An improvement study of biodiesel production from rice bran via non-catalytic in-situ transesterification using a subcritical water-methanol mixture

M Yasmin, F D Alfaty, H S Pradipta, M Rachimoellah and S Zullaikah
Deparment of Chemical Engineering, Institut Teknologi Sepuluh Nopember (ITS), Kampus ITS Keputih Sukolilo, Surabaya 60111 Indonesia
Email : szulle@chem-eng.its.ac.id

Abstract. A non-catalytic in-situ transesterification of biodiesel production from rice bran using subcritical water-methanol mixture was found to be unaffected by initial moisture and free fatty acids (FFA) contents. The method has been known as environmentally friendly conversion since no catalyst was used. Acid catalyst has an important role in in-situ transesterification due to their ability to accelerate the oil extraction from the bran and the reaction rate. In this study, CO$_2$ as pressurizing gas was added into subcritical water methanol mixture to increased yield and content of biodiesel. Effect of different operation pressure (P = 40-100 bar) at subcritical water methanol mixture (T = 200°C) and reaction time of 180 min on the yield and content of biodiesel were investigated. Rice bran with initial FFA content of 40.42 % has been subjected into hydrothermal reactor together with water methanol mixture to produce rice bran oil (RBO)-based biodiesel. The more CO$_2$ as pressurizing gas was added into the hydrothermal reactor, the more yield and content of biodiesel were obtained. The highest yield and content of biodiesel of 98.00±1.41% and 83.93%, respectively, were produced under P = 100 bar.

1. Introduction
Fossil fuels are still the most engage fuels to fulfill the energy demands in both industrial and transportation sectors. The negative effect to environment and depletion of fossil resource increase a demand of alternative fuels to replace fossil fuels utilization. Biodiesel, a promising and potential alternative fuel, is considered to replace petroleum diesel because of its non-toxicity, renewable, and environmentally friendly fuel [1-3]. Furthermore, biodiesel can also be blended with petroleum diesel or directly used in diesel engine [1,3]. Vegetable oils come from soybean, palm, rapeseed, and others are the most common feedstock used in biodiesel production on industrial scale. However, those feedstocks can drive high price of production cost [2,4]. Feedstocks which are cheaper, abundant, and sustainable can be an alternative to reduce the production cost. Rice bran, by-product of rice milling, becomes a potential feedstock for biodiesel production. Since it is abundant, cheap, and containing high oil content (10-26%) [4]. However, high free fatty acids (FFA) content in rice bran due to hydrolysis of triglycerides by lipase enzyme becomes an obstacle and cause a saponification which is reaction between...
oil and base catalyst. The saponification reaction can lower yield of biodiesel and hinder the separation and purification of biodiesel [5]. Various methods have been proposed to overcome those obstacles. Zullaikah et al [6] conducted two-step acid-catalyzed methanolysis to produce biodiesel from dewaxed/degummed rice bran oil (RBO) under low temperature for 8 hours. The conversion of 98% fatty acid methyl esters (FAME) was obtained under optimum condition. Ozgul-Yucel and Turkay [7] used simultaneous extraction and alkyl transesterification with acid catalyst at low temperature to convert rice bran oil into FAME. Shiu et al [2] investigated rice bran conversion using two-step in-situ transesterification from rice bran by acid and base catalyst simultaneously. While, Lai et al [8] used Novozym 435 and IM 60 as enzyme catalyst to accelerate reaction transesterification in biodiesel conversion. 98% of FAME and 81% of FAME was converted from RBO. Catalytic conversion technology is the common conversion method to convert biodiesel but the complicated separation and purification, lower rate of reaction, and longer reaction time become the drawbacks of those methods. Alternatively, non-catalytic conversion technology under sub/supercritical condition becomes an interest in rice bran-based biodiesel production due to insensitivity of FFA and water content of feedstock [4]. Kasim et al. [9] reported that 51.3% of FAME can be achieved using supercritical methanol at temperature 300 °C and pressure 30 MPa with CO2 as co-solvent. Supercritical CO2 can lower viscosity and have selectivity property [10]. While, Zullaikah et al. [4] proposed a non-catalytic in-situ conversion of rice bran using subcritical water-methanol mixture. The results showed that the higher yield of FAME (67.4 %) can be achieved under CO2 atmosphere with temperature 200°C, pressure 4 MPa, and reaction time for 3 h. However, high temperature of supercritical condition was a drawback since its charred the rice bran and lower yield of biodiesel [9]. Non-catalytic conversion under subcritical condition is a potential conversion method to produce biodiesel from rice bran because it obtained high biodiesel yield in a shorter reaction time [4]. Furthermore, Parvez et al [11] stated that subcritical water extraction can be considered as less energy intensive and environmentally friendly than other systems. Zullaikah et al. [4] stated that yield and content of biodiesel produced under CO2 atmosphere was higher than those under nitrogen (N2) atmosphere. CO2 becomes determined factor in non-catalytic conversion method. CO2 gas as co-solvent gave some positive effect in biodiesel conversion such as lower the operating condition, improve solubility, and increase efficiency of extraction [12]. Go et al [12] also stated that addition of CO2 gas as a co-solvent can improve the solubility and extraction efficiency of biomass, therefore higher yield of FAME can be achieved. They proposed in-situ transesterification method of J. curcas L. seed kernel under subcritical methanol, acetic acid, and water mixture to produce biodiesel using CO2 as pressurizing gas. Yield of FAME (98 %) based on extractable lipids of dry kernels can be achieved using this method. Miyazawa et al [13] also used CO2 in the form of dry ice to increase polysaccharide hydrolyses under hydrothermal condition. The result showed that yield of glucose increased with the increasing of the amount of loaded CO2 in the system. The effect of CO2 addition to increase the product yield can be considered as one of important and determined factor to improve performance in biodiesel production specifically in non-catalytic in-situ transesterification. In this work, the effect of pressurized CO2 injected in the in-situ transesterification of rice bran under subcritical water-methanol mixture on yield and content of biodiesel was investigated.

2. Experimental section

2.1. Materials
Rice bran (IR 64 variety) was obtained from local rice mill located in Banyuwangi, Indonesia. n-hexane and methanol were obtained from ANHUI FULLTIME (Anhui, China). CO2 gas as pressurizing gas was obtained from Aneka Gas (Indonesia) and other chemicals used was obtained from commercial sources.

2.2. Rice bran oil extraction
Initially, rice bran was separated from its impurities by sieving method. Then, rice bran (50 g) was extracted by n-hexane as solvent using a soxhlet extractor at 70 °C for 3 h. The mixture of crude rice bran oil (CRBO) and n-hexane was separated by a rotary vacuum evaporator (Yamato RE-46). The crude

IOP Conf. Series: Materials Science and Engineering 543 (2019) 012068   doi:10.1088/1757-899X/543/1/012068

IOP Publishing
The yield of FAME was determined as the weight ratio of FAME to CRBO as follows equation:

\[ \text{Yield of FAME (\%) = } \left( \frac{\text{crude FAME (g)} \times \text{FAME Content (\%)}}{\text{mass of CRBO (g)}} \right) \times 100\% \] (2)
3. Result and discussion

3.1. Effect of operating pressure to acidity (pH)

Operating pressure clearly affected the acidity of the system. Figure 1 shows that pH of the system slightly decreases with increasing loaded of CO$_2$ into the reactor. High amount of CO$_2$ loaded increased the operating pressure of the system. Peng et al [16] stated that pH of the CO$_2$ - water system decreased with pressure increment. Increasing solubility of CO$_2$ in water affected the acidity reduction and decreased the pH system. However, at high pressure, the reducing pH of CO$_2$ - water system is slowly with increasing of pressure. At pressure of 40 bar, calculated pH in the system was 3.82 and decrease to 3.78 at pressure of 100 bar. The decreasing of pH from pressure of 40 bar to 100 bar was only 1 % even though the amount of CO$_2$ was increased by 65 %. Furthermore, high operating pressure does not affect the reducing of acidity system significantly.

![Figure 1](image)

**Figure 1.** Effect of operating pressure to pH in the CO$_2$-water system at T = 200 °C

3.2. Effect of operating pressure on yield and purity of biodiesel (FAME)

The effects of increasing operating pressure on yield and content of FAME are shown in Figure 2. Yield of FAME increased significantly with increasing of operating pressure from 40 bar to 100 bar. At pressure 40 bar, yield of FAME was 35.00 ± 0.99% and kept increasing with the operating pressure. The highest yield of FAME (98.00 ± 1.41 %) was achieved at pressure 100 bar. The increment yield of FAME is caused by increment of pressure. When operating pressure in the system increase, the solubility of CO$_2$ in water system also increase [16]. The increasing of dissolved CO$_2$ in water can increase the acidity of the system due to the reaction of soluble CO$_2$ in water. The reaction can produce H$^+$ and makes the system more acidic [4,13]. In acidic condition, oil is more soluble therefore; the rate of oil extraction will be faster. Furthermore, the reaction rate of transesterification and hydrolysis of acylglycerols and esterification of FFA can also be faster. Figure 1 shows that the higher amount of loaded CO$_2$ introduced to the system, the lower acidity of the system. At pressure 100 bar, calculated pH in the system was the lowest and yielded the highest FAME. The highest percentage of increasing yield of FAME is obtained from pressure 80 bar to 100 bar which is 48%.
Figure 2. Effect of Operating Pressure on Yield and Content of FAME [T= 200 °C, reaction time = 3 h, rice bran/methanol/water ratio 1/4/4 (g/ml/ml)]

3.3. Effect of operating pressure on composition in crude biodiesel

The effects of increasing operating pressure on content of unreacted oils and other components are shown in Figure 3. Unreacted oils contain free fatty acids (FFA), triglycerides (TG), diglycerides (DG), monoglycerides (MG). Generally, the content of unreacted oils and other components in biodiesel was below of 10 %. It represented that the content of biodiesel produced under subcritical water-methanol mixture with CO₂ as pressurizing gas is mostly FAME. The initial FFA content in RBO was 40.42% and it lowered into below 4% under subcritical condition with varying pressure. However, the high amount of CO₂ added to the system did not affect the decreasing of FFA. The reaction pathway of FFA conversion is esterification in which FFA reacts with alcohol to form alkyl ester and water. However, the reaction pathway of acylglycerols conversion is transesterification with parallel reaction mechanism. In supercritical condition which needs high pressure and temperature, the reaction mechanism of transesterification is similar to the acid-catalyzed path. However, the reaction is much faster and completion of triglycerides to esters is more rapid than acid-catalyzed transesterification because the chemicals kinetics accelerate rapidly under supercritical conditions [17]. Ngamprasertsith and Sawangkeaw [17] proposed the mechanism reaction by the analogues between hydrolysis esters in supercritical water and transesterification of TG in supercritical alcohol. The assumption of mechanism reaction is initiated when the molecules of alcohol reacts with carbonyl carbon of TG due to the low hydrogen bond energy of alcohol and form alkyl esters and DG. Then, DG reacts with other alcohol molecules in a similar way to form alkyl esters and MG. In the last step, MG reacts with alcohol to produce alkyl esters and glycerol. The reaction mechanism proposed can be seen in Figure 4. The same reaction path also proposed by Asri et al [18] for thermal transesterification. The proposed reaction path of transesterification in supercritical condition can also be applied to subcritical condition. It is caused that those conditions need high temperature and pressure.
Figure 3. Effect of Operating Pressure on Composition in Crude Biodiesel [T= 200 °C, reaction time = 3 h, rice bran/methanol/water ratio 1/4/4 (g/ml/ml)]

Figure 4. The proposed reaction mechanism of transesterification under thermal conditions [17]

4. Conclusions
Carbon dioxide (CO₂) as pressurizing gas can substitute the absence of catalyst in non-catalytic conversion technology. The increasing of operating pressure due to the increment amount of introduced CO₂ to the system increased the yield of FAME and slightly increased the FAME content. The highest FAME yield and content was obtained under pressure 100 bar due to the lowering acidity in the system. The increasing of pressure does not affect unreacted oils and other components in biodiesel significantly.

References
[1] Gunawan S, Maulana S, Anwar S and Widjaja T 2011 Ind. Crops. Prod. 33 624-28
[2] Shiu P J, Gunawan S, Hsieh W H, Kasim N S, and Ju Y H 2010 Bioresour. Technol. 101 984-89
[3] Niawanti H and Zullaikah S 2017 Chem. Eng. Trans. 56 1513-18
[4] Zullaikah S, Rahkadima Y T and Ju Y H 2017 Renew. Energ. 111 764-70
[5] Ju Y H and Vali S R 2005 J. Sci. Ind. Res. 64 866-82
Acknowledgments
This research was financially supported by Ministry of Research, Technology and Higher Education and Institut Teknologi Sepuluh Nopember (ITS).