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Methyl Ester Production from Rice Bran Oil and Methanol with Calcium Carbonate Catalysts Using Esterification Method

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ABSTRACT: Rice bran oil is a type of oil with high nutritional value from rice bran. However, the free fatty acid content in it can increase by more than 60% with sufficient storage time. Free fatty acids contained in rice bran have the potential to be produced into biodiesel (methyl ester). This research aimed to determine the effect of methanol volume and esterification process time on biodiesel yield and to compare methyl ester yield to standard biodiesel. This research was conducted in two stages, namely rice bran oil extraction and esterification. In the extraction stage, rice bran was extracted with n-hexane for 3 hours at an operating temperature of 65ºC. The esterification process was carried out by mixing rice bran oil, methanol with a certain volume (100, 125, 150, 175, 200 mL), and calcium carbonate catalyst as much as 1% of the amount of methanol. Esterification was carried out with time variations of 1; 1.5; 2; 2.5 and 3 hours. The results in the form of rice bran oil were analyzed for the value of the biodiesel yield. The result of rice bran oil was analyzed for initial free fatty acid value. Pure biodiesel product in the form of methyl ester was obtained through separation with glycerol as a by-product. The optimum methyl ester *yield* was 81.70% at 175 ml methanol volume for 3 hours. The methyl ester results are in accordance with SNI biodiesel for density and kinematic viscosity values.

KEYWORDS: biodiesel, calcium carbonate, esterification, methyl ester, rice bran oil

1. INTRODUCTION

With an abundant supply of raw materials from rice bran, biodiesel production from rice bran oil is very promising. Depending on the rice variety and degree of milling, rice bran contains 16%-32% oil by weight [1]. About 60%-70% of rice bran oil cannot be used as food (*non-edible oil*) due to the stability and different ways of storing rice bran [2]. Rice bran oil is a type of oil with high nutritional value due to the presence of fatty acids, biologically active components, and antioxidant components such as: oryzanol, tocopherol, tocotrienol, phytosterol, polyphenol and squalene [2][3].

Bran is a by-product of milling grain into rice [2][4]. Bran contains 17%-23% fat which can be utilized as food oil. Bran also contains several minerals including: calcium (0.13%), phosphorus (2.39%), potassium (0.14%), sodium (0.24%), magnesium (0.14%) and silica (4.07%). It also contains iron (224 ppm.), aluminum, copper, manganese, tin and chloride [5].

In the oil extraction process, several types of solvents are usually used. One of them is n-hexane. n-hexane is a non-polar compound. Because of this non-polar nature, most compounds from the alkane group including n-hexane are soluble in nonpolar or slightly polar solvents such as diethyl ether or benzene. The industrially produced hexane fraction boils at 65-70ºC.

Rice bran oil is an important derivative of rice bran [6]. Depending on the rice variety and degree of milling, rice bran contains 16%-32% oil by weight. About 60%-70% of rice bran oil cannot be used as food (non-edible oil) due to the stability and different storage methods of rice bran such as research [2] and [4]. The characteristics of rice bran oil are presented in Table 1.

Table 1. Characteristics of Rice Bran Oil [5]

Characteristics	Value Range
Specific gravity at 20 /30ºC	0,916-0,921
Refractive index at 25ºC	1,47-1,473
Iodine Numbers	99-108
Saponification number	181-189
Titer (0ºC)	24-25
Free fatty acid (%)	3-60

Biodiesel is a promising alternative fuel that can be obtained from plant oils, animal fats or used oils through esterification with alcohol [3][7][8]. Ethanol, also called ethyl alcohol, is a type of solvent that is volatile, flammable, and colorless and has a distinctive aroma. Ethanol is a versatile solvent, miscible with water and many organic solvents including acetic acid, acetone, benzene, carbon tetrachloride, chloroform, diethyl ether, ethylene glycol, glycerol, nitromethane, pyridine and toluene. Ethanol is a good solvent in the biodiesel manufacturing process.

Biodiesel can be used without re-modification of diesel engines. The characteristics of biodiesel according to the

Indonesian National Standard are presented in Table 2.

Table 2. Indonesian National Standard for Biodiesel [9]

Parameters and their units	Value limit	Test method
Density at 40°C, kg/m^3	850-890	ASTDM 1298
Kinematic viscosity at 40oC, mm/s2	2.3-6.0	ASTDM 445
Acid number (mg CaCO3/g)	Max. 0.8	AOCS Cd3- 63
Alkyl ester content (%- weight)	Min. 96.5	Calculated

In Table 2, the alkyl ester content was calculated based on the saponification number, acid number, and total glycerol and free glycerol content.

One way to convert rice bran oil into biodiesel is through a transesterification reaction. Transesterification is the process of alcoholization of triglycerides that produces a mixture between alkyl esters (biodiesel) and glycerol that is separated and removed, so that it can produce products that have the same specifications as diesel [10].

Esterification is a reaction in which materials containing free fatty acids are reacted with alcohol to form esters and water. Esterification can only be performed if the feed being reacted with the alcohol contains high free fatty acids. Esterification reaction is shown in Fig. 1.

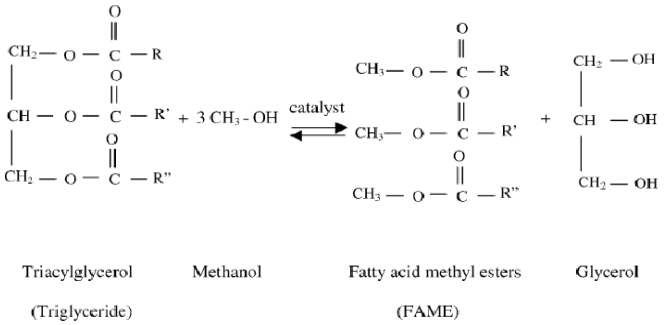

Fig. 1. Esterification reaction from triglyceride [11]

From Fig. 1, triglycerides plus methanol as an extract solvent and reactants react into methyl esters with the help of a basic catalyst in the form of calcium carbonate ($CaCO_3$) and by-products in the form of glycerol [12].

This research aims to study the effect of the amount of methanol used in the esterification process in making biodiesel and to study the effect of operating time on the esterification process in making biodiesel from rice bran oil with calcium carbonate catalyst.

2. METHODOLOGY

2.1 Tools and Materials

This research used rice bran obtained from Kweden Village, Bantul. The supporting materials were calcium carbonate, distilled water, ethanol 96%, phenolphthalein indicator, technical methanol, and n-hexane.

The tools used in this study were three-neck flask, measuring cup, heater, measuring flask, erlenmeyer, beaker glass, water bath, separatory funnel, thermometer, burette, dropper pipette, stative and clamp, pycnometer, socklet, cooler, and digital balance. The extraction tools set is shown in Fig. 2 and the esterification tools set is shown in Fig.3.

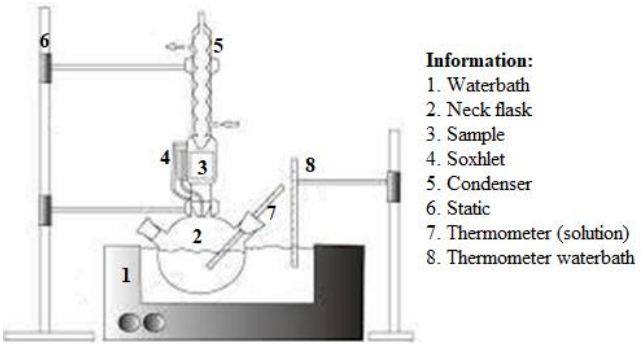

Fig. 2. The extraction tools set

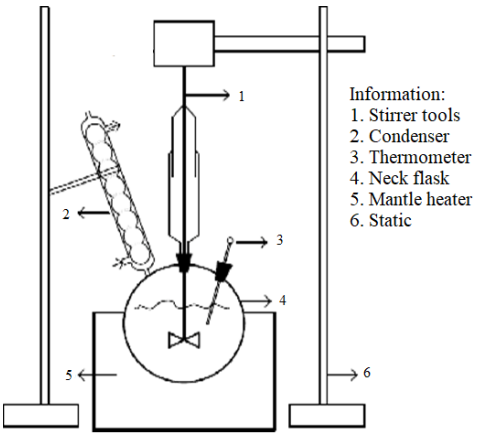

Fig. 3. The esterification tools set

2.2 Research methods

a. Raw material preparation, rice bran was matured for 4 months to increase the free fatty acid content in the bran.

b. Rice bran extraction process

Sample 100 g rice bran was wrapped and then put into the soxhlet. Then n-hexane was added 300 mL and heated for 3 hours with temperature of 65° C. The extracted result (rice bran oil) was separated from n-hexane by distillation and was weighted until a constant weight. The yield of rice bran oil was calculated in equation (1). This process was repeated until rice bran oil reached 100 mL.

$$\%yield = \frac{rice\ bran\ oil\ (g)}{sample\ rice\ bran\ (g)} \times 100\% \quad (1)$$

c. Esterification process

Rice bran oil 100 ml, methanol with a certain volume (100, 125, 150, 175 and 200 mL), and calcium carbonate 1%v as catalyst were put into a three neck flask and then processed at a temperature of 65ºC with a stirring speed of 450 rpm for a certain time (1; 1.5; 2; 2.5 and 3 hours). The resulting mixture of methyl ester and glycerol was separated in a separating funnel for 1 night. Then the separated methyl ester yields were calculated.

2.3 Research analysis

a. Moisture content analysis

Analysis of the moisture content of raw materials in the form of rice bran is carried out by weighing as much as 5 grams of rice bran then oven for 10 minutes followed by weighing until the weight is constant.

b. FFA (Free Fatty Acid) analysis

Analysis of free fatty acid content was carried out for rice bran oil by taking 5 g of rice bran oil into an erlenmeyer and adding 96% ethanol as much as 13 mL and then heated to a temperature of 45ºC. The solution was added 2-3 drops of phenolphthalein and titrated with NaOH solution 0.1 N. Free fatty acid levels can be calculated in equation (2).

$$FFA = \frac{(volume\ (mL) \times N)_{NaOH} \times Mr\ oil}{sample\ mass\ (g)} \quad (2)$$

c. Density of biodiesel (methyl ester)

Density testing was carried out based on SNI 04-7182-2015 [9]. Testing carried out using a pycnometer was clean and dry. Empty pycnometer weighed and recorded the results. Biodiesel heated to a temperature of 40 ℃. Pycnometer empty filled with biodiesel then closed until it overflows and nothing air bubble. After that the pycnometer containing biodiesel is weighed and recorded the result. Density of biodiesel can be calculated using equation (3).

$$density\ (\rho) = \frac{mass_{pycno+biodiesel}(g) - mass_{pycno}(g)}{volume\ biodiesel\ (mL)} \quad (3)$$

d. Kinematic viscosity

Kinematic viscosity testing was carried out based on SNI 04-7182-2015 with a viscometer Oswalt [9].

3. RESULTS AND DISCUSSION

From the results of the analysis of rice bran raw materials obtained moisture content of 12%. The extracted rice bran oil was analyzed for FFA (Free Fatty Acid) content, the FFA content was 0,3752 mg NaOH/g and the yield of rice bran oil was 10%. The FFA value in the study met the ASTM D6571-07b standard, namely a maximum of 0.5 mg KOH/g [13]. The effect of methanol volume on methyl ester yield can be shown in Table 3 and Fig. 4.

Table 3. The effect of methanol volume on methyl ester yield

Volume of methanol (mL)	Yield (%)
100	65,15
125	72,09
150	75,12
175	81,70
200	77,35

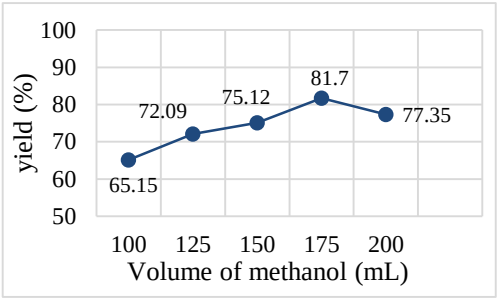

Fig. 4. The effect of methanol volume on methyl ester yield

The results in Table 3 and Fig. 4 show that the more the amount of methanol used, the greater the yield obtained. At 100 mL of methanol, the yield was 65.15% while the largest yield was obtained at 175 ml of methanol, which was 81.70%. The higher the amount of solvent, the greater the conversion will be obtained. This is because the use of one of the excess reactants will increase the possibility of collisions between molecules of reacting substances so that the reaction speed increases. However, in this study there was a decrease in yield in the addition of methanol by 200 ml due to the less than optimal stirring speed and temperature.

According to [14][15][16], the addition of methanol volume increases the biodiesel yield achieved. This is because the addition of one of reactants pushes the reaction in the right side, so the biodiesel product is greater. This is because of using one of the excess reactants increases the possibility of collision between reactant molecules thereby increasing the reaction rate [17].

The effect of processing time on methyl ester yield can be shown in Table 4 and Fig. 5.

Table 4. The effect of processing time on methyl ester yield

Time (hour)	*Yield* (%)
1	62,04
1,5	73,08
2	75,73
2,5	77,38
3	78,21

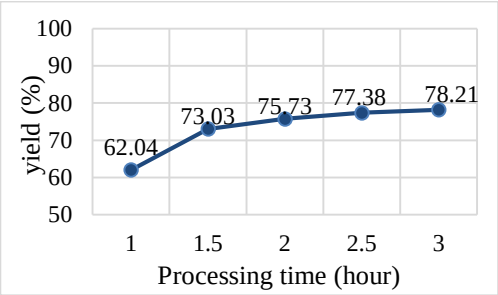

Fig. 5. The effect of processing time on methyl ester yield

From the research results in Table 4 and Fig. 5, it shows that the longer the esterification time, the greater the yield obtained. At 1 hour, the yield was 62.04% while the largest yield was obtained at 3 hours, 78.21%. The longer the time used for esterification, the greater the yield obtained. The above conditions are caused because the longer the reaction time, the greater the possibility of contact between substances, so that it will produce a greater yield as well [18].

Some of the standard biodiesel characteristic parameters used for comparison with the results of the study are shown in Table 5. The parameters used are kinematic density and viscosity values.

Table 5. Characteristics of biodiesel (methyl ester) results of research with Biodiesel standards

Parameter	Density at 40°C (kg/m^3)	Kinematic viscosity at 40°C (mm^2/s)
Biodiesel SNI 7182-2015 [9]	850- 900	2,3 – 6
Biodiesel (ASTM D6751-07b) [13]	-	1,9-6
Methyl ester with calcium carbonate research	865	3,94
Methyl ester with calcium oxide [19]	890	0,929

Table 5 shows that the density and kinematic viscosity values of methyl ester in this study have met SNI 7182-2015 [9] and ASTM 6751-07b [13] standards. The results of this study was better than the previous research conducted by [19].

The density value of the biodiesel in this study have met SNI 7182-2015 [9] and ASTM 6751-07b [13] standards, so that this biodiesel can be used as a substitute for diesel fuel. If the density of biodiesel exceeds the requirements, an imperfect reaction will occur in the oil conversion process. Biodiesel of this quality should not be used for diesel engines because it will increase engine fatigue, produce exhaust gases and damage the engine [20]. If the density value does not meet SNI it will cause incomplete combustion, increase emissions and make the engine thirsty [21].

The kinematic viscosity value of the biodiesel in this study have met SNI 7182-2015 [9] and ASTM 6751-07b [13] standards, so that this biodiesel can be used as a substitute for diesel fuel. If the viscosity is too low it will cause leaks in the fuel injection pump, and if it is too high it can affect the fast operation of the injector and make it difficult to ignite the fuel. However, if it is too high it can cause the fuel to be injected too quickly and complicate the fuel nebulization process [22].

4. CONCLUSIONS

Based on the research results, it can be concluded that:

1. Rice bran can be extracted into rice bran oil which was used as a raw material for making biodiesel. The free fatty acid content in rice bran oil was obtained at 37.52%, and yield of rice bran oil was obtained at 10%.
2. The optimum condition for the biodiesel (methyl ester) production with calcium carbonate catalyst was obtained at a methanol volume of 175 mL and a processing time for 3 hours. The largest yield value was obtained at 81.70%.
3. The density of methyl ester was obtained 865 kg/m^3 and the kinematic viscosity of methyl ester was obtained 3.94 mm^2/s. These two parameters still suited with the biodiesel standard values.

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