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BIODIESEL FROM LOW GRADE USED FRYING OIL USING ESTERIFICATION TRANSESTERIFICATION PROCESS

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Abstract

Biodiesel from Low Grade Used Frying Oil Using Esterification Transesterification Process. The aim of this research was to obtain the optimal condition for the production of biodiesel from low grade used frying oil through the esterification transesterification process. The experiment was arranged in Completely Randomized Design with Duncan's advanced test. Results showed that the biodiesel FFA content is ranged between 0.167 to 0.795% ($P < 0.01$) from the 0.5 to 3.06% initial rate, with the biodiesel yield between 69.7 to 94.2%. The esterification-transesterification stage were evidently able to increase the quantity and quality of biodiesel from used frying oil. By esterification, the yield increased and the FFA content reduced. Transesterification with 6:1 methanol molar ratio and 1.5% catalyst could increase the yield up to 9.9%. The testing of four biodiesel property parameters showed that biodiesel from used oil of tofu and chips factories, and chicken fast food 1 and 2 that had been esterified met the requirements of the Indonesian National Standard (INS) 04-7182:2006 for biodiesel. Whereas directly processed biodiesel (without esterification) from used oil of chicken fast food 1 known in terms of its acid number, did not meet the requirements.

Keywords: biodiesel, esterification, transesterification, used frying oil

1. Introduction

Indonesia's very high dependence on crude oil for fuel has quite a significant impact on its economy, especially after the prices of crude oil-based fuel (OBF) skyrocketed exceeding US\$ 70/barrel. The tendency of increasing OBF prices will apparently continue. In fact, some analysts assume that OBF prices could maintain its position around US\$ 80/barrel up to December 2007. Government policies that apply subsidy for domestic fuel prices appears to be very costly to the state. In macro economic sense, ongoing OBF price increases will have an impact on the national economy. This situation is brought out because the non-subsidy OBF or industrial OBF prices will increase around 15% and so will have an impact on the increase of energy supply cost, which will eventually increase the prices of industrial product goods and result in inflation increase.

Several policies have been launched by the government to respond to the energy price dynamics and to encourage the use of alternative energy sources including biodiesel fuel. If the efforts for the development of biodiesel could be happened, several national advantages would be obtained, among others are import charge reductions, fuel availability guarantee, manpower supplying and would contribute to

environment quality improvement, since biodiesel is a renewable energy source which emission is more environmental friendly compared to that of automotive diesel oil. Various researches on biodiesel related to raw materials, processing technology, testing in operation etc. are highly necessary to support the national energy policy in the future [1].

Currently, vegetable oils which are quite intensively studied as raw materials for biodiesel production are soybean oil, palm oil and castor oil [2]. Vegetable oil used for biodiesel production is must be clean with low water content and acid number (FFA). For large industries, there is nearly no problem to produce vegetable oil with the above mentioned quality. However, small industries using simple technology mostly produce low grade vegetable oil (rural produced castor oil) due to its condition of high water and FFA content. Actually the low grade vegetable oil can also be processed into biodiesel through the transesterification process. However, it is necessary to undergo a neutralization stage in advance, which may add to the cost and reduce yield. When neutralization is not conducted, the transesterification process will produce soap which may reduce the biodiesel yield and make the separation process difficult. One of the efforts to overcome the problem is by producing biodiesel in two

stages, i.e. the esterification and transesterification stages using a low pressure reactor. The use of low pressure (vacuum) plays a role to increase the efficiency of the esterification and transesterification processes by separating the water content and catalyst at the end of the process [3, 4].

Beside the rural produced low grade vegetable oil, the utilization of used frying oil as raw material for biodiesel production should also be taken into consideration. In 2005 it was predicted that the amount of the national frying oil consumption was 6 million tons [1] and if assumed that 30% of the consumption became used oil, the potential of used frying oil which might be utilized as raw material for biodiesel reached 1,8 million tons of used oil [5].

The optimal condition of the esterification and transesterification processes from low grade vegetable oil into biodiesel had to be studied in advance at a laboratory scale before it could be applied at a pilot project or field scale. Variables on the condition of the production process of biodiesel from low grade vegetable oil which needed to be studied included the temperature of reaction, period of reaction, ratio of methanol and oil, amount of catalyst and pressure used.

In order that the application of technology innovation of biodiesel production using raw materials from low grade vegetable oil can be spread wider in society so that it gives a meaningful contribution to the national economy, it is necessary to design a small-medium scale reactor (Small-Medium Enterprise – SME) which may be used by the society. The reactor is expected to be able to produce a high biodiesel yield. For that matter, the reactor performance test stages in the esterification and transesterification processes must be tested based on the optimum condition scale-up at the laboratory scale which have been found out from laboratory research results. The reactor performance in the esterification reaction is based on its ability to reduce the acid number, while the reactor performance for the transesterification process will be viewed from its ability to reduce viscosity and oil conversion rate into biodiesel [6]. The quality of biodiesel produced should also be tested referring to the ASTM D6751-3 standard.

The objective of the research is to obtain the best treatment condition on the esterification-transesterification process of low grade used frying oil and to conduct a one-stage transesterification process of various kinds of used frying oil as well as to test the quality of biodiesel produced referring to the ASTM standard.

2. Methods

Raw materials used in the research were used frying oil from tofu factory, chips factory, chicken fast food 1 and 2.

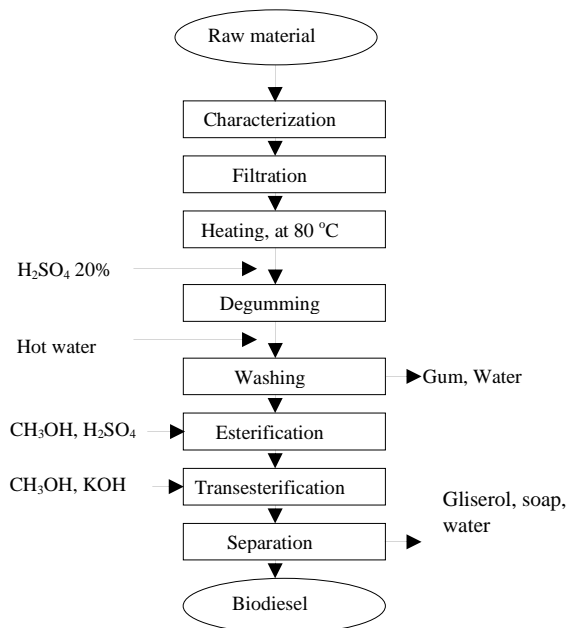


Figure 1. Flowchart of Biodiesel Production from used Frying Oil

The chemicals used were technical methanol, ethanol, benzene, H_2SO_4 , HCl , KI , NaOH , Na-tiosulfate, PP indicator, phosphate acid solution, and other chemicals for analysis. The equipment used were destilator, hot plate, stirrer, Erlenmeyer flask, separating funnel, vacuum pump, reverse cooler, pH meter, desicator, and other equipment for analysis.

The research was done at Djuanda University Agro-Industry Technology Laboratory, from May 2007 to November 2007. This study was conducted in four stages: 1) characterization of raw material, 2) optimization on the esterification process, 3) optimization on the transesterification process, and 4) one-stage and two-stage biodiesel production processes. The procedure of this researches are presented on Figure 1.

The testing of quality characteristics included water content, ash content, FFA content, acid number, iodine number, saponification number, peroxide number, density, and viscosity. Data from research results were analyzed using analysis of variance with Duncan's advanced test using a computer program package [3]. The best biodiesel from the esterification-transesterification process was tested referring to the ASTM D6751 standard.

3. Results and Discussion

Characterization of Used Frying Oil. The analysis results of used frying oil are presented on Table 1. The

viscosity of used frying oil from potato chips factory and tofu factory were lower compared to those of chicken fast food 1 and 2. The material of chicken fast food 1 had the lowest quality compared to the other used frying oils and so that particular used frying oil will further be given special attention through the esterification-transesterification treatments in this research.

Based on the analysis on used frying oil as raw material, there was a significant difference for the characteristics of water content, density, FFA content and peroxide number ($P < 0.01$); while iodine number, saponification number and sulfide ash were statistically not different ($P > 0.05$).

The average water content of used frying oil obtained was quite low ($< 0.5\%$) so that it met the requirements. According to Goff *et al.*, oil with a water content less than 0.1% can produce methyl ester more than 90% [7]. For density, the average densities of used frying oil from chicken fast food 1 and 2 were higher compared to those of used frying oil from tofu and potato chips factories. This was probably because the frying oil from chicken fast food 1 and 2 were used to fry materials containing high protein and fat so that some of the protein and fat are were dissolved in oil.

The testing of free fatty acid (FFA) was intended to find out the damage degree of used frying oil as raw material. Results of the test showed that frying oil used for frying chicken fast food 1 had the highest FFA average i.e 3.06%. That rate exceeds the requirement of the maximum 1% FFA content for biodiesel, while the three other raw materials met the requirements since they had an FFA average of less than 1%. For their peroxide numbers, the used frying oil of chicken fast food 1 and 2 were lower in average compared to those of tofu factory and chips factory. It is assumed that the low peroxide number of the chicken fast food frying oil was due to its source, i.e. oil having saturated fatty acid, while oil from the tofu factory and chips factory were assumed to originate from oil with many double bonds such as palm oil.

From the characterization results of the four kinds of used frying oil used, it was concluded that the used frying oil from fast food 1 had the lowest quality so that

it was chosen to be given an esterification treatment. The objective was to lower the raw material's FFA content since it was considered more effective compared to the neutralization process. To prove its effectiveness, a one-stage process biodiesel would be produced without undergoing the esterification process.

Optimization on the Esterification Process of Used Frying Oil. Overall, the condition of the four kinds of raw material studied could be used as raw material for biodiesel, since their FFA content were still below 1% except for the used oil of chicken fast food 1. Therefore the used oil from chicken fast food restaurant 1 was given a preliminary treatment i.e. esterification to lower its FFA content in order to obtain a higher biodiesel yield.

Optimization on the Methanol Molar Ratio with H_2SO_4 Catalyst. The esterification process resulted in a product with two layers in great contrast. The upper layer was methanol and the lower layer was oil which was a mixture of triglyceride, methyl ester and the remains of free fatty acid. The success of the esterification process is determined by the FFA decrease.

Results showed that the treatment with 20:1 methanol concentration and 6% H_2SO_4 resulted in the lowest FFA with an average rate of 1.15%, yet from Duncan's advanced test, the best treatment combination was 20:1 methanol concentration and 3% H_2SO_4 . The results of esterification on the used frying oil was in agreement with the results of esterification conducted on soybean oil containing 20% FFA with 9:1 methanol molar ratio:FFA, 60°C temperature for 1 hour with 5% H_2SO_4 catalyst, in which the acid number could be reduced from 41.33 to 1.77 whereas for an initial FFA content of 40%, the acid number became 18.82 [8]. The effect of methanol molar ratio between 20:1 to 40:1 on the esterification process was studied by Canakci and Van Gerpen which showed that the higher the methanol molar ratio, the greater the decrease of acid number [8]. Several literatures suggest quite a high molar ratio, such as the esterification conducted by Canakci and Van Gerpen on fat with 39.6% FFA with 20:1 methanol molar ratio, then continued by a second stage esterification with 40:1 methanol molar ratio [8].

Table 1. Characteristic Analysis Results for used Frying Oil as Raw Materials

| Raw material | Water content (%) | Saponification number (mg KOH/ g) | Density (mm ² /s) | Peroxide (mg O ₂ / 100 g) | FFA (%) | Iodine Number (mg I ₂ / 100g) | Sulfide content (%) |
|---------------------------|-------------------|-----------------------------------|------------------------------|--------------------------------------|---------|--|---------------------|
| Used oil of tofu factory | 0.067a | 190.3 a | 0.908 a | 17.3 b | 0.50 a | 16.82 a | 0.017 a |
| Used oil of chips factory | 0.030 b | 179.4 a | 0.907 a | 13.3 b | 0.18 a | 12.34 a | 0.074 a |
| Used oil of chicken FF 1 | 0.136 bc | 194.5 a | 0.923 b | 2.7 a | 3.06 b | 13.66 a | 0.074 a |
| Used oil of chicken FF 2 | 0.105 c | 188.1 a | 0.921 b | 9.1 abs | 0.83 a | 11.53 a | 0.072 a |

Note: the same letters in the columns show no difference at 0.05 level of significance ($P > 0.05$)

Optimization on temperature and esterification period. Based on Duncan's test, it was concluded that the best treatment was 70°C temperature for 30 minutes. The esterification 60°C temperature was used for soybean oil esterification by Canakci and Van Gerpen, for castor oil by Sudradjat *et al.* and 55-60°C esterification temperature was used for soybean oil and fat esterification by Canakci and Van Gerpen [8].

The results were in agreement with research results of Canakci and Van Gerpen for the esterification of soybean oil containing 20% palmitate acid FFA using 9:1 methanol molar ratio with 5% and 15% sulfide acid catalyst which concludes that the longer the esterification period (up to 0.5 hour), the greater the decrease of FFA content. However, between 0.5 hour and 1 hour, the difference in the decrease of FFA content was very little, whereas using methanol under the same conditions, the decrease of FFA content between 0.5 hour and 1 hour had no difference.

The production process of biodiesel directly from used frying oil was conducted on four kinds of used frying oil as raw materials. Different raw materials appeared to give different results. The water content of biodiesel produced had an average of about 0.5%. The average water content of biodiesel was not effected by the initial water content of the raw material. The rate was still classified as high since the requirement of the INS for Biodiesel is maximum 0.01%. The average highest biodiesel saponification number came from the raw material of used frying oil from chicken fast food 1, i.e. amounting to 229.15 and the lowest was from chips frying oil, amounting to 216.95; for density, the average rate amounted to 0.874 mm²/s, which still meets the criteria of the INS for biodiesel.

Free fatty acid (FFA) declined after the transesterification process. However, the analysis of varian results concluded that there was no difference in the FFA content of the biodiesel produced (Figure 2). The average FFA of biodiesel produced was 0.18% or 0.36

mg KOH/g acid number, except from used frying oil of chicken fast food 1, the average FFA rate reached 0.79% or 1.58 mg KOH/g acid number. Therefore, the biodiesel from used frying oil of chicken fast food 1 had not met the INS for biodiesel i.e. 0.8 mg/KOH/g, while the three other biodiesels did. The *iodine number* of biodiesel tended to increase compared to that of the initial raw material, yet was statistically not different ($P>0.05$). The iodine number of the biodiesel produced was categorized as low, less than <25, which met the requirements of the INS for biodiesel, i.e. maximum 115% iod/100 g.

Yield is the parameter of success on the process since it is immediately related to economical value. Based on research results, the highest biodiesel yield was obtained from used oil of tofu factory i.e. 94%, followed by used oil of chips factory and chicken fast food 2 at about 84%, while frying oil of chicken fast food 1 only resulted in 69% yield. The difference in yield was due to the characteristics of the raw materials used, in which the chicken fast food 1 materials had the highest FFA content, i.e. 3.06%. Such a condition may disturb the process so that it resulted in a low yield. The methanolysis reaction requires that the oil must be clean, without water and neutral. High free fatty acid will produce soap which will reduce the alkalinity of the catalyst and form a gel layer so that the separation and percipitation of gliserol becomes difficult [8]. The content of free fatty acid and and water exceeding 0.3% may reduce the yield of oil transesterification [9]. The transesterification yield can be increased from 25% to 96% by reducing the level of free fatty acid and water, each 10% to 0.23% and 0.2% to 0.02% respectively [10].

The Production Process of Biodiesel from Esterification Products. The two-stage biodiesel production through esterification-transesterification was aimed to improve the quantity and quality of the biodiesel

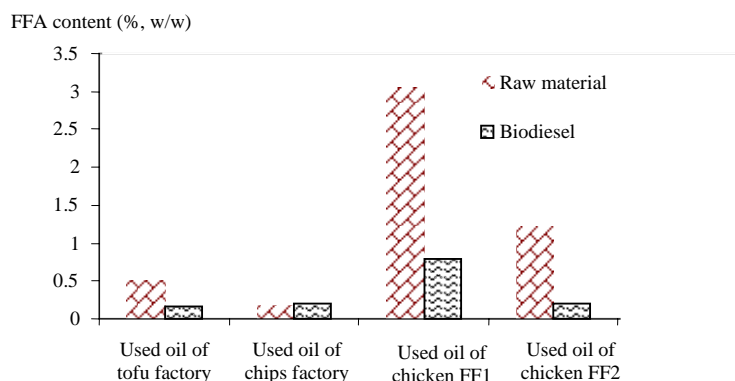


Figure 2. Average Difference in FFA Level of used Oil Before and After Transesterification Process

Table 2. Comparison on the Results of Direct and Indirect Transesterification

| Specification of process | Direct Transesterification | Transesterification of esterification products |
|------------------------------|----------------------------|--|
| Yield (%) | 69.700 | 77.400 |
| FFA content (%) | 0.795 | 0.340 |
| Acid number (mg KOH/g) | 1.590 | 0.680 |
| Density (kg/m ³) | 0.884 | 0.879 |
| Water content (%) | 0.580 | 0.570 |

Table 3. Testing on the Properties of Biodiesel from used Frying Oil (INS 04-7182:2006)

| No. | Parameters | Unit | Standard | Procedure | A | B | C | D |
|-----|------------------|--------------------|--------------|---------------|-------|-------|--------|--------|
| 1 | Density at 40 °C | kg/cm ³ | 850-890 | ASTM D 1298 | 865 | 871 | 875 | 879 |
| 2 | Sulfated ash | % m | maximum 0.02 | ASTM D 874 | 0.043 | 0.037 | 0.035 | 0.032 |
| 3 | Acid number | mg KOH/gram | maximum 0.8 | AOCS Cd 3d-63 | 0.410 | 0.390 | 0.330 | 0.680 |
| 4 | Iodine number | %- m (g-12/100 g) | maximum 115 | AOCS Cd 1-25 | 8.180 | 8.180 | 11.050 | 10.190 |

Note :

A : Biodiesel from used frying oil of chicken fast food 2

B : Biodiesel from used frying oil of potato chips factory

C : Biodiesel from used frying oil of tofu factory

D : Biodiesel from used frying oil of chicken fast food 1

produced. The esterification process could reduce the FFA content significantly from 3.06% to about 1.2%. The products as results of transesterification from esterified raw materials had the same appearance as the products of direct transesterification. The transesterification process was conducted under the conditions of 60°C temperature, 30 minute period, 6:1 methanol molar ratio and 1% NaOH catalyst.

Research results showed that esterification could increase the quantity and quality of the biodiesel produced (Table 2). Without esterification, the average yield was only 69.7%. However, the esterification process could result in 77.4% yield, increasing at 7.7%. The FFA content and acid number each declined respectively from 0.795% to 0.34% and 1.59 mg KOH/g to 0.68 mg KOH/g, and so did the density, while the water content relatively remained the same. Therefore, the esterification process was quite effective to increase the yield and quality of the biodiesel produced.

The yield of biodiesel produced in the transesterification process of esterification products significantly increased, yet relatively a little, only 77.4%, while it reached 90% for used oil from tofu and 85% from chips. Viewed in terms of the FFA content of the raw materials for transesterification, the FFA content resulting from the esterification process was still relatively high (1.20%) while for used oil from tofu (0.17%) and chips (0.20%), the low yield was probably due to the above problem. Lowering the FFA content among others could be conducted by double esterification with an increasing methanol molar ratio, the neutralization process, or by optimization of the transesterification process. From research results, by increasing the molar ratio from 6:1 to 9:1 at the same catalyst concentration, the biodiesel

yield could increase from 77.41% to 80.37% or increase at 2.96%. However, increase in catalyst amount rather had a negative effect since the yield rather declined significantly to 68.21%. Therefore, the transesterification with 9:1 methanol molar ratio and 1% KOH catalyst was the best.

Testing on the properties of biodiesel from used frying oil. The testing on the properties of biodiesel refers to the INS for biodiesel, yet only for certain characteristics, including density, acid number, iodine number and sulfated ash, as presented on Table 3. Based on the parameters of density, acid number and iodine number, biodiesel from used frying oil (coconut oil left after frying) met the parameter of the INS for biodiesel, while the sulfide ash and water content exceeded the acceptable margin. The sulfide ash that had not met the requirements was probably because the washing had not been optimum or mineral components from the fried material were included. However, concerning the specifications, the increase was relatively small, i.e. 0.02%. Therefore, with a mixture of 50% automotive diesel, it is expected to be able to reach the required biodiesel standard. Based on such a condition, biodiesel from used oil can technically be well used up to a level of 50%.

4. Conclusion

The characteristics of used frying oil vary in general, depending on the type of oil, the process it has undergone, the handling and period of storage. Based on the analysis results, there was a significant difference on the water content, density, FFA content, and peroxide number ($P < 0.01$); whereas the iodine number, saponification number and sulfide ash were statistically

not different ($P>0.05$). The used frying oil from chicken fast food 1 had the highest FFA content, water content and density, with an average rate of 3.06%, 0.136% and 0.923 respectively.

The engineering on the esterification and transesterification processes was conducted on the raw material with the lowest quality, i.e. the used frying oil of chicken fast food 1, since the quality of the other raw materials were relatively much better. The optimum concentration of methanol and H_2SO_4 was acquired at a treatment of 20:1 methanol molar ratio and a catalyst concentration of 6% H_2SO_4 . On the above mentioned condition, the average initial FFA content of the raw material at 3.06% could be reduced to 1.15-1.2%. On the best condition of treatment on the methanol and acid catalyst mentioned, the next step was to find the best temperature and period of the esterification process. The analysis of variance results concluded that the best treatment was obtained at 70°C temperature and 30 minute esterification period.

The process of biodiesel production through the process of transesterification directly from the raw materials were conducted on the four kinds of raw materials. Different raw materials turned out to result in different appearances. From the analysis results on the characteristics of the biodiesel produced, there was a significant difference on the saponification number and density ($P<0.01$), while the water content and FFA content did not show any difference ($P>0.05$). The saponification number and iodine number tended to show increases after the transesterification process. On the contrary, the density, peroxide number, and FFA content declined. The high initial water content of raw material from the used oil of tofu factory declined significantly while the water content of biodiesel from used oil of potato chips factory and fast food increased compared to their initial water content. The range of the biodiesel FFA content was 0.167–0.795% ($P<0.01$) from the initial rate of the raw material at the range of 0.5–3.06%. The yield of the biodiesel produced ranged between 69.68-94.16%. The highest yield came from the raw material of used oil from the tofu factory and the lowest came from the used oil of chicken fast food 1.

The process of biodiesel production through the stages of esterification-transesterification could improve the quantity and quality of biodiesel from used frying oil of fast food 1. Through esterification, the biodiesel yield increased from 69.7% to 77.4% and the FFA content could decline from 0.795% to 0.340%, the acid number declined from 1.59 mg KOH/g to 0.68 mg KOH/g. Transesterification with 9:1 molar ratio and 1% KOH

catalyst from esterified materials could increase the yield from 69.7% to 80.37%, whereas 6:1 methanol molar ratio and 1.5% catalyst could increase the yield from 69.7% to 79.61%.

The testing of the four biodiesel property parameters which included density, sulfated ash, acid number and iodine number showed that esterified biodiesel from used oil of tofu and chips factories, chicken fast food 2, and chicken fast food 1 met the requirements of the INS 04-7182:2006 for biodiesel. Whereas biodiesel produced directly from used oil of chicken fast food 1 (without esterification) viewed in terms of its acid number did not meet the requirements.

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