

An Efficient Method for the Production of Biodiesel from Rice Bran

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Abstract—A modified *in situ* esterification was employed for the economic competitiveness of biodiesel production from rice bran. The effects of methanol to rice bran ratio, acid catalysts, and reaction time on the biodiesel yield and purity were investigated. Biodiesel yield and purity of 17.99% and 67.04%, respectively, were obtained used acid catalyst (H₂SO₄) of 2.37%, ratio of methanol and rice bran of 15 (mL/g), and 5 h of reaction time. Recovery of crude biodiesel obtained was 92.45%. Based on the proposed method, the production process of biodiesel could be simplified and improved; therefore, the production cost probably could be reduced further.

Keywords—Biodiesel; Rice Bran oil; In Situ Process; Esterification; Transesterification.

I. INTRODUCTION

Petroleum is the largest single source of energy consumed by the world's population, it predicted to increase 40% by 2025 (Johnston and Holloway, 2007). Concerns about oil supply, energy security and environmental have motivated many countries to consider alternatives to imported petroleum.

Biodiesel produced by alcoholysis of plant oils or animal fats, is expected to serve as an alternative to fossil fuel. In addition, biodiesel is non-toxic, biodegradable, has low emission profiles, and environmentally benign. Biodiesel can be mixed with petroleum diesel in any proportion or used directly in diesel engines without modification (Sinha et al., 2008, Lin et al., 2009). However, most commercial biodiesels are produced from refined vegetable oils, such as soybean oil in US, rapeseed and sunflower seed oils in Europe, palm oil in Southeast Asia, and coconut oil in the Philippines (Yustianingsih et al., 2009). The cost of the raw materials comprises 70-80% of the production cost in commercial biodiesel production (Haas et al., 2004; Zullaikah et al., 2005; Lei et al., 2010).

In order to reduce the biodiesel cost, a number of efforts have been made. Used low cost raw materials, simplifying process, and utilization of by products from biodiesel production are expected to reduce the production cost. Indonesia produces more than 65 million tons of rice bran annually. As a by-product of rice milling, rice bran contains 10-25% of lipids (Zullaikah et al., 2005, Hatta et al., 2008, Gupta, 1989). Therefore, rice bran is commercially feasible for oil extraction. Due to the presence of active lipase in the bran and the lack of economic stabilization methods, most bran was used as livestock feed or boiler fuel and most of rice bran oil produced is not of edible grade. As a result, large amount of rice bran was utilized unreasonably nowadays. Therefore, rice bran is a potential low-cost feedstock and it would be an excellent candidate for biofuels production through biorefining. Biorefinery is a system that combines all the available technologies necessary to convert renewable low-value agricultural raw materials to high-value-added products.

Therefore, biorefinery is an efficient ways to reduce the production cost (Demirbas, 2009; El Boulifi et al., 2013).

Simplifying process by applying *in situ* method was studied to reduce the biodiesel cost. Consideration of the current *in situ* method, which is the liquid phase and solid oil-containing materials were mixed together in all of these studies. An additional step was needed to separate the solid and liquid phases, and more alcohol was needed to wash the solid to make that biodiesel and unreacted oil were transferred completely. Additional catalyst is usually required in this method (Ozgul-Yucel and Turkay, 2002, 2003; Yustianingsih et al., 2009; Shiu et al., 2010). There are few study on utilization of by products from biodiesel production (Kasim et al., 2009)

Based on the existing studies and problems, the objective of this work was to produce biodiesel from rice bran by modified *in situ* process. The effects of reaction conditions, such as methanol to rice bran ratio, acid-catalyst amount, and reaction time on the yield and purity of biodiesel were investigated systematically.

II. MATERIALS AND METHOD

A. Materials

Rice bran was donated by a rice mill located in Sidoarjo, Indonesia. Fresh bran was immediately passed through a mesh (< 0.6 mm) to remove foreign material, and stored in a sealed container at 40C to prevent the formation of free fatty acids (FFAs) caused by the hydrolysis of acylglycerols catalyzed by lipase contained in rice bran. Thin-layer chromatograph (TLC) aluminum plates (20cm x 20cm x 250µm) were purchased from Merck (Darmstadt, Germany). Standard fatty acid methyl esters (FAMES) were obtained from Sigma Chemicals Company (St. Louis, MO, USA). All solvents and reagents were either of high performance liquid chromatography (HPLC) grade or of analytical reagent grade and were obtained from commercial sources.

B. Extraction of Crude Rice Bran Oil (RBO)

Rice bran (10 g) was packed into an extraction thimble filter (35 x 120 mm) and the top surface was covered with cotton to prevent natural contaminations. Crude RBO was extracted from the rice bran by soxhlet extraction with methanol (150 mL) as the solvent, which was put in a 250 mL round-bottom flask and heated. After a predetermined time (0.5, 1, 3 and 5 h), the extraction process was stopped; the product was distilled to separate methanol from the crude RBO and dried in an

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oven at 80°C for 2 h. The yield of crude RBO was obtained by dividing the weight of the methanol extract (crude RBO) by that of the rice bran. The solid by product (defatted rice bran) was dried and measured gravimetric.

C. Modified In Situ Esterification

A Soxhlet extractor used in the extraction of crude rice bran oil, equipped with a magnetic stirrer, a heater and a condenser was employed in the modified in situ esterification. Rice bran was dried in an oven at 80°C for 2 h to reduce its water content. Rice bran (10 g) was packed into an extraction thimble filter (35 x 120 mm) and the top surface was covered with cotton to prevent natural contaminations. A solution that was prepared from methanol (150 mL) and H₂SO₄ (0.1, 0.2 and 0.5 mL) was put into a 250 mL round-bottom flask at 68±2°C and atmospheric pressure. After a predetermined time (0.5, 1, 3 and 5 h), the modified in situ esterification process was stopped. The product was distilled to recover methanol from the oil product. After that, FAMES was extracted with hexane (3x50 mL) from the liquid phase. The mixture was washed with distilled water until neutral pH. The mixture was separated into an upper organic layer and a lower aqueous layer. The lower layer was removed and discarded. The hexane was recovered from the pooled organic layers using distillation; the remaining substance was dried in an oven at 80°C for 2 h to remove its water content and was referred to as the reaction product. The product was analyzed by gas chromatography and TLC.

D. Determination of FFAs

FFAs contents as oleic acid were determined according to Rukunudin et al., (1998). Sample was dissolved in ethyl alcohol, 95% at 60°C and FFAs contained in the sample were neutralized with NaOH solution. The sample mass and the volume of NaOH solution used were used to calculate the contents of FFAs.

E. TLC and GC analyses

Individual components in each sample were identified by using authentic standards (Gunawan et al., 2008). Spots on each plate were visualized by exposing the chromatogram to iodine vapor (Fried, 1996).

The sample was dissolved in n-hexane and 0.5 µL of this sample was injected into the GC. External standard calibration curves were obtained by using 0.2-20 mg pure standard. Oleic acid methyl ester was selected for the determination of FAMES calibration factor and was used for all FAMES. Chromatographic analysis was performed in a HP 6890 (Hewlett-Packard Inc., Avondale, Pennsylvania, USA) gas chromatograph equipped with a flame ionization detector. The column used was HP-1 crosslinked methyl siloxane column (60m x 0.25mm i.d. x 1µm film thickness, Hewlett-Packard Inc., Avondale, Pennsylvania, USA). The operating conditions were: the injector and detector temperature were set at 250°C, the column temperature was held at 200°C for 2 min, and then was raised to 300°C at 15°C/min and was held for 10 min. Helium was used as the carrier gas with a linear velocity of 40 cm/s at 200°C. The yield of FAMES was obtained by

dividing of the weight of the FAMES in the oil product by that of the rice bran.

III. RESULT AND DISCUSSION

A. Extraction of Crude Rice Bran Oil (CRBO)

Since in situ operation conditions such as ratio of rice bran to methanol and time dependent on the extraction operation condition, the process of the extraction of RBO with methanol was carried out first before biodiesel production through modified in situ esterification. In this work, ratio of rice bran to methanol of 1:15 (g/mL) was used due to equipment constrain. In general ratio of 1:4 - 1:15 were used during in situ production of biodiesel from rice bran (Ozgul-Yuzel and Turkay, 2002, 2003; Yustianingsih et al., 2009; Shiu et al., 2010; Lei et al., 2010; Lei et al., 2011).

The effect of extraction time on crude RBO yield and FFAs content was shown in Table 1. It can be seen that the yield of crude RBO increasing with time. Crude RBO yield of 6.10% was obtained for 30 min of extraction time and increases to 19.46% for 5 h of extraction time. Crude RBO obtained for 5 h of extraction time with hexane was lower than that of methanol (data not shown). This is due to the presence of polar compounds extracted by methanol (Shiu et al., 2010). Since, the extraction rate decreasing with time, 5 h of extraction time was appropriate for extraction of crude RBO (Lei et al., 2010).

The extraction time has significant effect for the FFAs content in the obtained crude RBO if extraction time prolonged to 5 h (Table 1). The FFAs content increases from 32.27% to 53.53% for extraction time of 0.5 h to 5 h, increasing of the FFAs contents due to hydrolysis of the glycerides to FFAs (Lei et al., 2010).

B. Modified In Situ Esterification

In this study, biodiesel was obtained through in-situ esterification process, in which the oil extraction process and the reaction carried out simultaneously with the addition of an acid catalyst (Özgül-Yücel and Türkay, 2003). Esterification reaction with acidic catalysts was used because rice bran containing high level of FFAs (> 30.00%). Effect of reaction time and different catalyst amount on product obtained is shown in Figure 1. It can be seen that crude biodiesel (product) obtained increases with time. Similar trend was shown with crude RBO obtained during extraction. However, different amount of catalyst added gave not significantly different on product obtained. Therefore, adding 0.1 mL of H₂SO₄ (2.37%) was enough to accelerate esterification reaction compare with that of the conventional in situ esterification that used high amount of H₂SO₄ (> 18.4%) (Ozgul-Yuzel and Turkay, 2002, 2003; Yustianingsih et al., 2009; Shiu et al., 2010, Gunawan et al., 2011).

The effect of reaction time and different catalyst amount on FAMES yield, FAMES content and FFAs content in the product was shown in Table 2. The yield of FAMES increases with time on different catalyst amount. During in situ acid-catalyzed esterification, the FAME yield increases significantly when reaction time was increased from 0.5 h to 1 h. An increase in FAMES yield was not significant after reactions were performed at a longer time (> 1 h). The results are probably because the reaction between methanol and FFAs catalyzed by

acid is very fast in the first an hour (Shiu et al., 2009). The highest FAMES yield of 17.99% was obtained for 5 h of reaction time. These results are in agreed with the previous research (Lei et al., 2010, Lei et al., 2011). The amount of H₂SO₄ added to the reactor varies from 0.1 mL (2.37%) to 0.5 mL (9.20%). However, The FAMES yield not affected by different amount of H₂SO₄ (Table 2). In the conventional in situ esterification H₂SO₄ was mixed with rice bran and methanol, therefore more catalyst and methanol were needed. In this work, H₂SO₄ was added in the liquid phase, therefore could minimize the used of catalyst amount. In the biodiesel production, 1-5% of catalyst was used to accelerate the reaction (Lotere et al., 2005, Zullaikah et al., 2005, Zullaikah and Ju, 2013). In addition, the use of excess catalyst can result in dark color of the FAMES product (Özgül-Yücel and Türkay, 2002, Zullaikah and Ju, 2013).

Acid-catalyzed methanolysis has an important advantage over base-catalyzed one in that the performance of the acid catalyst is not affected by the presence of FFAs in the feedstock. In fact, acid catalyst can simultaneously catalyze both esterification and transesterification. Thus, a great advantage with acid catalysts is that they can directly produce biodiesel from low cost lipid feedstocks that generally associated with high FFAs content.

However, reaction rate of acylglycerols into FAMES much slower (Lotere et al., 2005). Therefore, more H₂SO₄ was needed to accelerate the reaction. It can be seen in **Table 2** that FAMES content increases with time and catalyst amount. High content of FAMES (74.92%) was obtained for 5 h of reaction time and 0.5 mL of H₂SO₄ (9.2%).

The complete FFAs conversion was achieved when the reaction was performed for 1 h. The FFA was not detected after prolongation time was performed. According to Gunawan et al (2011), during acid catalyzed esterification, the FFAs was converted rapidly into FAMES within an hour. After extending time, the conversion rate was slower than before. When using higher amount catalyst 4.75 % and 9.2 %, the complete conversion was achieved when the reactions were conducted for 0.5 h. The higher amount of acid catalyst could accelerate the complete reaction of esterification.

IV. CONCLUSION

A modified in situ esterification for the efficient production of FAMES has been successfully developed. The proposed method has been proved to decrease the amount of catalyst (H₂SO₄) and methanol.

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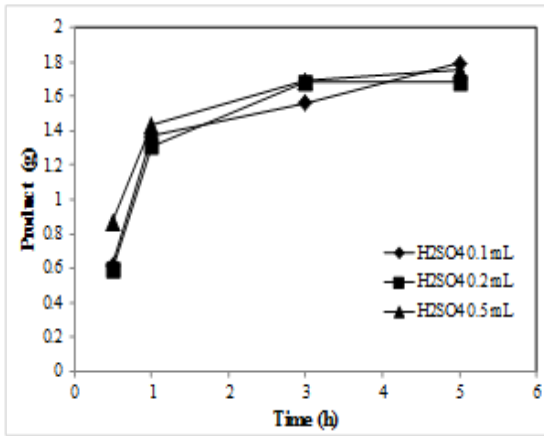


Figure 1. Effects of catalyst amount and reaction time on the product

TABLE 1.
EFFECT OF EXTRACTION TIME ON YIELD OF CRUDE RBO, FFAs IN
CRUDE RBO AND TOTAL SUGARS IN THE DEFATTED RICE BRAN^A

Time (h)	Crude RBO Yield (%)	FFAs Content (%)
0,5	6.10 ± 0.28	32.27 ± 1.99
1	14.97 ± 0.47	35.07 ± 1.98
3	17.90 ± 0.85	36.47 ± 1.98
5	19.46 ± 0.36	53.53 ± 3.63

Extraction conditions: rice bran = 10 g, T = 68±2°C, and methanol to rice bran = 15 mL/g.

^A Averages of two independent measurements.

TABLE 2.
EFFECTS OF CATALYST (H2SO4) AND REACTION TIME ON YIELD AND
PURITY OF FAMES^A

H ₂ SO ₄ (mL)	Time (h)	Crude Methyl Ester		FAMES Yield (%)
		FAMES content (%)	FFAs content (%)	
0.1	0,5	48.77 ± 0.14	5.61 ± 0.00	6.21 ± 0.28
	1	55.53 ± 0.24	ND	13.70 ± 0.47
	3	66.13 ± 0.32	ND	15.68 ± 0.64
	5	67.04 ± 0.32	ND	17.99 ± 0.61
	0,5	53.4 ± 0.05	ND	5.95 ± 0.09
0.2	1	60.37 ± 0.25	ND	13.13 ± 0.57
	3	64.04 ± 0.50	ND	16.83 ± 0.95
	5	73.26 ± 0.51	ND	16.76 ± 1.04
	0,5	62.5 ± 0.29	ND	8.71 ± 0.58
	0.5	1	66.24 ± 0.42	ND
3		74.15 ± 0.33	ND	16.97 ± 0.67
5		74.92 ± 0.45	ND	17.47 ± 0.91

Extraction conditions: rice bran = 10 g, T = 68±2°C, and methanol to rice bran = 15 mL/g.

^A Averages of two independent measurements.