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Transesterification and Physical Properties of Fatty Acid Methyl Ester from Rubber Seed Oil.

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ABSTRACT

Biodiesel from rubber seed oil has been successfully synthesized through two-stage transesterification. The first stage is the pre esterification with catalyst H₂SO₄ to obtained fatty acids methyl ester, the second stage transesterification using KOH catalyst and biodiesel maximum was found 97.55%. Analysis GC-MS results of rubber seed oil biodiesel consists of methyl palmitate, methyl linoleate, methyl stearate, methyl arakhidat, and methyl behenate. Characterization of rubber seed oil biodiesel was obtained kinematic viscosity at 40°C = 5.49 cSt, density: 0.857, 0.822 and 0.804 g/cm³ at: 15 °C, room temperature and 40 °C respectively. Distillation characteristics 245.6 °C, 348.3 °C and 368 °C for T10, T50 and T90 respectively. Pour point 7 °C, cetane number 54.06 and water content 0.0279 %, overall the results of the transformation characteristics of rubber seed oil biodiesel have met the requirements set standard ASTM.

Keywords: Transesterification, Rubber seed oil, Biodiesel, Fatty acid methyl ester.

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INTRODUCTION

The use and utilization of energy derived from natural energy sources materials unrenewable such as petroleum, natural gas and coal should be reduced and reduced reserves of energy considering this type diminishing returns and the impact on the environment as a result of its use [1-3].

More over biodiesel has gained significant attention as it is a renewable, biodegradable, less pollutant emitting, non-toxic and more environmentally friendly fuel source as compared with the fossil diesel fuel available at present. It is a renewable and biodegradable fuel that consists of fatty acid methyl esters (FAMES). It is carbon neutral because the carbon content in the exhaust is equal to the amount initially fixed from the atmosphere. Most of the research activities reported so far is about the production of the biodiesel from the edible oils and fats [4-7].

Biodiesel is defined as the mono alkyl esters (methyl and ethyl esters) of long chain fatty acids derived from vegetable oils or animal fats, for use in compression-ignition (diesel) engines. It is formed from transesterification of vegetable oils with methanol (or ethanol). Biodiesel has many merits as a renewable energy resource that include being derived from a renewable, domestic resource, thereby relieving reliance on petroleum fuel, and it is biodegradable and non-toxic. Further, compared to petroleum-based diesel, biodiesel has a more favourable combustion emission profile, such as low emissions of carbon monoxide, particulate matter and unburned hydrocarbons. In addition, using biodiesel on a large scale will promote plantations of crops used to produce its feedstock. This would result in more carbon dioxide recycling by photosynthesis, thereby minimizing the impact on the geenhouse effect. Biodiesel has a relatively high flash point (150 °C), which makes it less volatile 1 and safer to transport or handle than petroleum diesel [8-11].

Some renewable energy sources and renewable materials have been found and promises, which are plant oils such as palm oil, coconut oil, jatropha oil, and castor oil. In Indonesia, one source of vegetables that is highly prospective for use as raw material for biodiesel is the rubber seed [12]. The results from the sap of the rubber plantations and fruit. Until now only the rubber is widely used. In addition to seeds, can be taken rubber seed and its meal oil [13]. Indonesia is the largest rubber producing countries in the World. Based on statistical data, extensive rubber plantations in Indonesia reached an estimated 3,318,105 ha and is capable of producing rubber seed oil for 25.622.406,8 L/year to date, has not been widely used rubber seeds [14].

In this work, rubber seed oil has been isolated and transformed into biodiesel through two stage transesterification method. The products were characterized via GC-MS, viscosity, density, distillation characteristics, cetane number, pour point and water content.

MATERIALS AND METHODS

Rubber seed (Figure 1), potassium hydroxide (Merck), acetic acid (Merck), methanol (Merck), anhydrous magnesium sulfate (Merck), sulfuric acid (Merck) and the solvent petroleum ether (Merck).



Figure 1: Rubber seeds before peeled (a) and after peeled (b).

Rubber seeds was boiled at 80 °C and then dried and then crushed. Extraction process executed by the solvent extraction method sokhlet using petroleum ether. The extraction is run for 4 hours. The results of

the extraction of petroleum ether was distilled to remove the residue and dried in an oven at 105 °C. The results of the extraction put in desiccator that has been filled with anhydrous calcium chloride. The oil obtained was then filtered and put in a erlenmeyer flask for subsequent analysis.

The first stage transesterification with catalyst H₂SO₄.

Methanol 20 ml was added to the distillation flask of 500 ml capacity equipped with a magnetic stirrer and concentrated sulfuric acid is added as much as 0.6 ml, the mixture was cooled and then added 120 ml of oil, the mixture is stirred and refluxed for 4 hours at 90 °C. The results of reflux put into a separating funnel. The bottom layer is the glycerol and the top layer is fatty acid methyl ester. The bottom layer is separated from the top layer. The top layer was made for transesterification process by KOH catalyst.

The second stage transesterification with catalyst KOH.

Methanol 11 5 ml has incorporated into the three-neck flask 200 ml capacity equipped with a magnetic stirrer and then added KOH. The mixture was heated and stirred until dissolved then added 45 ml of the oil, the mixture was stirred and refluxed for 2 hours. The results of reflux put into a separating funnel. The bottom layer containing glycerol while the top layer is mixture of esters. The top layer was washed with acetic acid and distilled water until neutral. Ester layer coupled with anhydrous MgSO₄ aimed to absorb the remaining water. This procedure has repeated for variations of KOH 0.2001 g, 0.3015 g, 0.3987 g, 0.5003 g and 0.6011 g.

Characterizations

Identification of the constituent components of biodiesel by GC-MS, chromatogram and spectra from the analysis GC-MS were compared against a reference standard of the bank-the National Institute of Standards Technology (NIST) -62 Library (62 entries). 229 Willey Library and Library Pesticid.

Determination of the viscosity (η) of the oil carried by the ball viscometer (*haake*), kinematic viscosity was calculated by the formula: $v = \eta/\rho$, v = kinematic viscosity (cSt), η = dynamic viscosity (mPa.s), ρ = biodiesel density (g/cm³). Oil density has determined using a pycnometer. Determination of distillation characteristics, biodiesel incorporated into tubes containing biodiesel and then placed into a reactor equipped with a heater and thermocouple connected to the condenser. The reactor was heated at 500 °C. Temperature measurement has done at the time of distillate volume has reached 10%, 50% and 90% of the sample volume. Determination of cetane number based on equation ASTM D-976. Determination of pour point of biodiesel, biodiesel has inserted into a test tube, then put in the freezer. Test tubes containing biodiesel observed each 5 minutes. Furthermore, the temperature recorded at the time of biodiesel began to form a gel (no longer pourable) which means that biodiesel has reached the pour point of biodiesel. Determination of water content performed by gravimetric methods.

RESULTS AND DISCUSSION

At stage of the transesterification catalyst concentrated sulfuric acid at 90 °C for 4 hours, it aims to reduce the free fatty acid content dropped to 2%. At the end of the reaction obtained two layers where the bottom layer is then separated from the glycerol which is the top layer of fatty acid methyl esters. In this research note that the raw material for rubber seed oil, effective molar ratios between oil and methanol are 6:1 and concentrated sulfuric acid catalyst 0.667% by volume of oil used is a optimum conversion with a yield of fatty acids produced 95.83%. The aims this stage, transesterification with catalyst concentrated sulfuric acid to reduce free fatty acid content dropped to 2%. Previous transesterification have been reported and a reaction temperature near the boiling point of the alcohol (e.g. 60 °C for methanol) and a 6:1 molar ratio of alcohol to oil were recommended [15-17].

Transesterification on the catalyst potassium hydroxide (KOH) was conducted to determine the effect of the amount of the base catalyst is added to the volume of biodiesel produced. In this study, the second stage of the transesterification reaction carried out with molar ratios between fatty acids and methanol 9:1 with KOH catalyst 0.2001 g, 0.3015 g, 0.3987 g, 0.003 g and 0.6011 g for 2 hours at 65 °C. At the end of the reaction layer formed over two layers which are separated methyl esters, methyl ester was washed with

distilled water until neutral and then carried out the process of drying and filtration. Variations amount of KOH as catalyst was used to the yield of biodiesel produced showed that the increase or decrease the amount of catalyst used is influential on the yield of biodiesel produced. To know the effect of the amount of potassium hydroxide catalyst used to the volume of biodiesel produced showed in Figure 2.

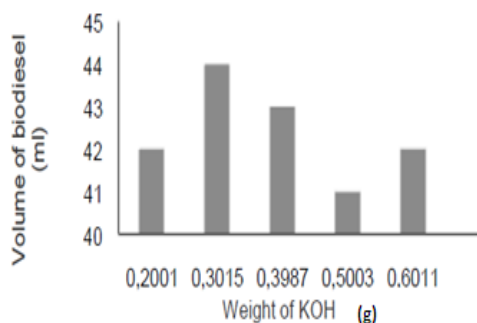


Figure 2: Influence the amount of catalyst on the volume of biodiesel

The volume of biodiesel increased with the addition of a catalyst to achieve optimum conditions. Furthermore, the volume of biodiesel decreased with the addition of KOH catalyst. This is probably caused by an excess amount of catalyst or possibly at the beginning of the mixing KOH catalyst, catalyst not soluble in methanol resulting in direct contact between KOH with oil so that there is a saponification reaction. From the measurement volume is known that the volume of the largest biodiesel obtained on the addition of 0.3015 g KOH catalyst is 43.9 ml, these results suggest that the second stage of the transesterification reaction, total of 97.55% fatty acid reaction products first stage converted into methyl esters (biodiesel). The alkali-catalyzed system was studied and the reaction mechanism was formulated [18]. A commercial continuous alkali-catalyzed transesterification process to produce methyl esters on an industrial scale under high pressure (90 bar) and at high temperature (240 °C) was demonstrated [19].

From the analysis chromatogram has known that biodiesel results of the transformation of rubber seed oil has 14 peaks were detected at different retention times, which are listed in Figure 3.

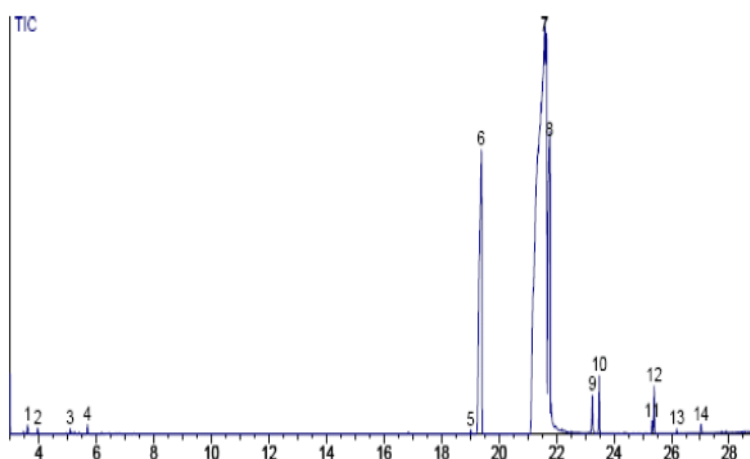


Figure 3: The chromatogram GC of rubber seed oil.

These peaks are identified using mass spectroscopy to know the similarities and the fragmentation pattern of the molecular weight of the compounds identified by the fragmentation pattern and molecular weight compounds. The results of the identification of the components making up the biodiesel methyl esters of rubber seed oil transformation results are listed in Table 1. It appears there are 8 peaks can be identified

from the 14 peak. Peaks are identified peaks 1, 6, 7, 8, 10 and 11, the sixth peak is identified constituent components of biodiesel methyl esters of rubber seed oil is methyl palmitate, methyl linoleate, methyl stearate, methyl arakhidat, and methyl behenate.

Table 1: Components of methyl esters of rubber seed oil (biodiesel).

No. of Peak	Components	Formula of Molecule	Retention time (minute)	Conc. (%)
1	Dimethyl benzene	C ₈ H ₁₀	3.608	0.16
2	Not identified	-	3.956	0.09
3	Not identified	-	5.083	0.05
4	Not identified	-	5.692	0.12
5	Not identified	-	19.018	0.06
6	Methyl palmitate	C ₁₇ H ₃₄ O ₂	19.383	13.68
7	methyl linoleate	C ₁₉ H ₃₄ O ₂	21.592	72.12
8	Methyl stearate	C ₁₉ H ₃₈ O ₂	21.758	11.21
9	Not identified	-	23.250	0.66
10	Methyl arakhidat	C ₂₁ H ₄₂ O ₂	25.492	0.81
11	Methyl behenate	C ₂₃ H ₄₆ O ₂	25.325	0.18
12	Not identified	-	25.400	0.67
13	Not identified	-	26.183	0.05
14	Not identified	-	27.033	0.13

From the test results, it is known that before it is transformed into methyl esters of rubber seed oil viscosity at 40 °C is 27.76 cSt. After transformed into methyl esters (biodiesel) through a two stage transesterification reaction, the oil viscosity decreased significantly. Biodiesel viscosity at 40 °C is 5.49 cSt. These results indicate that the biodiesel meets the standards of ASTM, both set limits to the characteristics of the diesel oil from petroleum viscosity maximum is 6.5 cSt. Various viscosity of biodiesel from vegetables oil been reported [7, 11, 12].

Viscosity is one of the physical properties that are important for diesel engine fuel. Viscosity is very influential on the ease of drainage system through the fuel injection pump, if the viscosity is too high biodiesel use can complicate the process of formation of a gain of fog at the time of atomization of fuel into the engine so it will cause incomplete combustion process but if the viscosity of the material too low can result in fuel leakage at the fuel injection pump. Both of these can cause problems in diesel engines, so the value of the viscosity of the fuel is one of the essential requirements in the standard and quality of biodiesel.

The density of a fuel can be defined as the ratio of the mass of fuel to the fuel volume at a given temperature. In this study the density measurement is performed on a laboratory scale using a pycnometer. Density testing is performed at three different temperature levels at 15 °C, room temperature and at 40 °C. Density at 40 °C is used to calculate the viscosity of biodiesel at 40 °C. While the value of the density at 15 °C was used in the calculation of cetane number of biodiesel. Density at 15 °C is 0.857 g/cm³ while the density at room temperature is 0.822 g/cm³ and density at 40 °C is 0.804 g/cm³. From these data it can be seen that the lower the temperature measurements taken, the greater the density of biodiesel obtained. Referring to the ASTM standard, that only the density at 15 °C which is one of the requirements of diesel oil from petroleum. The results were obtained at 15 °C density have met the standards established by ASTM where the density characteristic imposes limits on the temperature of 15 °C for diesel fuel is 0.80 up to 0.90 g/cm³. Density results of this study are similar to previous studies [7, 11, 12].

Distillation temperature is volatility or the tendency of a liquid turns into a gas phase. Volatility is not directly and closely related to the economic factors of diesel fuel. Distillation temperature also affects the viscosity, flash point and cetane number of the fuel. Volatility medium (50% recovery) related to the likelihood of smoke, it may be caused by the influence of fuel injection and mixing that causes incomplete combustion. Distillation temperature measurement at the time of distillate evaporates as much as 10%, 50% and 90% by volume, should be done with test method ASTM D-86. In this study, the determination of distillation characteristics was performed using a simple distillation column designed himself. It was observed that the average temperature at the time of distillate has reached 10%, 50%, and 90% for 368 °C, 245.6 °C, and 348.3 °C respectively.

Based on the Indonesia standard and the quality of biodiesel in Indonesia, no longer include the temperature limits for 10% and 50% by volume, but only imposes limits maximum heating temperature (T90), which amounted to 370 °C.

Cetane number is a measure of the ignition quality of biodiesel in the compressed state. Cetane number than conventional biodiesel is influenced by the structure of its constituent molecules. Cetane number of biodiesel also vary widely depending on the components of the primary constituent such as for biodiesel methyl esters of palmitate and stearic fatty acids have a cetane number to 75, while the cetane number of methyl linoleic only reached 33. Biodiesel consists of various components, the cetane number of total methyl esters have been calculated using the equation $CN = CI - 2$ which cetane index (CI) was calculated by the equation ASTM D-976 which is a correlation between Density 15 °C and the evaporation temperature of 50% by volume. ASTM D-976 equation used is valid for biodiesel, methyl ester and a mixture of methyl ester with biodiesel. Cetane number of biodiesel from rubber seed oil was 54.06. Referring to both biodiesel quality standards set by ASTM which requires cetane number for diesel fuel is at least 40, then the biodiesel has qualified defined. Cetane number from this research similar to cetane number of various vegetables that have been reported [11]. From the test results pour point of biodiesel is known that the pour point of biodiesel from rubber seed oil is at 7 °C, this means that the pour point of rubber seed oil biodiesel 3 degrees lower when compared with diesel oil from petroleum in general which has a pour point of 10 °C. Based on Indonesia standards set in 2006 where the characteristic pour point of petroleum maximum of 18 °C.

Biodiesel is made from rubber seed oil has water content of 0.0279%. By comparison with the ASTM standards, to the characteristics of the water content of diesel fuel is allowed for maximum of 0.05%, so it can be said that the biodiesel from rubber seed oil that meets the requirements specified above both fuel standard [7, 11,12]. Water content contained in diesel fuel in small quantities, especially in hot climate countries is actually not very harmful for the engine. Because the small amounts of water to form a dispersion of the fuel will evaporate after the engine in hot conditions. However, in winter countries, the water content contained in the fuel can block the flow of fuel into the engine. In addition, the presence of water in the engine will cause corrosion [7, 11, 12, 13,18].

CONCLUSIONS

In the present work , we have performed isolation and transformation of rubber seed oil into biodiesel through the transesterification reaction of two stages. In the first stage of the transesterification conversion of fatty acids methyl esters were obtained 95.83 % and the second stage the transesterification catalyst 0.3015 g KOH obtained the optimum yield 97.55 % . Characterization test results are known that rubber seed oil biodiesel has a water content of 0.0279 % , kinematic viscosity at 40 °C 5.49 cSt. Density at 15 °C, at room temperature and 40 °C were 0.857 g/cm³ , 0.822 g/cm³ and 0.804 g/cm³ respectively. Distillation characteristics 245.6 °C , 348.3 °C and 368 °C for T10 , T50 and T90 , respectively. The pour point of biodiesel from rubber seed oil is at 7 °C, and cetane number 54.06 . The results of GC-MS analysis of methyl esters have known that the constituent components of biodiesel are methyl linoleic 72.12 % , methyl palmitate 13.68 % and methyl stearate 11.21 % . Overall the results of the transformation of biodiesel characteristics of rubber seed oil meets the requirements specified ASTM standards.

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