Sub critical water-methanol condition of rice bran oil for biodiesel production

G Prihandini* and L Elizabeth

Department of Chemical Engineering, Politeknik Negeri Bandung, Bandung, Indonesia

*ghusrina.prihandini@polban.ac.id

Abstract. Biodiesel produced in conventional way by using catalyst make environment harmful. Subcritical water is a new method, green technology which can be employed to convert rice bran with water and methanol to fatty acid methyl ester (FAMEs) or biodiesel with adding CO2 and N2 gas as co-solvent. The aim of this study to investigates the influence of operation condition of biodiesel production from rice bran oil. Some solvents concentrated, range of temperature, pressurized gas and reaction time were applied in this research. Rice bran, water, and ethanol were put into subcritical water reactor in a certain ratio at 40bar to carried out the reaction under subcritical condition. The best condition 30/10 methanol-water (v/v), t= 7 h, T = 200 °C, CO2 as co-solvent was highest yield oil obtained 18% with oleic acid methyl ester as the major identified biodiesel.

1. Introduction

The growing population all over the world lead to increasing fossil fuel demand. To substitute fossil fuel, an alternative renewable energy source must have found. Biodiesel is promising alternative to mineral fossil fuel.

Biodiesel is defined as a mixture of long chain fatty acid alkyl esters, which is made from triacylglycerols (TAGs) from different biological renewable recourses with an excess methanol or ethanol, in the presence of an acid, base or enzyme catalyst, although non-catalytic process are possible also. However, the utilization of catalyst in biodiesel production making environmental pollution. Biodiesel production using supercritical condition was proposed to overcome the drawbacks related to homogenous and heterogeneous catalytic process, recently. The advantages of supercritical using methanol were mixing properly, high conversion in short reaction time without any catalyst. In this case, there wasn’t catalyst added making no formation soap arise with high FFA and water content. In Supercritical fluid has high mass transfer rate and permeating capacity due to its lower viscosity and larger diffusion coefficient [1]. However, the high temperature and pressure were required for carry out reaction to supercritical condition. The large amount of energy will be consumed, making supercritical fluid is an inefficient way. Therefore, it still searching for better methods for biodiesel production with low energy consumption and environmentally friendly [2].

Recent trend of biodiesel production is subcritical water (SCW) method which is environmentally friendly with wide range application such extraction, hydrolysis, wet oxidation of organic compounds. SCW is interpreted as water at temperatures between normal boiling point (100 °C) and critical point
(374 °C) under high pressure to maintain in liquid phase [3]. Dielectric constant of water in SCW is the main factor as an extraction solvent. It decreases from 80 at room temperature to 27 at 250 °C, which is almost equal with that of organic solvent at room temperature. Increasing attention also led to comprehensive research for hydrolysis and biomass conversion to valuable compounds [4].

The forecast of the global biodiesel price will remain almost unchanged until 2024 because of the projected decrease in vegetable oil. High production cost due to high contribution (70-95%) of used biodiesel feedstock to the total production cost is considered to the biodiesel commercial [5]. Therefore, biodiesel feedstock should be examined in order to reduction of biodiesel production, oil containing and waste. Rice bran is a by- product of rice milling to produce white rice. Rice bran is the outer layer of the brown rice kernel; it contains 12-23% crude oil which mainly consist of TAGs depending on the rice origin [6]. After the milling process, rice bran deteriorates rapidly due to formation of Free Fatty Acids (FFAs) which is resulted from hydrolysis of TAGs increase acidity making soapy taste [7]. Hence, rice bran required particular method to overcome due to the presence of FFA. Like supercritical, there weren’t any soap formation in SCW method with high FFA content. Therefore, rice bran was fitted feedstock for biodiesel production using SCW method.

The aim of this study is to investigate the effects of treatment temperature, reaction time, ratio methanol/water of subcritical water treatment will be combined with pressurized gas CO₂ and N₂.

2. Material and methods

2.1. Material
Dried rice bran was obtained from Lamongan, East Java. Rice bran variant IR 64 was filtered to remove the impurities and kept in refrigerator to avoid increasing of FFA content. Any solvents and pressurized gases were purchased from commercial source. Filter paper No. 2, thickness 0.26 was purchased from Merck.

2.2. Biodiesel production in sub-critical water condition
Rice bran (5 g), methanol and water in certain ratio came into subcritical reactor equipped with external heater. Reactor was made from stainless steel, withstand 85 MPa maximal pressure. The set temperature on electric heater was measured at thermocouple. The pressurized gas (CO₂ and N₂) were injected into reactor to push pressure shifted to subcritical condition.

After achieving reaction time, gas pressure inside reactor was released immediately. The shocking temperature making reaction stopped as dropping pressure and temperature due to no more at subcritical condition. The released vapor was condensed in ice water bath. Liquid in the reactor was collected and added with 50 mL n-hexane. Both were shaken with magnetic stirrer and centrifuged then. The upper phase was hexane which contained rich FAME. Rotary vacuum evaporator was utilization to separate FAME from n-hexane. The extraction procedure was repeated three times. Ester conversion was estimated from the percentage area in gas chromatography (GC-MS) analysis of the product.

2.3. GC-MS analysis method
Quantitative analysis of Me-OH in each sample was performed on Shimadzu equipped with spilt injector and MSD detector. Separation was carried out on a HP-5MS 5% Phenyl Methyl Siloxane capillary column (30 m x 250 um i.d, 0.25 um film thickness), model Agilent number 19091S-433. The temperature program was set at 100 °C and maximum increase to 370 °C at 15 C/min and hold for 16 min. Total analysis time was 28 min. Helium was used as gas carrier with average velocity at 37cm/sec at 200 °C. Data analysis were carried out by HP 6890 GC Method.
2.4. Statistical analysis
Each experiment was performed in triplicate values were expressed as mean standard deviation. The difference associated with p<0.05 were considered significant for validity and reliability.

3. Result and discussion

3.1. Reaction time affected biodiesel production
The highest yield oil was obtained 13,82% ± 0,16 at 7 h reaction time using water-methanol as a solvent with CO$_2$ as a pressurized gas. Employing N$_2$ as a pressurized gas has same trends with CO$_2$ but less quantity about 12,75 % ± 0,071. Yield oil were increase as increasing temperature using both CO$_2$ and N$_2$ as pressurized gas. As the bran and water-methanol were mixed incompletely at initial reaction time making the yield oil low enough. However, when the reaction time keep longer than 7 h, the yield oil is decrease significantly. The decreasing yield oil due to a longer reaction time, fatty acid could not polymerize well [8]. The high presence of H$^+$ and OH$^-$ in subcritical condition impact for occurrence acid-base reaction. In addition, the use of CO$_2$ as pressurized gas making medium run closer into acid, might result in a high conversion of yield oil [9]. Hence, the CO$_2$ get higher yield oil than that of N$_2$ due to its properties.

![Figure 1](image1.png)

Figure 1. Reaction time affected yield oils. Under operation condition: Methanol/H$_2$O : 20/20 ml, T = 200 °C, P = 40 bar.

3.2. Temperature affected biodiesel production
Temperature has great influence in subcritical condition to maintain the medium in liquid state. Oils are greatly extracted from the bran depend on solvent type and temperature. In subcritical condition Water ionic product were higher in subcritical condition (10$^{-12}$) than that of ambient (10$^{-14}$) [9]. High density ascending at that condition also. These pushed ionic reaction make yield oil enhance.

![Figure 2](image2.png)

Figure 2. Effects of reaction time to yield oils. Operation condition: Methanol/H$_2$O : 20/20 ml, T = 200 °C, P = 40 bar.
The increasing temperature effected rising diffusion rate and decreasing viscosity, surface tension. Therefore, diffusion of subcritical water into matrix ran quickly [10]. Yield oils increase constantly as increase temperature. Under high solubility condition (>170 °C), it appears that oil was extracted immediately and diffusion-controlled extraction is reached, whereas Under low solubility (<170 °C) not all oil is extracted even after 7 h. The highest yield oils 13.82% ± 0.16 at 200 °C with CO₂ as a pressurized gas were described at Fig. 2. However, yield oils decrease to 13.14% ± 0.67 at 215 °C. The same trend was occurred at N₂ as pressurized gas. The increasing extraction temperature above the certain value gives rise to the degradation of the essential oil components. The possibilities explanation, as increasing temperature, the extraction rate come faster due to an increase in diffusion rate of subcritical water decrease viscosity and surface tension [11].

3.3. Ratio water-methanol affected biodiesel production
The amount of ratio solvent has correlation with polarity. The polarity water (10.2) and methanol (5.6) is totally different. However, under subcritical condition, the dielectric constant of water decrease to 27, same with dielectric constant of methanol at ambient temperature. Therefore, water can act as solvent to non-polar compounds [12]. The adding of organic solvent namely methanol could increase yield of rice bran oil.

Yield oils increase as increasing ratio methanol to water. The highest yield (17.43% ± 0.04) oils was obtained at ratio 30/10 methanol to water used CO₂ as a pressurized gas. The N₂ also has the same trend but the yield oils lower than CO₂ figure 3. When the amount of methanol increase to ratio 35/5, the yield oils decrease slightly. It’s proved that the excess of methanol, disposed to extract more polar compounds. The greater amount of solvent, the bigger extraction efficiency. However, the abundant solvent doesn’t extract more, the certain amount of solvent can extract optimally [13].

3.4. Quantitative analyses
Total biodiesel composition quantifications in GC-MS method. It was necessary to identification and integration area of biodiesel from C14 to C18. Results will be expressed in % area with two decimal place. The relative percentage areas of biodiesel from rice bran oil investigated are shown in figure 4 that described biodiesel arise at 10 until 19 retention time. Table 1 provides percentage of biodiesel. The GC-MS were identified as myristic acid methyl ester (0.91%), palmitic acid methyl ester (21.57 %), palmitic acid (3.95 %), oleic acid methyl ester (63.08%), stearic acid methyl ester (2.54%) and ascorbic acid (7.95%). Almost 80 percent of rice bran oil were converted into biodiesel. Oleic acid methyl ester was the major identified biodiesel, it was proved that subcritical water -methanol is a new promising way for economically and environmentally friendly biodiesel production.
3.5. FAME composition
FAME characteristic profile in reaction product was determined by GC-Shimadzu and the result was summarized in table 1. Oleic acid methyl ester (C18:1, 63.08%) was the most abundant FAME followed by palmitic acid methyl ester (C16:0, 21.5%) and stearic acid methyl ester (C18:0, 2.54%). The amount of FAMEs obtained in this study was greater than using esterification and transesterification method (data not shown).

![Figure 4. Gas chromatography analysis of biodiesel from rice bran oil.](image)

Table 1. GC-MS Analyses of Biodiesel with variable 200 °C, P: 40 bar, 8 h reaction time.

| RT  | Component                              | %Area |
|-----|----------------------------------------|-------|
| 10.17 | Myristic acid methyl ester (C14:0)   | 0.91  |
| 13.08 | Palmitic acid methyl ester (C16:0)   | 21.5  |
| 14.19 | Palmitic acid (C16:0)                 | 3.95  |
| 17.76 | Oleic acid methyl ester (C18:1n-9)    | 63.08 |
| 18.54 | Stearic acid methyl ester (C18:0)     | 2.54  |
| 19.05 | Ascorbic acid                          | 7.95  |

Biodiesel or fatty acid methyl ester (FAME) production using subcritical methanol-water from rice bran oil without presence catalyst. The absence of catalyst made reaction running slow due to oil feedstock and methanol were unmixed completely.

Subcritical methanol-water work at 100 °C to 374 °C with pressurized gas CO₂ and N₂ to keep water-methanol in liquid state. In that of condition, water can act as a reagent, acid-base catalyst and environmentally solvent. Acting as efficient acid-base catalyst, it has a high dissociation constant [9]. High dissociation constant of water at SCW almost equal with organic solvent in room temperature. So that of benefits, SCW has been applied in various reactions as extraction, hydrolysis, autocatalysis and decarboxylation. In this case, the principle of SCW as catalyst convert oil into biodiesel [10]. Biodiesel production from subcritical water methanol was carried out at different temperature, reaction time and ratio water–methanol.

4. Conclusion
By reacting methanol and water in subcritical condition, a newly method for the environmentally friendly biodiesel production from rice bran has been developed. This method doesn’t need any catalyst,
acid nor base catalyst. The proposed is simple with high yield obtained. However, further research is necessary to reduce the amount of methanol required in reaction.

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