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Biodiesel Production from Crude Palm Oil Using Kapok Skin KOH (*Ceiba Pentandra*) Catalyst as Solid Green Catalyst

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ABSTRACT

Biodiesel is one type of renewable alternative energy that has great potential to be developed. Biodiesel is a fuel consisting of a mixture of mono-alkyl esters of long-chain fatty acids made from renewable sources, such as vegetable oils or animal fats, one of which is crude palm oil (CPO). Crude palm oil contains free fatty acids in high levels, so treatment is needed to reduce free fatty acids by a reaction known as the esterification reaction. Then, the transesterification process is carried out to produce biodiesel (methyl ester). The purpose of this study was to analyze the effect of catalyst mass, a mole ratio of CPO to moles of methanol and the effect of adding THF co-solvent to biodiesel purity. The catalyst used is a heterogeneous catalyst from kapok fruit peel waste. Kapok fruit rind was calcined at 700°C for 8 hours. The independent variable varied the mole ratio of oil to methanol in a 1:4 ratio; 1:6; 1:8; and 1:10 with a catalyst weight variation of 3 and 4%. Meanwhile, for the addition of co-solvent, variations of THF: methanol v/v 1:1 and 2:1, were carried out. The biodiesel properties such as density, viscosity, water content and acid number, were evaluated and compared with the Indonesian National Standard. The results showed that the transesterification reaction with the addition of co-solvent resulted in a higher methyl ester content than that without the addition of co-solvent. The highest yield of methyl ester without the addition of co-solvent was 79.16%, while the yield of the methyl ester with the addition of THF co-solvent with a ratio of 1:1 and 2:1 v/v to methanol was 90.09 and 94.09%, respectively. The highest methyl ester content (94.09%) was achieved by the addition of THF: methanol = 2:1, CPO: methanol molar ratio = 1:6 and 4 wt% catalyst weight. The results obtained in this study indicate that a green catalyst made from kapok skin can be used to produce biodiesel and also the addition of co-solvent can increase the yield of methyl esters, so that high purity is obtained.

Keywords: biodiesel; crude palm oil; high purity; *Ceiba Pentandra*; THF.

INTRODUCTION

The rate of population growth and GDP (Gross Domestic Product) is the cause of the increasing world energy demand. Fossil energy sources, especially petroleum, require people to look for other alternatives as energy sources. In the search for new energy sources, much attention is focused on biomass as a renewable and usable source capable of meeting most of the energy needs (Fan et al., 2009; Meher et al., 2006). Currently, biodiesel is considered as an alternative fuel to replace diesel fuel because of its advantages. Over the years, various efforts have been made to save our world through the provision of environmentally friendly alternative energy sources. Biodiesel is a clean-burning fuel derived from renewable raw materials such as animal fats or oils. Biodiesel production being developed today generally comes from vegetable oils (soybean oil, canola oil, rapeseed oil, crude palm oil), animal fats (beef fat, lard, chicken fat, lard) even from spent cooking oil (yellow oil) (Fan et al., 2009). Currently, the development of biofuels is more focused on increasing the production of raw materials and developing new heterogeneous catalysts (Ueki et al., 2011). The availability of raw materials and production catalysts is the greatest challenge facing the biofuel industry worldwide (Altes, 1989; Ueki et al., 2011; Yuji, Ueki., Tamada, 2009). Crude palm oil is one of the vegetable oil products that can be used as raw material for making biodiesel. Crude palm oil is the basic crude product obtained through the extraction of the oil palm fruit. Crude palm oil contains high levels of free fatty acids. The way that can be done to reduce free fatty acids is by reacting free fatty acids with alcohol with the help of a strong acid catalyst. This reaction is known as an esterification reaction. The esterification process aims to reduce the activation energy with the help of an acid catalyst such as sulfuric acid (H_2SO_4) (Altes, 1989; Bodger et al., 1982). Biodiesel from CPO oil can be made through a transesterification reaction assisted by using a heterogeneous catalyst. The heterogeneous catalyst that is often used is potassium. One of the materials that have the potential to be used as a catalyst due to its less than optimal utilization is kapok skin.

Kapok (*Ceiba Pentandra*) is a plant that grows in the tropics. The kapok tree has been used for the manufacturing of containers, plywood, furniture, and raw material for making paper. Kapok fiber has been used in the manufacturing of mattresses, whereas commercial fiber sources and the seeds are used as an oil; in turn, the skin tends to be discarded. Kapok fruit peel ash contains 50.78% potassium carbonate (K_2CO_3), 26.27% sodium carbonate (Na_2CO_3) and 4.37% sodium hydroxide (NaOH) (Kolakaningrum et al., 2021; Turner, 2005). On the basis of the background described above, it is planned to conduct research on the production of biodiesel from high purity CPO using a natural catalyst from kapok fruit peel with the addition of tetrahydrofuran (THF) as co-solvent and using a simple, low-temperature single reactor to produce biodiesel products. which has high purity.

The use of co-solvent is an appropriate alternative to overcome the problem of solubility. A single-phase reaction can be formed by adding a solvent that can increase the solubility of the oil, the solvent hereinafter referred to as a co-solvent (Mahajan et al., 2006). The co-solvent is highly soluble in alcohol, fatty acids and triglycerides. The selected co-solvent has a boiling point close to methanol which can facilitate the separation process at the end of the reaction. Several co-solvents have been used for the transesterification reaction, including n-hexane, diethyl ether, acetone, 2-propanol, tetrahydrofuran, or ethyl acetate. This study aimed to investigate the effect of CPO: methanol feed ratio on biodiesel yield, and the addition of co-solvent on biodiesel yield using heterogeneous catalysts from kapok fruit peel, as well as determine the methyl ester content contained in biodiesel by GC-MS analysis and the characteristics of the catalyst using FTIR, XRD, and SEM.

METHODOLOGY

Materials

The main ingredient of this research is crude palm oil. The reagents used in this study were 96% methanol, tetrahydrofuran, aquadest, PP (Phenoftalin) indicator, NaOH, H_2SO_4, and KOH. Kapok skin is used as a catalyst for the transesterification process. The reaction was carried out on a laboratory scale using a three-necked round bottom flask equipped with a back cooler, thermometer and magnetic stirrer.

Preparation of CPO and Kapok Skin

Preparation of raw materials was carried out by screening Crude Plam Oil using filter paper and Performing FFA analysis on Crude Plam Oil. The crude palm oil used as raw material in the study had an initial %FFA of 5.2 wt%; thus, pretreatment was necessary to reduce its fatty acid content. The method chosen is the esterification reaction with the reaction conditions: the amount of 0.5 wt% H_2SO_4 catalyst against oil, a reaction time of 2 hours, 60°C and atmospheric pressure. After the esterification reaction, the fatty acid content in the oil will decrease. The kapok fruit skin was cleaned and then dried in an oven at a temperature of 110°C ± 4 hours, then placed into a furnace at a temperature of ± 700°C for ± 8 hours, then placed into a desiccator. After drying, the kapok skin was used as a catalyst.

Transesterification process

CPO was placed in a three-neck flask, heat the oil at a temperature of up to 60°C. The kapok fruit peel powder catalyst was dissolved in methanol, a solution of kapok skin powder, methanol and THF with a ratio of THF: Methanol 1:1 and 2:1 v/v was added, the magnetic stirrer was turned on at 250 rpm for 60 minutes. After the reaction time was reached, the solution mixture was filtered from the heterogeneous catalyst, then the mixture was separated using a separating funnel and left to stand for 24 hours. The separated biodiesel was then purified by a distillation process which aims to separate biodiesel from methanol and water.

Characterization

The tests performed percent yield to compare the weight of CPO and biodiesel weight and density using a pycnometer. Furthermore, characteristic testing using the Fourier Transform Infrared FTIR) spectroscopy is used to analyze functional groups of materials as well as theinteractions between groups. Before modification, the samples tested with KBr were used as background in the analysis of the powder (solid) samples and infrared wavelengths in the range of 600 cm^{-1} to 4000 cm^{-1}. Meanwhile, 50% of the sample weight was homogenized with 50% KBr using a mortar and then pressed into the cell in the Shimadzu IRPrestige-21 spectrophotometer. Morphological analysis was conducted using Scanning Electron Microscope (SEM) JEOL-6510 – LA. In order to determine the crystal size, the Shimadzu XRD-D7000 device, equipped with a Maxima X-Ray Diffractometer where X-rays are scanned continuously from an angle of 10 to 80 degrees 2-theta at a speed of 2.0 degrees per minute, was used. The target X-ray tube was Cu with a voltage of 40.0 kV and a current of 30.0 mA. The two samples were crushed with pestle and mortar before being placed in a stainless-steel sample holder. To determine the fatty acid composition contained in biodiesel, an analysis of the Gas Chromatography-Mass Spectrophotometer (GC-MS) was carried out.

RESULTS AND DISCUSSION

Methyl ester yield

In this study, the ratio of reactants of CPO: methanol was varied: 1:4, 1:6, 1:8, and 1:10 with variations in weight of kapok fruit rind catalyst, 3% and 4% by weight of oil. Variations in the ratio of co-solvent (THF): methanol 2:1 and 1:1 and without the addition of co-solvent. This can be seen in Figure 1.

Figure 1 shows a comparison of the two weight variations of the catalyst to the oil. From the figure above, it can be concluded that with a larger weight of the catalyst, the resulting yield is greater. With a catalyst weight of 4% from each mole ratio of oil: methanol, everything looks superior, this can be seen in the molar ratio of 1:10 by weight of the catalyst with 3% the yield reaches 72.6%, while with a catalyst weight of 4% the yield reaches 74.2%. The catalyst serves to speed up the reaction by lowering the activation energy but does not affect the equilibrium position. In addition, the use of alkaline catalysts in large quantities can neutralize free fatty acids in triglycerides. Thus, the greater the amount of base catalyst used, the more methyl esters formed (Jumina et al., 2021; Konur, 2021).

Figure 2 show the yield of biodiesel (%) with a ratio of THF: Methanol 2:1 has a higher yield than the ratio of 1:1. This is because the more co-solvents, the easier it will be to dissolve fatty acids into methyl esters. The largest biodiesel yield was produced from a 1:6 mole ratio with a THF: Methanol ratio of 2:1, which was 94.09%. The yield was higher than that obtained by Jitputti et al. with the same molar ratio and reaction time

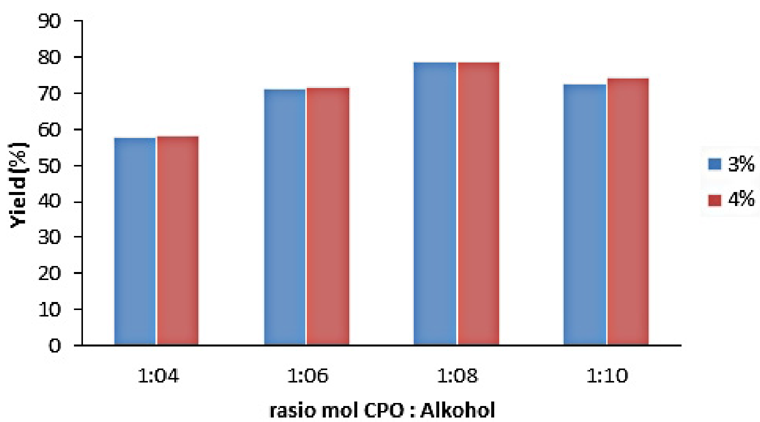


Figure 1. Biodiesel yield without the addition of co-solvent with two variations of catalyst weight

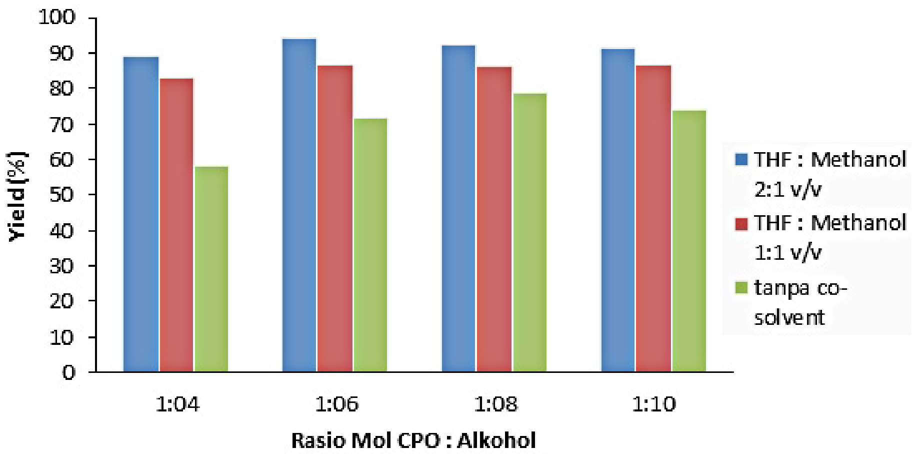


Figure 2. Biodiesel yield with a ratio of THF: Methanol 1:1 and 2:1 and without the addition of co-solvent with a catalyst weight of 4%

(Jitputti et al., 2006). The yield of biodiesel (%) with a ratio of THF: Methanol 2:1 has a higher yield than the ratio of 1:1. This is because the more co-solvents there are, the easier it will be to dissolve fatty acids into methyl esters. The largest biodiesel yield was produced from a 1:6 mole ratio with a THF: Methanol ratio of 2:1, which was 94.09%. The yield is higher than that obtained by Jitputti et al. with the same molar ratio and reaction time (Jitputti et al., 2006). The density of the biodiesel produced was found to be between 0.804 to 0.893 g/ml, and was close to that of biodiesel from cottonseed oil, soybean oil, peanut oil, palm oil, and sunflower oil, 0.885, 0.883, 0.880 and 0.860 g/ml, respectively (Sakarkar et al., 2012).

Fourier Transform Infrared

FTIR (Fourier Transform InfraRed) spectroscopy was used to understand the functional groups and their molecular bond structures in the range of 4000 cm^{-1} to 400 cm^{-1}. The function of FTIR is to determine the functional groups present in the kapok fruit peel waste catalyst. In this study, the catalyst activation process was carried out on the kapok fruit skin thermally using a furnace at a temperature of 700°C for 8 hours. In this case, the buffer function of the calcination of kapok fruit peel powder is used as a heterogeneous catalyst. Figure 3 shows the FTIR analysis of kapok rind powder. The appearance of the C-Br (Alkyl Halide) functional group is indicated at the wavenumber

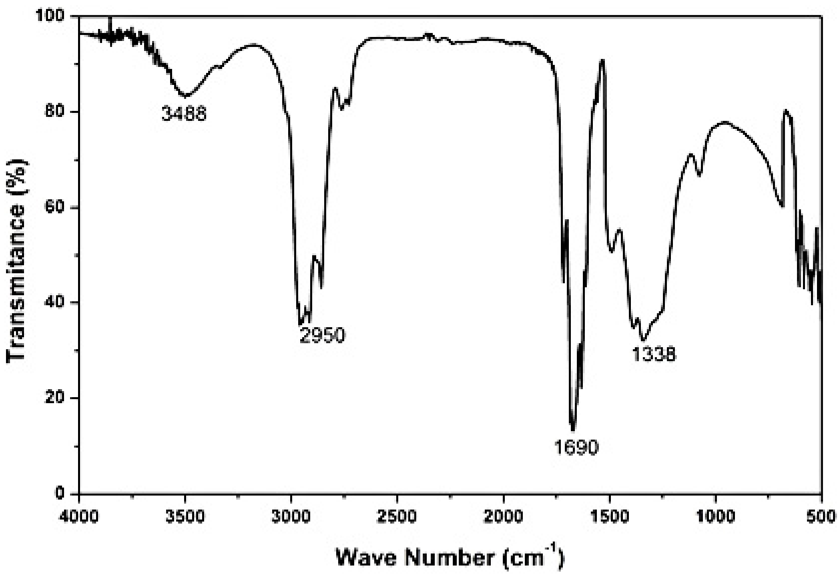


Figure 3. Results of FTIR analysis of catalyst

of 636.51 cm^{-1} and the C=C alkene (lignin) functional group, where this group is indicated at the wavenumber of 983.70 cm^{-1}. The peak of 1296.16 cm^{-1} was characterized as a stretching C-O structure of the functional groups of alcohols (cellulose, hemicellulose and lignin), carboxylic acids, esters and ethers. Then, at the peak of 1469.76 cm^{-1}, it was characterized as a C-H flexible bond from the alkane functional group (cellulose, hemicellulose and lignin). The appearance of a peak at the 1747.51 cm^{-1} waves indicates the presence of a C=O (Aldehyde/ketone/carboxylic acid) functional group. In the double bond region (1950–1550 cm^{-1}), stretching vibrations of the carbonyl groups can be characterized here, such as aldehydes, acids, aminola, carbonates, indicated at a wave value of 1924.96 cm^{-1} in the presence of the C=C functional group =C. At the wave value of 2252.86 cm^{-1}, there is a functional group N=C=O (Isocyanate).

The peak in the hydrogen stretching region (3700–2700 cm^{-1}), occurs due to the stretching vibration of the hydrogen atom with other atoms. The frequency is so much greater than the interaction is negligible. The absorption peak occurs in the 3700-3100 cm^{-1} region due to stretching vibrations of O-H or N-H (Algharib et al., 2021). After that, another wavelength appears at the peak of the wave 3200–3800 cm^{-1} which may indicate the presence of the O-H functional group hydrogen/phenol bond alcohol, which usually appears at that wavelength.

Crystal size and morphology analysis

Figure 4 shows that there are six prominent components in this catalyst sample, namely potassium sulfate, sodium cadmium sulfate, sodium silicate, potassium carbonate, potassium chloride and calcium carbonate. These components are found in the activated kapok fruit skin. XRD test showed that the preparation of potassium catalyst which was calcined at 700°C for 8 hours had not been successfully formed. With high potassium content, kapok rind powder can be used as a catalyst in the manufacture of the transesterification process in the manufacturing of biodiesel from CPO, this is also evidenced by the formation of methyl esters from CPO. From Figure 5, it can be seen that the surface profile of the catalyst at 1000× magnification shows that the surface structure tends to be rough and agglomerated, while after being enlarged to 5000×, it shows the presence of pores that are covered by irregular surface structures.

GC-MS

To determine the fatty acid composition contained in biodiesel, a GC-MS. analysis was performed. The results of the GC-MS from Figure 6 analysis showed that the methyl ester compounds obtained in biodiesel were methyl laurate, methyl palmitate, methyl linoleate, methyl oleate, and methyl stearate. The methyl ester compounds obtained are partially in accordance with the fatty acid content found in palm oil (Kuan et al., 2019) which is a by-product of incineration process from palm oil industry, creates environmental sustainability issues. This is due to the method of handling solid waste material of industry by simply dumping it on an open land area. The previous study of POCM including physical and mechanical properties of solid present showed promising results of utilizing POCM as a packing media for treatment

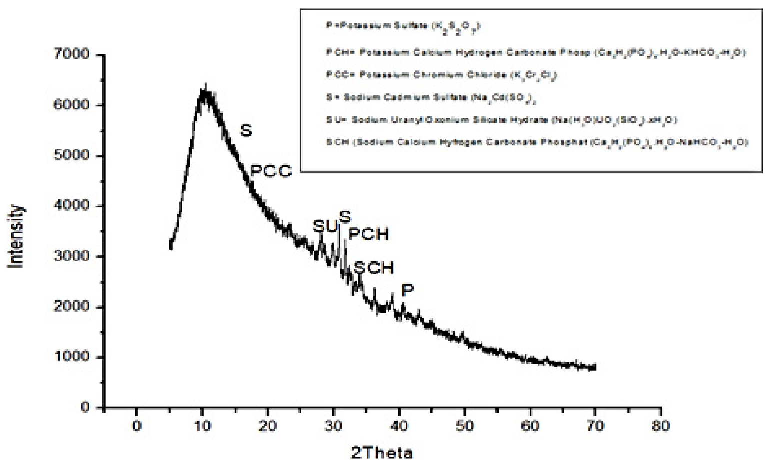


Figure 4. Results of XRD analysis of catalyst

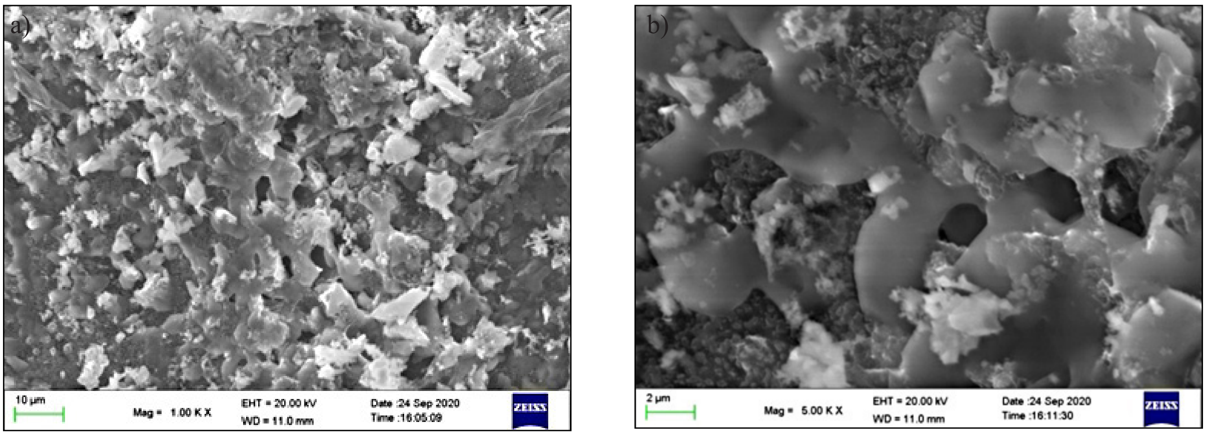
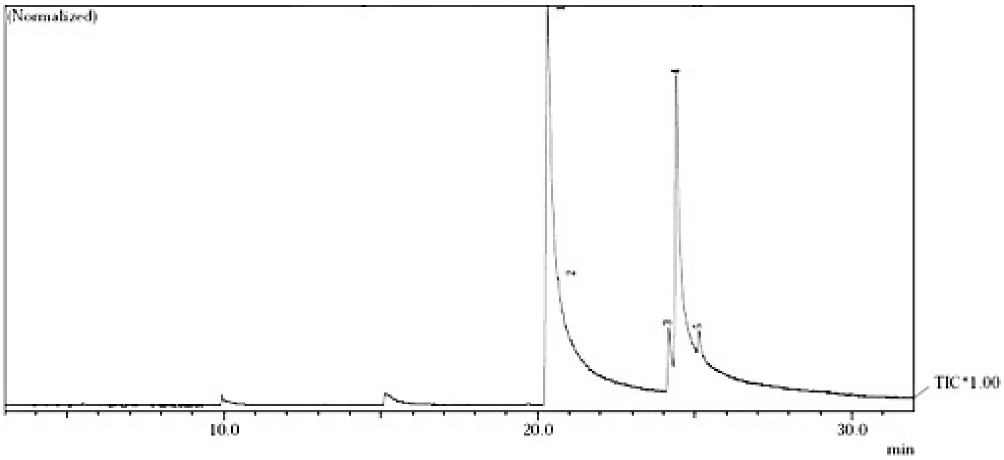


Figure 5. SEM of catalyst with magnification (a) 1000× (b) 5000×



Peak Report TIC

Peak#	R.Time	Area	Area%	Name
1	20.325	17468169	40.28	Hexadecanoic acid, methyl ester (CAS) Methyl palmitate $$ Methyl hexadecanoate
2	20.650	6615652	15.26	Hexadecanoic acid, methyl ester (CAS) Methyl palmitate $$ Methyl hexadecanoate
3	24.183	1672792	3.86	9,12-Octadecadienoic acid (Z,Z)-, methyl ester $$ Linoleic acid, methyl ester
4	24.411	13871262	31.99	9-Octadecenoic acid (Z)-, methyl ester (CAS) Methyl oleate $$ Oleic acid methyl ester
5	25.123	3736232	8.62	Cyclopentanetridecanoic acid, methyl ester (CAS) $$ Methyl dihydrochaulmoograte
		43364107	100.00	

Figure 6. GC-MS biodiesel analysis

of domestic wastewater industry. The packing media can be used in the process of biological wastewater treatment system in Sequencing Batch Reactor (SBR. The content of biodiesel can be calculated by comparing the area of methyl esters contained in biodiesel with the total area analyzed in the GC test. The biodiesel content obtained is with a purity of 94.75%.

CONCLUSIONS

The obtained data shows that the effect of adding co-solvent to the transesterification process can increase the yield. This can be seen during the transesterification process with a catalyst weight of 3% without the use of co-solvent, the maximum yield obtained was 78.69%, while with the addition of co-solvent THF: methanol in a ratio of 1:1 and 2:1, by 84.86% and 89.81%, respectively.

Meanwhile, the use of green catalysts derived from kapok fruit waste is effective for the transesterification process, because the yield obtained is quite large, which can reach 79.16% with 5% catalyst weight percent. As for the density and viscosity, almost all data are included in the SNI standard, which is 0.85–0.089 gr/ml respectively.

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