Effect of acid-catalysed in one step production of biodiesel on total sugars of defatted rice bran

M Yasmin¹, S Zullaikah¹,², A Permatasari¹, I Marita¹ and M Rachimoellah¹

¹Department of Chemical Engineering, Institut Teknologi Sepuluh Nopember (ITS), Kampus ITS Keputih Sukolilo, Surabaya 60111 Indonesia

Abstract. Defatted rice bran is a major byproduct of rice bran-based biodiesel and rich in carbohydrate. The high amount of carbohydrate (starch) from its process can be utilized as energy fuel feedstock. In this work, the effect of acid catalyst amount and reaction time on the yield of oil and carbohydrate products in in-situ transesterification from rice bran was investigated. The longer reaction time was used; oil products (FAMEs yield and its content) and carbohydrate product (total sugars content and recovery) showed the opposite trendline. The longer reaction times was achieved, the more yield of FAMEs was obtained but the lower total sugars content on defatted rice bran. While, the less amount catalyst was enough to faster reaction and produce high total sugars content.

1. Introduction

An increase of emissions as a consequence of excessive consumption of fossil fuels leads to some negative effects to environment security. Therefore, a demand of renewable fuels to substitute the recent fuels increases year by year. The potential renewable and alternative diesel fuel is biodiesel. Biodiesel has attracted a wide attention as clean, biodegradable, and environmentally benign fuel. Biodiesel can be mixed with petroleum diesel in any proportion or used directly in diesel engines without modification [1].

Biodiesel can be directly converted by transesterification of oil and alcohol with the presence of catalyst. Commercial biodiesel production still relies on 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 [2,3]. However, those renewable sources arise 70-80% cost in biodiesel production [3]. The economic competitiveness in biodiesel production can utilize low-cost raw materials such as rice bran, a byproduct of rice milling. It can be a potential feedstock due to high lipids content (10-25%) and available in large quantity [4].

In recent years, in-situ process has drawn considerable attention as a way to reduce the production cost further [5]. Rice bran oil (RBO) based biodiesel under in-situ acid esterification [6], rice bran-based biodiesel with ultrasound assisted in-situ esterification [2], in-situ transesterification under supercritical condition [7], two steps in-situ process of rice bran-based biodiesel [5], and in situ subcritical transesterification [4] had been conducted as the economic competitiveness to produce biodiesel.

Most of those researches still focus on yield of biodiesel can be achieved and its optimization. While, rice bran-based biodiesel production yielded a high amount of defatted rice bran as a byproduct. Defatted rice bran is rich in carbohydrate and can be used as bioethanol feedstock. However, information of total
sugars on defatted rice bran as a byproduct of rice bran-based biodiesel is rarely found. Therefore, the objective of this work is to investigate the effect of acid-catalyst amount and reaction time on FAME and total sugars from in situ transesterification process.

2. Materials and methods

2.1. Materials
Rice bran was obtained from local rice mill in Sidoarjo, Indonesia. Fresh rice bran was immediately separated from its impurities by sieving method (<0.6 mm mesh) and stored in a sealed container at 4°C to prevent the formation of free fatty acids (FFAs) by lipase enzyme. Rice bran was put at 80°C in an oven for 2 h to reduce its water content before it is used as feedstock in the process. 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 were obtained from commercial sources.

2.2. Extraction of rice bran
Rice bran (10 g) was extracted by Soxhlet extraction method using extraction thimble filter (35 x 120 mm) and methanol (150 ml) as a solvent. The extraction was conducted at 65°C in predetermined time (0.5, 1, 3, and 5 h). The liquid product was distilled to separate methanol from crude rice bran oil (CRBO). Then, the CRBO was analyzed and weighed to know the initial FFAs content and yield of the extraction. The yield of CRBO was determined as the weight ratio of CRBO to the rice bran and the FFAs analysis was determined according to Rukunuddin et al [8]. The solid product (defatted rice bran) was dried at 65°C for an hour and analyzed to know the total sugars content. Total sugars content was determined by Luff-Schoorl method according to Egan et al [9]. The initial total sugar in rice bran was 41.82%.

2.3. In-situ production of biodiesel
Soxhlet extraction apparatus equipped with magnetic stirrer was employed in this work [3]. In general, rice bran (10 g) was put in the extraction thimble filter (35 x 120 mm) while methanol (150 ml) as solvent and reactant with sulfuric acid as catalyst was put in round-bottom flask. The in-situ process was conducted at 65°C in predetermined time and amount of catalyst. The liquid product was distilled to recover methanol from the oil product. Then, the oil product was extracted by n-hexane for three times (50 ml each) and washed by distilled water until neutral pH. The mixture formed two layers, upper layer (organic phase) and bottom layer (aqueous layer). The aqueous layer was removed and discarded while the organic layer was distilled to recover hexane from its FAMEs product. The FAMEs product was dried at 80°C for an hour to remove the remaining water. The FAMEs were weighed and analyzed to know its yield and purity. The yield of FAMEs was determined as the weight ratio of FAME to its crude oil while the FAMEs content was analyzed by gas chromatography (GC). The solid product (defatted rice bran) was dried at 65°C for an hour and analyzed to know total sugars content. Total sugars content was determined by Luff-Schoorl method according to Egan et al [9].

2.4. Product analysis
Total sugars were determined by Luff-Schoorl method, which is based on iodometric determination of the unreduced Cu (II) ions remaining after the reaction with reducing sugars [9]. Titratable acidity expressed by anhydrous citric acid was determined by titrating sample with 0.1 M NaOH. The recovery of total sugars was determined as the weight of total sugars in defatted rice bran to the initial weight of the total sugars in rice bran.

FAMEs content of the sample was determined by gas chromatography. The sample with n-hexane dilution (0.5 µL) 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 silicone 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 the weight of the FAMEs in the oil product by that of the rice bran.

3. Results and discussion

3.1. Effect of extraction time on yield of CRBO and total sugars

In this work, ratio of rice bran to methanol used was 1:15 (g/ml). Table 1 shows the effect of extraction time on yield of CRBO and FFAs content. The yield of CRBO increased along with increasing of extraction time. At 0.5 h, yield of CRBO was 6.10% and it increased to 19.46% for extended time of extraction (5 h). Shiu et al [5] stated that extraction lipid from rice bran was a slow process so that it needs longer time to extract the lipids. However, the increment of extraction time affected the extraction rate. The longer extraction time used, the rate will be slower. Lei et al [10] reported that time to complete extraction of rice bran with methanol was 5 h.

The FFAs content in CRBO depended on extraction time significantly. When extraction was prolonged to 5 h, the FFAs content increased rapidly. The increasing of FFAs content can be caused by hydrolysis of the glycerides such as triglycerides (TG), diglycerides (DG), or monoglycerides (MG) into FFAs [3].

Table 1. Effect of extraction time on yield and FFAs content of CRBO.

| Time (h) | Yield of CRBO (%) | 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: mass of rice bran = 10 g, T=65°C, and rice bran to methanol = 1:15 (g/ml).

Table 2. Effect of extraction time on total sugars in defatted rice brana.

| Time (h) | Total sugars |
|---------|--------------|
| 0.5     | 37.97±0.18 (90.79±0.44) |
| 1       | 32.25±0.83 (77.12±2.00)  |
| 3       | 28.02±0.56 (66.99±1.34)  |
| 5       | 27.45±0.56 (65.63±1.34)  |

Extraction conditions: mass of rice bran = 10 g, T=65°C, and rice bran to methanol = 1:15 (g/ml).
a Values reported as content (wt. %) with recoveries (%) in parenthesis

Total sugars on defatted rice bran was also affected by extraction time. The longer of extraction time, both of content and recovery of total sugars decreased. The initial total sugars content in rice bran was 41.82% and it decreased until 27.45% for 5 h of extraction. The highest loss of sugars in rice bran was 14.37% after 5 h of extraction. The decline of total sugars can be caused by utilization of methanol as polar extraction solvent. The more polar the solvent is, the more carbohydrate can be preferentially extracted [1,5].
3.2. Effect of reaction time
In this study, biodiesel was obtained through in-situ transesterification process, in which the oil extraction process and the reaction was carried out simultaneously with the addition of acid catalyst [6,10]. The selection of sulfuric acid as catalyst was due to high level of FFAs (>30%) in rice bran and to prevent saponification reaction between base catalyst and FFAs [3,11].

Effect of reaction time on FAMEs yield and content is shown in Fig 1. Both of FAMEs yield and content increased along with increasing of time. The FAMEs yield was 8.71% (at 0.5 h) and it increased to 17.47% as the reaction time increased to 5 h. The highest increasing of FAMEs yield (5.6%) was obtained when reaction time was increased from 0.5 h to 1 h. Gunawan et al [1] stated that the conversion FAMEs from rice bran oil was rapid at the first hour and slower for further hours. Therefore after 1 h of reaction, an increment of FAMEs yield was not too significant. FAMEs yield also depended on the oil extraction rate rather than reaction rate of transesterification [4].

Total sugars content and recovery were also affected by reaction time. Figure 2 shows that total sugars content in defatted rice bran slightly decreased from 5 min to 30 min of reaction. The trend of total sugars content was opposite with FAMEs yield. The decline of sugars content in defatted rice bran can be caused by acid condition. Acidic condition as a result of acid catalyst presence in the system might hydrolyze starch (as the major carbohydrate in rice bran) into monomer sugars [4]. Therefore, the content of starch decreased along with increasing of reaction time. Recovery of total sugars in defatted rice bran has the same trendline with its content. The longer reaction time used, the recovery of total sugars decreased gradually.

![Figure 1. Effect of reaction time on FAMEs yield and content (T=65oC, ratio rice bran to methanol = 1:15 (g/ml), volume of catalyst = 0.5 ml).](image-url)
3.3. Effect of catalyst amount

The reaction between methanol and oils catalyzed by acid is very fast [4]. Figure 3 shows that adding more catalyst did not increase FAMEs yield significantly and the highest FAMEs yield (17.99%) was obtained by using 0.1 ml of catalyst. Zullaikah et al [3] stated that adding less catalyst amount was enough to accelerate the reaction. Therefore, adding less amount of catalyst was appropriate to faster the reaction and prevent darker color of FAMEs [3,12].

Total sugars content did not affect significantly when amount of catalyst was added. Figure 4 shows that the trendline is similar with FAMEs yield. The more catalyst was added, both of FAMEs yield and total sugars content was not affected significantly. Less amount of catalyst used in the system will decrease total sugars content so that utilization of less amount of sulfuric acid was enough to produce high total sugars content in defatted rice bran. Recovery of total sugars decreased along with more sulfuric acid added into the system. Therefore, less amount of sulfuric acid was enough to prevent loss of total sugars in defatted rice bran.
Figure 3. Effect of Catalyst amount on FAMEs Yield and Content (T=65°C, Ratio rice bran to methanol =1:15 (g/ml), Reaction time = 5 h)

Figure 4. Effect of Catalyst amount on Total Sugars Content and Recovery (T=65°C, Ratio rice bran to methanol =1:15 (g/ml), Reaction time = 5 h)

4. Conclusion
Reaction time and acid catalyst amount affected total sugars on defatted rice bran as major byproduct from catalytic in situ biodiesel production. The longer reaction time can lower total sugars on defatted rice bran even though increasing biodiesel yield. Therefore, less amount of catalyst was enough to increase FAMEs yield and did not lower total sugars in defatted rice bran significantly.
Acknowledgments
This research was financially supported by Directorate General of Higher Education, Ministry of National Education, Indonesia and Institut Teknologi Sepuluh Nopember through project No. 0392/IT2.7/PM/2012.

References
[1] Gunawan S, Maulana S, Anwar S and Widjaja T 2011 Ind Crops Prod 33 624-28
[2] Yustianingsih L, Zullaikah S and Ju Y H 2009 J. Energ. Inst 82 133-37
[3] Zullaikah S, Rahkadima Y T, Rachimoellah M, Widjaja T and Sumarno 2014 IPTEK. Journal of Proceeding Series 1 351-54
[4] Zullaikah S, Rahkadima Y T, and Ju Y H 2017 Renew. Energy 111 764-70
[5] Shiu P J, Gunawan S, Hsieh W H, Kasim N S and Ju Y H 2010 Bioresour. Technol. 101 984-89
[6] Ozgul-Yucel S and Turkay S 2003 J. Am. Oil Chem. Soc. 80 81-4
[7] Kasim N S, Tsai T H, Gunawan S and Ju Y H 2010 Bioresour. Technol. 100 2007-11
[8] Rukunudin I, Whitea P, Bernb C, and Baileye T 1998 J. Am. Oil Chem. Soc. 75 563-68
[9] Egan H, Kirk R, and Sawyer R 1981 Sugars and preserves 152-53
[10] Lei H, Ding X, Zhang H, Chen X, Li Y, Zhang H, and Wang Z 2010 Fuel 89 1475-79
[11] Ju Y H and Vali S R 2005 J. Sci. Ind. Res. 64 866-82
[12] Ju Y H and Zullaikah S 2013 J. Taiwan Inst. Chem. Eng. 44 924-8