colloidal formed was removed from the oil by filter paper. Then, FFA was converted to esters in an esterification process using an acid catalyst of sulphuric acid of 1% by weight of oil to reduce the acid value of WCO below 2 mg KOH/g. A methanol to oil molar ratio of 5 was used to investigate their influence on the acid value of WCO. The progress of the reaction was monitored by measuring the acid value at every 20-minute interval. The decrease in the acid value showed the forward progress of the esterification process. After the reaction, the mixture was allowed to settle for about 2 h and the methanol-water fraction that separated at the top was removed in a separating funnel. The bottom product having acid value below 2 mg KOH/g was used as the raw material for the transesterification process.

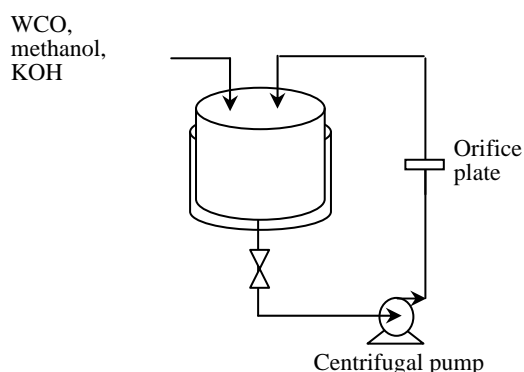


Figure 1. Schematic Representation of Hydrodynamic Cavitation Apparatus Used in this Study

The transesterification reaction was carried out with methanol to oil molar ratio of 3, 6, 9, and 12. KOH with concentration of 1.5% (w/w) of oil was used as an alkaline catalyst. The reaction was carried out at 60°C of reaction temperature and specified of reaction time. After reaction, the mixture was allowed to settle overnight. The lower layer that contained impurities and glycerol is drawn off. The ester (called biodiesel) remains in the upper layer. Biodiesel is washed using hot distilled water to remove the entrained impurities and glycerol, then, it was taken for analysis.

Both of esterification and transesterification were conducted by using hydrodynamic cavitation apparatus. Schematic diagram of the hydrodynamic cavitation apparatus used in this study is presented in Figure 1. Details of the hydrodynamic cavitation experiment is described elsewhere [20].

The mechanical stirring was carried out in a similar operating condition as the one explained for hydrodynamic cavitation experiment. The mechanical stirring with an agitation speed of 600 rpm was performed for comparison with hydrodynamic cavitation experiment.

3. Results and Discussion

Esterification. Acid-catalyzed esterification is an equilibrium reaction. Therefore, much more methanol than that given by the stoichiometric 1:1 molar ratio of oil to methanol is required to drive the reaction to completion, i.e., to form 1 mole of FAME from 1 mole of oil. In addition, excess methanol was used since the water being formed during the esterification reaction gets dissolved in the excess methanol. Thus, equilibrium limitation due to the reversibility of the reaction can be shifted towards the right side of the reaction. The esterification reaction can be written as follows:



which is catalysed by acids. In this work, R_1 was a methyl radical, and R_2 was a linear chain of 11-17 carbon atoms. The conversion of FFA as indicated by the reduction of acid value as function of reaction time, is shown in Figure 2.

From Figure 2, it was observed that the reaction rate increased with the increasing reaction time. The reaction progressed rapidly during the first 100 min showing over 50% conversion of FFA. After 100 min, there was no significant improvement in the FFA conversion. This might be due to the effect of water produced during the esterification of FFA, which prevented further reaction [21-22]. The dilution of the acid catalyst by the water formed in the reaction reduced its catalytic activity.

Transesterification. Figure 3 shows the relationships between the product yield and reaction time at various methanol to oil molar ratio under the hydrodynamic cavitation condition. In the transesterification of WCO by means of hydrodynamic cavitation, an upward trend for all of methanol to oil molar ratio with an increase in the reaction time was noticed. This indicated that transesterification has occurred, in which WCO was transformed to biodiesel. In the first 60 min, relatively rapid increase in the yield was observed for all of methanol to oil molar ratio. In the range of methanol to oil molar ratio studied, biodiesel yield of around 65-75% was achieved in the first 60 min. The results indicated that the reaction rate was higher at lower reaction times. At longer time, only gradual increase in yield was observed, attributed to high concentration of methyl ester in the reaction vessel to promote reverse reaction [23]. Omar *et al.* [24] reported that the optimum yield of biodiesel could be obtained in 100 to 200 min.

Figure 3 also shows the effect of various methanol to oil molar on biodiesel yield. Methanol to oil molar ratio is one important parameter in biodiesel production process. The transesterification reaction stoichiometry requires three moles of alcohol per mole of oil to yield three moles of biodiesel and one mole of glycerin. In the range of methanol to oil molar ratio studied, a similar trend of experimental result was observed. From Figure 3, it was observed that with an increase in the methanol to oil molar ratio from 3 to 6, the yield of biodiesel increased from 79.5 to 89.4% at 150 min of reaction time. However, further increase in the methanol to oil molar ratio to 9 and 12, the yield of biodiesel decreased slightly to 85.6 and 85%, respectively. It was supposed that at higher oil to methanol molar ratio, the separation of ester from glycerol layer becomes difficult [25]. The methanol to oil molar ratio of 6 can be considered as the optimum operating ratio.

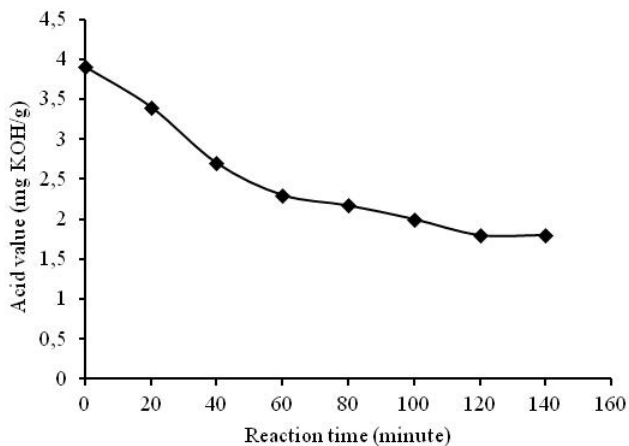


Figure 2. Effect of Reaction Time on Acid Value in Esterification Process

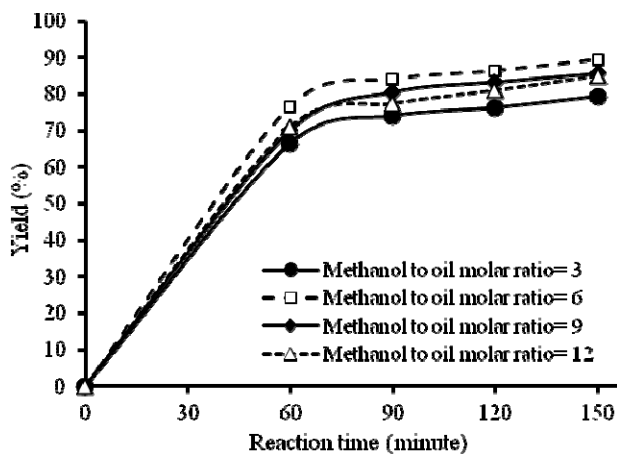


Figure 3. Product Yield as Function of Reaction Time at Various Methanol to Oil Molar Ratio

To demonstrate the effect of the presence of hydrodynamic cavitation, two experiments were carried out where in one case only hydrodynamic cavitation was used and in other case only agitation was used with all other reaction parameters viz. reaction time of 150 min and methanol to oil molar ratio of 6 were kept constant. The obtained results have been listed in Table 1. It was observed that the use of hydrodynamic cavitation enhances the yield of biodiesel for all of methanol to oil molar ratios. Thus, the use of hydrodynamic cavitation is effective both in enhancing the rate of reaction as well as in shifting the equilibrium for resulting a higher product yields. Hydrodynamic generated cavitation results in conditions of intense turbulence and micro-scale liquid circulation currents which help in uniform mixing at micro-level and hence in the elimination of the mass transfer resistances [14]. The phenomena reaction under hydrodynamic cavitation can be explained as follows; formation of

cavitation bubbles could be stimulated by hydrodynamic of fluid flow with sufficient energy. The symmetric collapse of the cavitation bubbles disrupts the phase boundary to create micro jets. As a result, oil and methanol form microscale fine emulsions, and they easily suspend each other. The promotional effect by hydrodynamic cavitation was ascribed to the increase in interfacial area and activity of the microscopic and macroscopic bubbles formed.

It can be seen from Table 1 that hydrodynamic cavitation results in 89.4% as the highest yield at methanol to oil molar ratio of 6 whereas the conventional stirring method results in lower extent of the highest yield of 86.2% at methanol to oil molar ratio of 9. It can be deduced that the reactions under hydrodynamic cavitation consumed a lower quantity of methanol and provided a higher yield than those under the mechanical stirring process.

Properties of biodiesel. In general, the biodiesel obtained from each experiment was very similar in appearance of clear yellow liquid. Compositions of samples were analyzed by gas chromatography-mass spectrometry (GC-MS). The typical GC-MS total ion chromatogram of components in biodiesel product can be seen in Figure 4. Meanwhile, biodiesel components analysis results by GC-MS are presented in Table 2. Only component with composition more than 1% is presented. The GC-MS analysis indicated that biodiesel mainly contained five fatty acid methyl esters and methyl oleate was the highest component. Biodiesel contained 98.1% of methyl ester. In addition, it can be concluded that the composition of biodiesel was similar

Table 1. Comparison between Ultrasonic Cavitation and Mechanical Stirring

Methanol to oil molar ratio	Yield (%)	
	Mechanical stirring	Hydrodynamic cavitation
3	78.7	79.5
6	81.5	89.4
9	86.2	85.6
12	84.8	85.0

*reaction time = 150 min.

Table 2. GC-MS Result of Biodiesel

Component	Composition (%)
methyl oleate	45.7
methyl palmitate	39.4
methyl linoleate	7.9
methyl stearate	4.1
methyl myristate	1.0

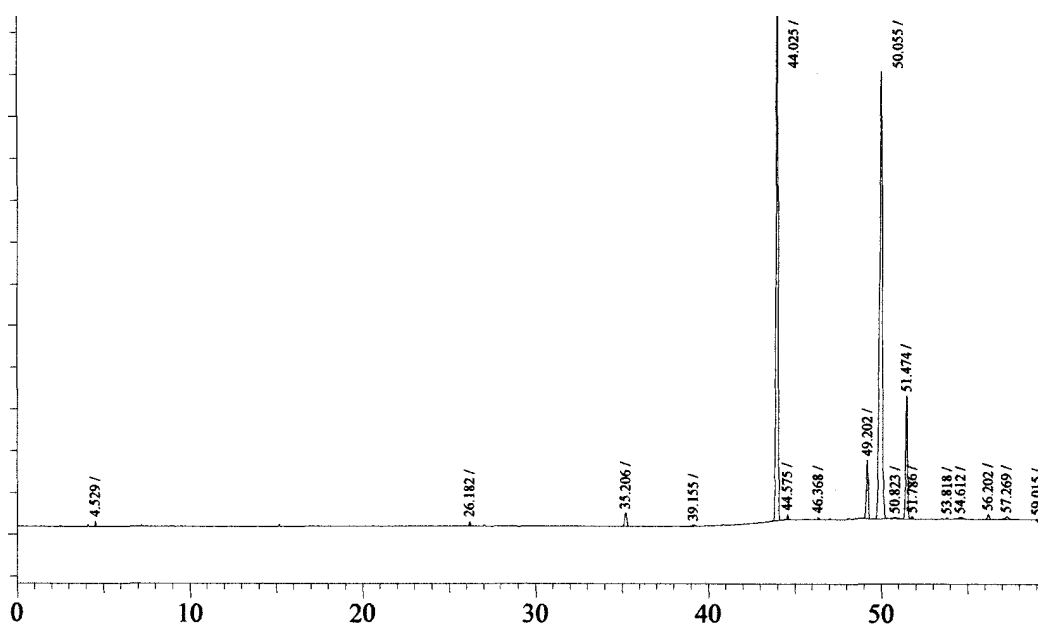


Figure 4. Typical GC-MS Total Ion Chromatogram of Components in Biodiesel

Table 3. Analysis Results of Biodiesel

Parameter	Experiment	SNI
Acid value (mg KOH/g)	0.4	max. 0.8
Density at 40 °C (kg/m ³)	878	850-890
Kinematic viscosity at 40 °C (mm ² /s)	4.2	2.3-6.0
Cetane number (-)	68.9	min. 51
Flash point (°C)	178	min. 100
Cloud point (°C)	10	max. 18

with the composition of fatty acid of palm oil as the source of WCO.

Generally, the properties of biodiesel produced must be able to fulfill Indonesian National Standard (INS) No. 04-7182-2006 before it can be used as the fuel source. Therefore, the biodiesel produced under the optimum condition was characterized for its fuel properties and compared with INS. The properties of six biodiesel property parameters comparison of acid value, density, kinematic viscosity, cetane number, flash point and cloud point with INS is shown in Table 3. It was observed that all of the fuel properties met the parameter of the INS for biodiesel. This proved the ability of hydrodynamic cavitation to produce biodiesel from WCO that complied with INS.

4. Conclusions

The production of biodiesel from low-cost of WCO using hydrodynamic cavitation was investigated. A two-step processes esterification and transesterification was

conducted to convert WCO to biodiesel. The result of esterification process with methanol to oil molar ratio of 5 and temperature of 60°C showed that the initial acid value of WCO of 3.9 mg KOH/g can be decreased to 1.81 mg KOH/g in 120 minutes. The highest yield of biodiesel in transesterification process of 89.4% obtained at reaction time of 150 minutes with methanol to oil molar ratio of 6. The properties of biodiesel met the INS for biodiesel. The experimental results clearly established the efficacy of cavitation as an excellent way to achieve process intensification of biodiesel production.

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