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Biodiesel Synthesized from a Mixture of Used Cooking and Sunflower Oils: Effect of Activated Fly Ash Catalyst and Oil to Methanol Ratio

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ABSTRACT

The purpose of this study is to determine thea yield ofbiodiesel synthesized from mixed of used cooking oil and sunflower oil by optimizing of oil to methanol (mole) ratio and applying a fly-ash catalyst. Biodiesel can be produced by utilizing vegetable oil or animal fat through an esterification or trans-esterification process with the support of methanol and catalyst. Used cooking oil was used as a raw material and mixed with sunflower oil to reduce freefatty acid (FFA) levels. The flyash catalyst was activated by sulfuric acid and impregnated with calcium carbonate. The process of producing biodiesel consists of catalyst preparation which includes activation and impregnation, esterification process and trans-esterification process. Esterification was carried out at 60^{o}C, the ratio of oil: methanol was 1:12, weight of catalyst H_2SO_4 1%-wt/wt oil, by mixing of 400 rpm for an hour. Trans-esterification was carried out at a molar ratio of oil:methanol (1:10; 1:12; and 1:14) and the mass of the catalyst (2, 4 and 6%) of the oils. The optimum yieldof 81.48% was obtained in the molar ratio of oil:methanol=1:12 with a catalyst mass of 2%. The biodiesel produced has a density of 0.87 g/mL, acid number 0.28 mg-KOH/g and moisture content 0.02%. The gas chromatography analysis shows the largest components of biodiesel produced are methyl hexadecanoicacid and cis-methyl-9-octadecanoic acid,therefore it can be simply concluded that the biodiesel compoundsare actually produced

Key words: fly ash, biodiesel, used cooking oil, esterification, trans-esterification

1. INTRODUCTION

Diesel oil is a fraction of petroleum that is widely used as fuel in industry and transportation, but the increasing number of needs results in the availability of raw materials which are increasingly depleting. Biodiesel is one of the promising alternative energy sources because its raw materials derived from renewable materials make its availability guaranteed.

Used cooking oil is used as raw material because the utilization of used cooking oil has several advantages, besides being easily obtained because it is a domestic household waste and can overcome the waste generated from the disposal of used cooking oil. The use of vegetable oil has advantages that are easy to process, easy and fast manufacturing process, and high conversion rates. In this study, the sunflower oil is mixed with used cooking oil to reduce the high FFA levels in used cooking oil.

Coal fly ash catalyst is the residual solids of combustion in coal, oil and biomass production. Fly ash consists of metal oxides of SiO_2, Al_2O_3 and Fe_2O_3 as the main components and other small compounds such as Na_2O, CaO, MgO, TiO_2, BaO, K_2O, and others [1]. The coal fly ash catalyst can be increased by activating it with an acid and base solution.

The activation of fly ash catalyst can multiply the active side of the catalyst by dissolving impurity ions that are on the surface of the catalyst [2]. Here, the fly ash catalyst is activated by H_2SO_4. Activation of coal fly ash with mineral acids can dissolve impurities or compounds which can reduce the adsorption capacity so that the adsorption ability increases [3]. The catalyst is also impregnated with calcium carbonate. $CaCO_3$ is used because one of the supporters of fly ash catalyst is CaO, which calcium content may increase biodiesel yield. The selection of heterogeneous catalysts is more advantageous than homogeneous catalysts. In addition to being easily separated physically, the solid catalysts also can be reused.

2. METHOD

This research aims to produce biodiesel from used cooking oil and sunflower oil through two stages, the esterification and the trans-esterification process. Several tests were carried out to determine the biodiesel content produced.

The standardized tools were used in this research. All the analytical grade of chemicals, for example,sulfuric acid (H_2SO_4), calcium carbonate ($CaCO_3$), ethanol, methanol, potassium hydroxide (KOH), and sodium hydroxide (NaOH) were bought from e-Merck. Theused cooking oil waste was taken from household nearby, the sunflower oil was bought from local market, and the coalflyash was obtained from local industry of PT. Indo AcidatamaTbk, Karanganyar, Indonesia.

2.1 Preparation of fly ash catalyst

The first step in making the catalyst is,the fly ash is sieved with a size of -100 + 200 mesh. The activation process of fly ash by means of 50 grams of fly ash from the sifting results mixed into 100 mL of H_2SO_4 solution. The mixture is stirred using a magnetic stirrer for 24 hours at room temperature with a stirring speed of 600 rpm. Then the pH of the top layer is checked and the sulfuric acid is separated. The precipitate was further neutralized using aquadest to pH ± 7. Then dried for 24 hours in order to remove the water content with a temperature of 80^{o}C.

The impregnation of fly ash was carried out by put 5 grams of fly ash into porcelain cups plus 5 grams of $CaCO_3$ and stirred evenly. After that, it was calcined in the furnace at ± 700 ° C for 4 hours, then cooled in a desiccator 5 minutes.

2.2 Esterification step

Oil as much as 200 mL with the ratio of used cooking oil: sunflower oil is 3:1, then put into a three-neck flask that has been installed with a condenser. A three neck flask is placed in a water bath on a hot plate to maintain the reaction temperature of 60^{o}C. Once the reaction temperature is reached, the methanol reagent that has been prepared in a ratio of 1:12 as an oil-methanol molar ratio and 1% H_2SO_4 catalyst is added to the reactor with a stirring of 400 rpm. After the reaction lasts for an hour, the esterification product is put into the separating funnel and allowed to stand until two layers are formed. The bottom layer is separated from the top layer as H_2SO_4 catalyst and the remaining methanol,then proceed to the transesterification stage. Before proceeding to the lower layer transesterification stage of the esterification product, the FFA level is calculated first. If the FFA level> 2%, it is necessary to do the esterification process first, if <2% then the oil does not need to be processed esterification and directly to the trans-esterification process.

2.3 Trans-esterificationstep

The transesterification process is carried out by reacting oil and methanol with a molar ratio of oil:methanol (1:10, 1:12, and 1:14) and catalyst mass of 2, 4, and 6% of 20 mL of oil to speed up the reaction while accompanied by heating at 80°C for 3 hours. The transesterification product is then put into a separating funnel to separate methyl ester (biodiesel) and glycerol, remaining methanol and catalyst residue.

To remove the remaining glycerol, methanol and the catalyst then was washed using hot aquadest. Aquadest is inserted into the separating funnel and then allowed to stand for a few moments to form a layer of water at the bottom. The water layer is removed. Washing is done to show whether the resultant is methyl ester. The result of washing in the form of methyl ester is removed into a beaker glass container, then dried in the oven at a temperature of 100 ± 2 ° C for an hour. The dried methyl ester is cooled in a desiccator for 5 minutes. Once already cool, methyl esters are weighed. Then, a methyl ester test which includes density, acid number, water content and GC analysis is performed [11-12].

3. RESULTS AND DISCUSSION

X-ray diffraction (XRD) test was carried out to identify the characteristics of crystals in coal fly ash catalyst. From the XRD test on the fly ash catalyst, Fig. 1, it was found that the crystals formed inside the catalyst were detected. This can be seen from the formation of new peaks in the fly ash test results after preparation compared before preparation. The peak generated on the graph after preparation shows a higher number than without preparation, this shows an increase in the intensity of the components contained in the coal fly ash after preparation. The peak location (2θ) on the fly ash catalyst before preparation was 26.83, while the peak location of the catalyst peak after preparation slightly moved to 29.42 which is the highest intensity.

According to the researchers[4-5], the results of the XRD test with the peak are dominated by quartz compounds (SiO_2), and mullite ($Al_6Si_2O_{13}$) at the peak. While the $CaCO_3$ and calcium content can also be seen at peak 48.47 which can be seen through the Match2 XRD program application. The use of $CaCO_3$ is intended because the calcium content can increase biodiesel yield.

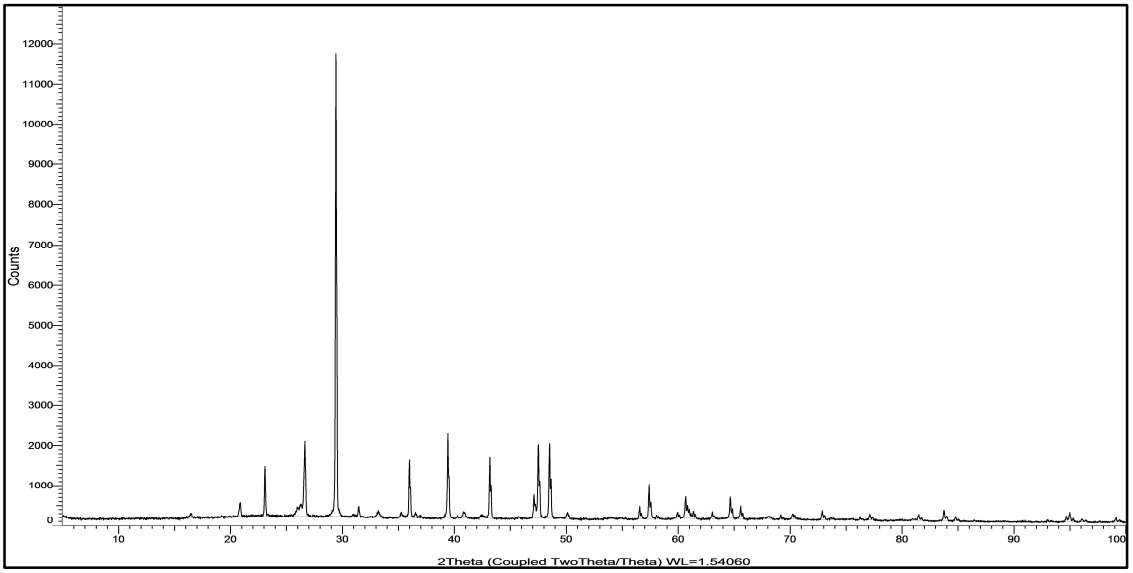

Figure 1: X-ray diffraction of fly ash after activation and impregnation process

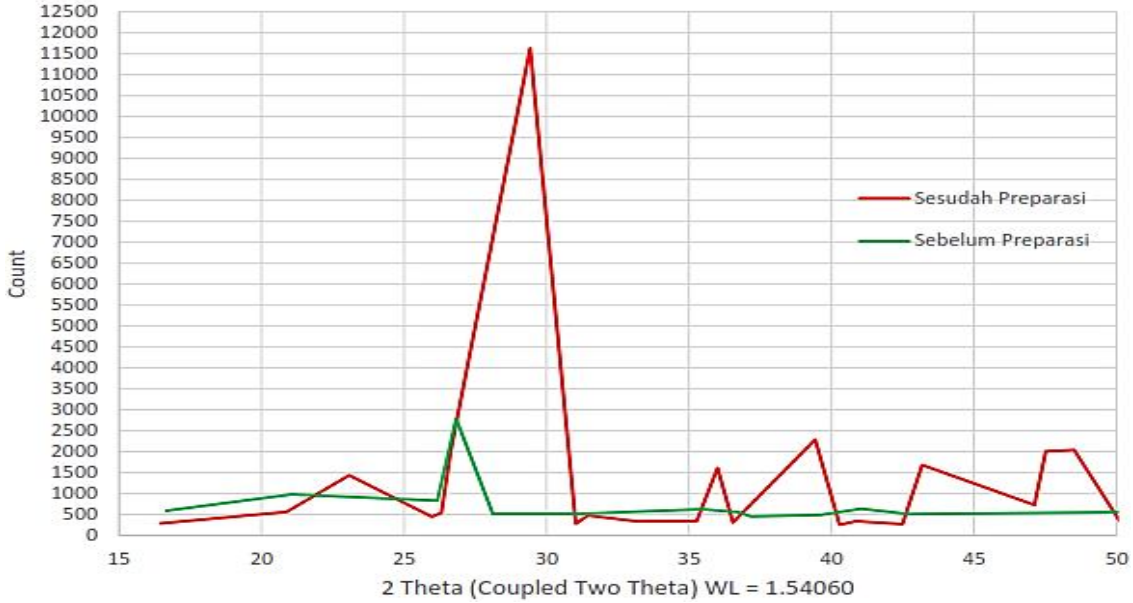

Figure 2: Comparison XRD pattern before and after catalyst preparation

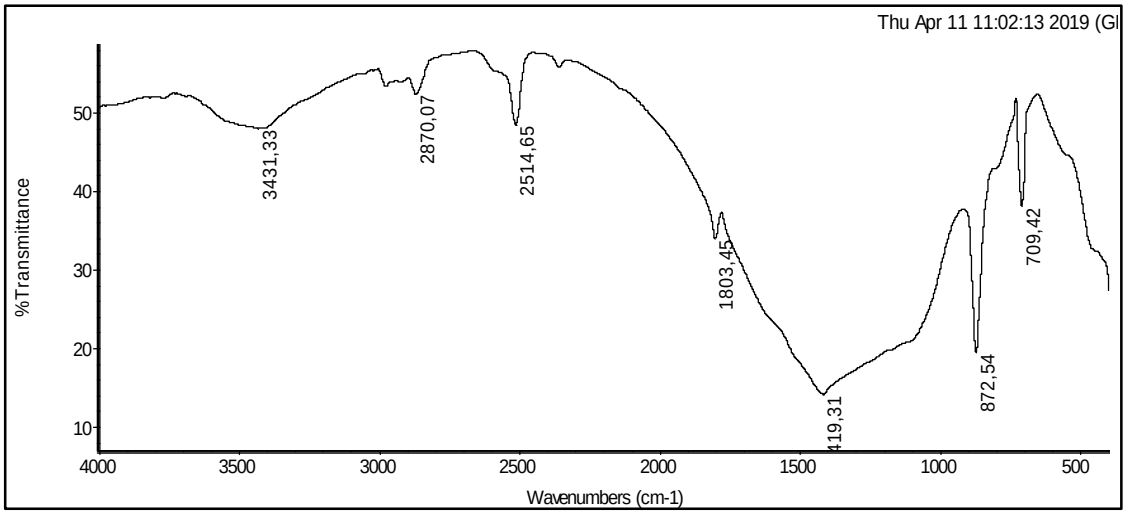

Figure 3: FTIR spectra for fly ash catalyst after activation and impregnation process

Table1: Interpretation of FTIR spectra of fly ash catalyst

Wave number range	Before impregnation	After impregnation	Interpretation
3,200-2,550	2,923.07 3,032.90	2,514.5 2,870.07	Hidroxyl radicals (-OH)
1,320-980	1,088.08	1,419.21	Vibration Spans Si-O or SiO_4
650-850	782.37	709.42	Symmetrical stretching vibrations SiOandAlO
500-420	458.21	-	Symmetrical bend vibrationsSiOandAlO

Table 2: Yieldof biodiesel at various mass of catalysts

Molar ratio (oil:methanol)	Yield (%)		
	Mass of catalyst		
	2%	4%	5%
1:10	67.30	65.40	57.70
1:12	81.48	68.52	66.67
1:14	75.00	67. 86	64.29

The catalyst formed is then analyzed with a Fourier transform infrared (FTIR) spectrophotometer, this analysis is needed to determine the material and determine the components of the mixture formed and provide information in estimating the molecular structure of these components. The results of FTIR for fly ash catalyst after preparation is shown in Figure 3.and the interpretation listed in Table 1.

The transesterification process is carried out to produce biodiesel by varying the mole ratio of oil:methanol with time, so as to obtain the following yield.

From Table 2, it can be seen that the resulting data decreases with each test. Theoretically explained that the greater the ratio of oil to methanol molar ratio will produce a greater yield due to the use of increasing methanol. But in this study an increase from the ratio of mole ratio of 1:10 to 1:12, but when using the ratio of mole ratio of 1:14 actually decreased. The use of excess methanol, above the optimum, the formation of biodiesel and glycerol is faster. The resulting glycerol reaches the stoichiometric amount, the glycerol which is then formed will react with the active side of CaO which is the content of the CaCO3 catalyst to produce calcium glyceroxide. Calcium glyceroxide is less active in catalyzing the transesterification reaction, so that the formation of biodiesel is disrupted as a result of the reduced number and activity of $CaCO_3$ as a catalyst [6].

In addition, the catalyst weight also determines the yield produced, but as more catalysts are used the resulting yield will decrease as it may cause a bounce reaction. As we can see from the graph, the more catalysts are used then the lower the number of catalysts in use [7-8].

Based on this, in this study the best conversion was achieved at a molar ratio of oil: methanol 1:12 with a catalyst weight of 2% at a reaction time of 3 hours and a reaction temperature of 80^oC.

The methyl esters obtained from the transesterification reaction were further analyzed using GCMS. This analysis produces chromatogram peaks, each of which shows a specific type of methyl ester. The results of the GCMS biodiesel adsorption results are shown in Figure 7:

Based on the results of Fig. 4, there are 2 dominant peaks, the main components contained in biodiesel samples are methyl hexadecanoate and cis methyl-9-octadecenoate.

From these data it can be stated that biodiesel compounds are indeed true, i.e. methyl esters. Analysis with GCMS shows that there are no free fatty acid compounds contained in biodiesel. This shows that the adsorption process is able to produce biodiesel in the form of methyl esters [9-10].

Density testing was carried out using a picnometer with a liquid temperature of 40oC according to SNI 2015 standards. The limit of biodiesel density according to SNI-7182: 2015 is 0.850-0.890 g / m3. The test results obtained on biodiesel produced amounted to 0.8728 grams / m3. This figure shows that the density of the biodiesel products produced has met the SNI standards on biodiesel.

In addition to the density test, a moisture content test was carried out on biodiesel. To find out the water content in biodiesel, the mass difference calculation of biodiesel is done before and after the evaporation process is carried out at 100^{o}C for an hour. From the process, the moisture or water content data of 0.02% was obtained.

Acid numbers determine the quality of biodiesel, in the process of transesterification of fatty acids with a catalyst to form a reaction to form soap. The indicator to find out the soap content is by knowing the free fatty acid value of 0.28 mgKOH/g, the number indicates that the acid number in the biodiesel has met the Indonesian National Standard (SNI) where SNI for acid numbers in biodiesel is 0.5 mgKOH/g.

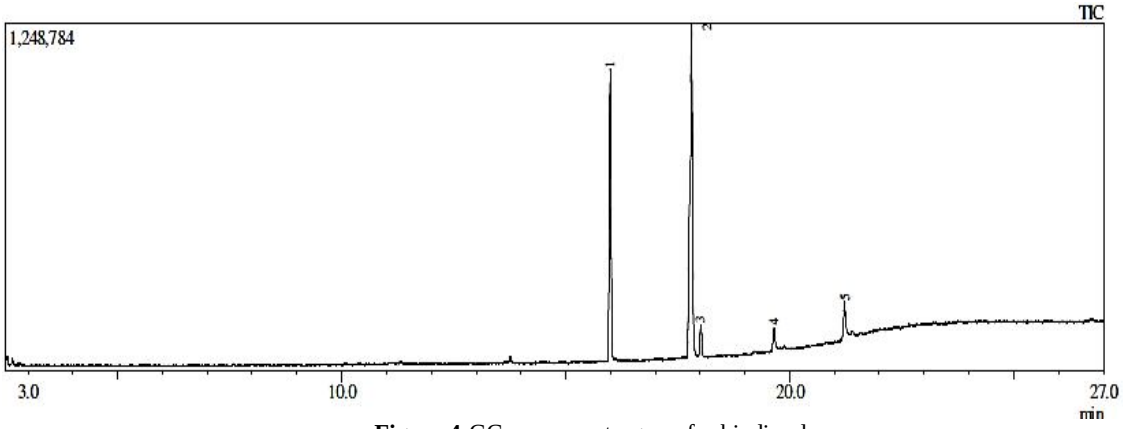

Figure 4:GC mass spectrogram for biodiesel

4. CONCLUSIONS

Based on the results of research that has been done, it can be concluded as follows:

1. H_2SO_4 activated coal fly ash catalyst is very influential on the yield of biodiesel produced
2. Biodiesel can be synthesized from waste cooking oil with sunflower oil with a ratio of 3: 1 oil through two stages, namely esterification and trans-esterification. From 27 mL of used cooking oil and sunflower oil, there was 22 mL of biodiesel or 81.48%
3. The results of biodiesel synthesis are indeed identical to biodiesel. This can be seen in the GC-MS results, from the gas chromatogram and mass spectrum that have been adjusted to the data base, there are two methyl ester compounds (biodiesel),i.e. methyl hexadecanoate and cis methyl-9-octadecenoate
4. The greater the weight of the catalyst will reduce the biodiesel yield because it causes a saponification reaction, while for the molar ratio of oil: methanol the greater the ratio the higher the yield, but if it is too large the ratio will interfere with the formation of biodiesel
5. The results of testing the density, acid number, and moisture content have met the SNI standard.

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