VOL. 11, NO. 1, JANUARY 2016 ISSN 1819-6608
ARPN Journal of Engineering and Applied Sciences

www.arpnjournals.com

IN SITU TRANSESTERIFICATION OF STERCULIA SEEDS TO PRODUCTION BIODIESEL

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ABSTRACT

Sterculia seeds is one of potential sources of vegetable oil. Oil from the sterculia seeds not classified as a food oil even though it contains highly unsaturated fatty acids. The main constituent fatty acids in the sterculia oil are sterculic acid. The existence of very large sterculic acids in the sterculia oil affect characteristics that are sensitive to heat. Therefore, to take advantage of this sterculia oil as raw material for biodiesel production, it is necessary to study the conversion of oil into biodiesel directly from the seeds. In this study the oil extraction process has been carried out simultaneously with the transesterification process in one unit *in-situ* transesterification, in order to shorten the stages of biodiesel production while maintaining the characteristics of the unsaturated fatty acids in the sterculia oil which then become the raw material transesterification reaction. Base on this research we can conclude that in-situ transesterification can be performed to convert the oil in sterculai seeds into biodiesel without oil extraction in advance, with product properties acid number in the range 1.064 -1.283, mg KOH / g sample, saponification numbers in the range 149.95-157.13 mg KOH / g sample, iodine numbers in the range 1275-6298, g I_2 / 100 g sample and the viscosity in the range of 0.036 to 0.026.

Keywords: in-situ transesterification, biodiesel, sterculia seeds.

INTRODUCTION

Sterculia seeds (Kepoh Seeds) has a weight in the range of 2-2.5 grams, containing 53-58% of the core grains total weight of seeds. The core seeds contain oil-fat high enough that 44-54% of weight, the rest is 23-24% protein, and 6-8% water (Pasae, 2010).

Sterculia oil can be turned into a gel when heated for 10 minutes at 250 °C. These changes result from the polymerization of the oil. Because of the tendency of the polymerization, the previous researchers recommend that the oil extraction and refining performed at low temperatures, through cold compression or by using a cold extraction solvent with boiling point less than 60 °C.

This oil contains high enough of unsaturated fatty acids with the main component of sterculic acid with the molecular formula $C_{19}H_{34}O$ as shown in Figure 1. These fatty acids can be used as ingredients of various industrial products such as cosmetics, soaps, shampoos, fabric softeners, paints, and plastics. Fatty acids in sterculia oil can also be used as a raw material for making biodiesel or additives (Pasae, 2013).

The main characteristics of the fatty oils from sterculia oil are specific gravity (40 °C) 0.9239, molecular weight 294.5 g/mol, saponification number 177.5 mg KOH/g sample, Iodine Numbers 74 g I_2/g sample. Constituent of fatty acids in weight percentace are 5-8% myristic acid, palmitic acid 8-11%, stearic acid 0-1%, 8-9% Oleic Acid, Linoleic Acid 2-3% and sterculic acid 69-73%.

Sterculic acid had a melting point of 18.2 to 18.3 °C and a refractive index (n_{25}) 1.4643. Very unstable in the Free State. Even at room temperature, the acid is polymerized into a liquid as thick as a colorless syrup. Conversion of sterculic acid most useful is to create branched fatty acids that utilize the unique presence of cyclic bonds in the chain sterculic acid by ring opening and converts metilen siclopropen group into the side chain in the form of methyl groups. Branched fatty acids have widespread use as an additive reduction in pour point and gatherers various components of lubricants, soap, softener textile/fabric, cosmetics, plastics, and food products. Conversion to branched fatty acids also produce metiloctadecanoic potential for widespread use in the industry.

Production process of biodiesel from sterculia seeds generally done through the stages of oil extraction from the seeds, oil refining, and transesterification of oil into biodiesel. Extraction step is generally done mechanically using expeller or hydraulic press, followed by extraction using a solvent. Crude oil purification by degumming and neutralization is done before the transesterification process. Degumming process carried out to removes gum or slime and colloidal suspensions such as phospholipids, carbohydrates and nitrogen compounds contained in the crude oil. After extraction and purification stages, the next stage is transesterification. Transesterification reaction is carried out to obtain biodiesel often called alcoholysis reaction. This reaction is reversible and produces monoalkyl fatty acid esters (biodiesel) and glycerol (Knothe G., 2008).

The stages of the process to be followed in the manufacture of biodiesel leads to low efficiency and high energy consumption, resulting in high production costs of biodiesel. Therefore, it is necessary to develop the biodiesel manufacturing process that is simple, efficient,

and energy-efficient, and can produce high quality biodiesel through in-situ transesterification process. In situ transesterification is much simpler in producing biodiesel by eliminating the process of extraction and purification of oil so as to lower the cost of production (Haas *et al*., 2004). Triglycerides are used in situ transesterification process comes from the source of raw materials derived from oil and not oil that has been extracted and purified in advance (Qian *et al.*, 2008).

In-situ transeterification process has certain advantages when compared to conventional biodiesel production process. Other advantages are the in situ transesterification will eliminate phase extraction and refining of oil so that the process becomes much simpler, as well as low production costs. Haas *et al*. (2004) stated that in the biodiesel production process, more than 70% of the cost of consumables used for the extraction and refining of oil.

Based on these advantages, this research studied biodiesel production process from seed sterculia directly through in-situ transesterification process. This process is also influenced by several factors. These factors include temperature, stirring speed, and duration of the process. Therefore, in this study also examined the effect of time in-situ transesterification process to the yield and quality of biodiesel.

Mechanism of in situ transesterification process according Georgogianni *et al*. (2008) is the raw material of oil resources into direct contact with a solution of alcohol and acid or base catalyst. Alcohol serves as an oil solvent in the material at the same reactants in transesterification process. Haas *et al*., (2004) stated that the alcohol will enter and destroy parts of the cell, and then dissolving the oil contained in the raw material. The oil is then treated in the transesterification process.

The rate of a chemical reaction increases with rising temperature. Keenan (1986) states that a temperature rises of 10 ° C will fold two or three rates of reaction. When the temperature is raised 10 °C, the reactant molecules collide more frequently with larger collision because the molecules move faster. Energy obtained from these collisions result in a chemical reaction can take place more quickly.

Previous research on situ transesterification was also performed by Siler-Marinkovic and Tomasevic (1998) with the raw material for seeds. The yield of ester obtained from this process reached 98% at the reaction conditions and processes as follows: temperature 64.5 ° C and the processing time of 1 hour or 30 ° C and the processing time of 4 hours with a molar ratio of methanol / oil contained in the materials / H_2SO_4 at 300: 1: 9.

Ozgul-Yucel and Turkay (2003) in his research on in situ transesterification of rice bran oil with an acid catalyst (H_2SO_4) showed that methanol gives higher ester yield than ethanol, propanol, and butanol. Reagent ethanol, propanol, and butanol gave a higher yield of ester in the case of in situ transesterification of soybean seeds (Ozgul-Yucel and Turkay, 2002) where increasing the reaction time, the molar ratio of the amount of methanol and the catalyst does not have a significant effect on yield.

Haas, *et al.* (2007) in his research on the in situ transesterification of soybean seeds with NaOH catalyst showed that the amount of methanol and catalyst usage can be reduced respectively by 60% and 56% when the water content in the material is reduced to 0.8%. Optimal conditions with a yield of 100% was obtained at a 10-hour processing time, material moisture content 0.8%, and the concentration of 0:10 N NaOH in methanol up to 12 ml.

Georgogianni, *et al* (2008) conducted in situ transesterification of sunflower seeds using 2% NaOH catalyst, at a temperature of 60 ° C, and a mechanical stirrer 600 rpm. The yield of methyl esters obtained amounted to 95%. The yield of the reaction time can be achieved in 20 minutes and the ratio of the mass of fuel / methanol at 1: 10. While in situ transesterification of cottonseed were carried out by Qian (2008), the conversion of oil to methyl ester can reach 98% under the conditions of the seed moisture content <2%, 0300-0335 mm particle size material, the concentration of NaOH 0.1 mol / L methanol, the molar ratio of methanol / oil 135: 1, as well as the temperature and reaction time were 40 ° C and 3 h.

In the case of in situ transesterification sterculia seed, process condition parameters that will be done is the influence of the water content of the material (0.5, 2, 3, and 4%), the particle size of the material (10, 20, 35 mesh), the ratio of methanol / material (v / b) (2: 1, 4: 1, 6: 1), and the concentration of KOH (0:05, 0075, and 0.1 mol / L methanol) on the biodiesel yield and quality (Kartika et al., 2009). The operating conditions are set at 60 ° C, time 240 minutes, and stirring speed of 700 rpm.

METHODS

The main ingredient used in this study is sterculia seed. Chemicals used for in situ transesterification process include methanol, sodium hydroxide, hexane, and distilled water. Chemicals used for sample analysis, namely ethanol, PP indicator, 0,1N KOH solution, chloroform, Hanus reagent, 20% KI solution, distilled water, Kanji solution, 0.5 N alcoholic KOH and HCl 0.5 N.

In situ transesterification process sterculia seeds carried in a three-neck flask equipped with a thermometer, condenser, and a stirrer were placed on the heater. Operating conditions carried out at a temperature of 30 ° C (room temperature), and the time transesterification process 4, 6, and 8 hours.

NaOH dissolved in methanol and reacted with stirring to form a solution of methanolic-KOH. Further into methanolic-KOH solution included sterculia seeds that have been smoothed. Once the seeds are inserted sterculia, to the mixture was added 500 ml of hexane. The mixture was continuously stirred with the speed, time and temperature of 30 ° C (room temperature) in accordance

with the treatment. Once the process is complete, the mixture was allowed to settle overnight then separated from the pulp. Filtrate obtained is a mixture of oil, methyl esters, glycerol, methanol, and hexane. Filtrate evaporated using a rotary evaporator to separate oil, methyl esters, and glycerol from methanol and hexane. Methanol and hexane evaporated, leaving a mixture of oils, methyl esters, and glycerol. This mixture is then separated by separator flask. Glycerol layer is beneath the semi-solid and tangible.

Once separated, the oil and methyl ester is then washed with distilled water until the pH is neutral. Further analysis to determine the yield, acid number, saponification number, iodine number and viscosity using Indonesian National Standard (SNI).

RESULT AND DISCUSSIONS

In this study, the process of oil extraction and transesterification reactions sterculia conducted simultaneously in the reactor. Seeds of sterculia, hexane, and methanol were spiked simultaneously enter the catalyst in a reactor equipped with a stirrer. The transesterification process is varied at a time of 4, 6 and 8 hours each hour was measured triplo.

In situ transesterification process includes two stages of the research that is the raw material preparation stage and the stage of primary research. Raw material preparation stage is carried out prior to in situ transesterification process; the raw materials used are dry beans. Sterculia dried seeds was prepared by stripping sterculia seeds to separate the seeds from the shell after it was crushed and then transesterified in stirred tank reactor using a room temperature of 30 ° C.

In the main study phase NaOH reacted with methanol to meperoleh methanolic-KOH solution. Further into methanolic-KOH solution included sterculia seeds that have been smoothed. Then added 500 ml of hexane. The mixture was stirred at the speed, time and room temperature in accordance with the treatment. Once the process is complete, the mixture was allowed to settle overnight then separated from the pulp. The filtrate obtained is a mixture of oil, methyl esters, glycerol, methanol, and hexane. The filtrate was evaporated using a rotary evaporator to separate oil, methyl esters, and glycerol from methanol and hexane. Methanol and hexane evaporated, leaving a mixture of oils, methyl esters, and glycerol. This mixture is then separated by separator flask. Glycerol layer is beneath the semi-solid and tangible.

Once separated, the oil and methyl ester is then washed with distilled water until the pH is neutral. The parameters measured to characterize biodiesel produced include yield, acid number, saponification, iodinium number and viscosity. Methyl esters obtained in this study are presented in Table-1.

Table-1. Results of in situ transesterification after evaporation.

Time (hr)	**run**	**sterculia seeds** (g)	**Methanol** (ml)	**Hexane** (ml)	**NaOH** (g)	**Methyl ester** (g)	**Average of methyl ester** (g)
4	1	100	560	500	1,8	131,43	
	2	100	560	500	1,8	107,16	144,08
	3	100	560	500	1,8	193,65	
6	1	100	560	500	1,8	138,21	
	2	100	560	500	1,8	190,70	184,51
	3	100	560	500	1,8	224,63	
8	1	100	560	500	1,8	328,95	
	2	100	560	500	1,8	202,71	247,75
	3	100	560	500	1,8	211,61	

Based on the data in Table-1 it is known that the longer the reaction time, the higher the acquisition methyl ester. Obtaining the highest on the reaction time of 8 hours at an average 247.75 g. When compared with the results of previous studies in which the extraction process is carried out separately by the transesterification reaction (Pasae, 2011), the required time is 9 hours altogether, with details of the gradual extraction time was 6 hours, and the transesterification reaction time of 3 hours. Thus it can be said that the process of making biodiesel from seed sterculia through in-situ transesterification reaction is more economical and efficient than the process of making biodiesel through transesterification extraction and separately.

Table-2. Results of the analysis of the acid number, saponification number, iodine number and viscosity.

Run (hr)	Acid number (mg KOH/g sample)	Saponification number (mg KOH/g sample)	Iodin number (g I_2/100 g sample)	Viscosity (cSt)
4	1.283	157.13	6.298	0,036
6	1.277	155.80	3.537	0,033
8	1.064	149.95	1.275	0,026

Acid number indicates the amount of free fatty acids contained in the oil or fat. Based on the data in Table 2, the results for the acid number of the reaction products obtained during 4 hours, 6 hours and 8 hours respectively 1, 283, 1, 277, and 1, 064 mg KOH / g sample. This indicates that the longer the reaction time, the amount of free fatty acids in the smaller product. The presence of high free fatty acids in the product is not desirable, as it may cause damage to the methyl ester.

Saponfication number indicates the number of bases (mg KOH) required to saponified 1 gram of oil. The high rate of saponification depends on the molecular weight of the oil, the greater the molecular weight, the lower the saponification numbers. This can be explained, with the length of the hydrocarbon chain of oil, it will be the smaller the molar proportion of carboxylic groups that will react with bases. According Ketaren (1986) in the saponification number of oil is affected by the presence of the compounds was saponified in the oil can reduce the strength of the oxidation of polyunsaturated fatty acids. Based on data in Table 2, saponification number for the products obtained from the reaction for 4 hours, 6 hours and 8 hours respectively 157.13, 155.80, and 149.95 mg KOH / g sample. This indicates that the longer the time the lower the number saponification reaction product.

Iodine number showed unsaturated fatty acids constituent of oil and fat. Unsaturated fatty acids are able to bind iodine and form a saturated compound. The amount of iodine in the connective indicates the number of double bonds. Unsaturated fat can easily be united with iodinium (two atoms iodinium added to each double bond in the fatty). The more iodinium used the higher the degree of lack of saturation. Based on data in Table-2, the number of iodine to the product obtained from the reaction for 4 hours, 6 hours and 8 hours respectively are 6.298, 3.537, and 1.275 g I2 / 100 g sample. This indicates that the longer the reaction time, the lower the number of iodine products.

The viscosity of a molecule determines the ease of moving because of friction between the material layers. Because of the viscosity indicates the level of resistance of a fluid / oil flowing. The greater the viscosity, the flow will be slow. The amount of viscosity is affected by temperature, tensile force between the molecules and the size and number of soluble molecules. In liquids, the viscosity due to the cohesive forces (attractive forces between like molecules). Based on data in Table-2, the number of iodine to the product obtained from the reaction for 4 hours, 6 hours and 8 hours respectively 0,036, 0,033, and 0, 026 cSt. This indicates that the longer the reaction time, the lower the viscosity of the product.

CONCLUSIONS

a) In-situ transesterification can be performed to convert the oil in sterculia seeds into biodiesel without oil extraction in advance.
b) The reaction time affects the amount of the product obtained and the physical properties of the product.
c) Product characteristics transeterifikasi in-situ form of the acid number is in the range 1.064 -1.283, mg KOH / g sample, saponification numbers in the range 149.95-157.13 mg KOH / g sample, iodine numbers in the range 1275-6298, g I_2 / 100 g sample and the viscosity in the range of 0.036 to 0.026.

ACKNOWLEDGEMENTS

Thanks to director of Research and Public Service Directorate General of Higher Education, Ministry of Education and Culture of the Republic of Indonesia, for research funding through the National Strategic Research Grant in 2014.

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