TRANSESTERIFICATION OF VEGETABLES OIL USING SUB- AND SUPERCRITICAL METHANOL

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Abstract

A benign process, non catalytic transesterification in sub and supercritical methanol method was used to prepare biodiesel from vegetables oil. The experiment was carried out in batch type reactor (8.8 ml capacity, stainless steel, AKICO, JAPAN) by changing the reaction condition such as reaction temperature (from 210°C in subcritical condition to 290°C in supercritical state with of 20°C interval), molar ratio oil to methanol (1:12-1:42) and time of reaction (10-90 min). The fatty acid methyl esters (FAMEs) content was analyzed by gas chromatography-flame ionization detector (GC-FID). Such analysis can be used to determine the biodiesel yield of the transesterification. The results showed that the yield of biodiesel increases gradually with the increasing of reaction time at subcritical state (210-230°C). However, it was drastically increased at the supercritical state (270-290°C). Similarly, the yield of biodiesel sharply increased with increasing the ratio molar of soy oil-methanol up to 1:24. The maximum yield 86 and 88% were achieved at 290°C, 90 min of reaction time and molar ratio of oil to methanol 1:24, for soybean oil and palm oil, respectively.

Keywords: free catalyst; sub-and supercritical methanol; transesterification; vegetables oil

INTRODUCTION

Currently biodiesel is very promising alternative energy to be developed as a replacement for diesel oil (Joelianingsih et al., 2008; Asri et al., 2010). Biodiesel has many advantages, especially; it is friendly to the environment, due to its characteristics, lack of aromatic compound, high biodegradability, low SO₂ and particular matter content (Schuchardt et al., 1998; Michael and McCormick, 1998; Ma and Hanna, 1999). Biodiesel is derived from renewable...
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材料如植物油、动物油、藻类和食用油。此外，生物柴油具有减少污染物和致癌剂的潜力。目前，生物柴油通常是通过传统的方法来生产的，这些方法使用均相基催化剂（Joeliamingsih et al., 2008; Asri et al., 2010; Imahara et al., 2008; Minami and Saka, 2006）。在这个过程中，通常存在一些问题，例如脂肪酸含量（FFA > 0.5%）与催化剂反应，生成皂化产物，这些产物不是所需的，因此需要通过过程来清洁催化剂和产品。这个过程需要更多净化步骤来消除皂化产品，作为催化剂，最终在较低的油中获得生物柴油。此外，生物柴油生产的总成本不具有竞争力。因此，需要进一步的研究来找到一个有效的生物柴油生产过程，具有低成本和最小的环境影响。

同质催化剂是一种最具有前景的替代方法来生产生物柴油从植物油，因为它可能能够克服均相催化剂的弱点。同质催化剂的催化过程被期望能成为一个有效的过程并提供一个最小的环境影响。同质催化剂的催化过程被期望能成为一个有效的过程并提供一个最小的环境影响。Kouzu et al. (2008) 进行了油酸甲酯与甲醇的反应，使用了钙氧化物（CaO）作为固体基质。结果表明，在一个小时内，脂肪酸甲酯的产率随温度升高而升高，达到99.3%。此方法的另一个优点是，它不使用催化剂，因此可以容易地分离。此外，可以克服扩散问题，因为在超临界甲醇中，由于其高密度，水的密度增加，这有助于甲基酯的形成。

在超临界状态下，甲醇具有疏水性，这有助于克服扩散问题。另一方面，它的存在增强了油酸甲酯的形成。然而，它的不稳定性是生物柴油的一个问题。目前，生物柴油的生产过程是通过一系列的反应来完成的，例如：二甲基硫酸盐甲酯的合成，以及生物柴油的生产。在超临界甲醇中，水的存在不会影响甲醇的生产。

同样，几乎没有关于油酸甲酯在甲醇中的反应的资料。因此，这项工作集中在没有催化剂的油酸甲酯的生物柴油生产上。这项研究使用了Wako纯化学品公司制造的甲醇和六烷基。甲醇和六烷甲基酯标准（甲基棕榈酸，甲基棕榈酸，甲基棕榈酸和甲基棕榈酸）是使用Wako纯化学品公司制造的甲醇和六烷基酯的标准。

MATERIAL AND METHODS

Material

棕榈油和大豆油为起始材料由Wako纯化学品公司提供，日本。甲基棕榈酸，甲基棕榈酸和甲基棕榈酸酯的标准（甲基棕榈酸，甲基棕榈酸，甲基棕榈酸和甲基棕榈酸）由Wako纯化学品公司提供，日本。同样，几乎没有关于油酸甲酯在甲醇中的反应的资料。因此，这项工作集中在没有催化剂的油酸甲酯的生物柴油生产上。这项研究使用了Wako纯化学品公司制造的甲醇和六烷基酯的标准（甲基棕榈酸，甲基棕榈酸，甲基棕榈酸和甲基棕榈酸）是使用Wako纯化学品公司制造的甲醇和六烷基酯的标准。
The reactor was firstly charged with the mixture of palm oil and methanol in a certain molar ratio. Then the reactor was inserted to the electric furnace. Prior, one series of experiment was done to measure the temperature and pressure inside the reactor during the reaction procedure. The effect of different operational parameters (reaction temperature, reaction time and molar ratio) on the yield of biodiesel were observed. After reaching the set point of temperature, at which point the reaction was kept until the time of reaction was achieved. Afterwards, the reactor was removed from the electric furnace and immersed in water bath for cooling in order to stop the reaction. The treated liquid discharged from the reactor into a sampling bottle. Two ml of water were added into the solution mixture for diluting the excess of methanol. Subsequently, the solution mixture was centrifuged to separate it into two phases. The top phase was FAMEs (biodiesel) and a small amount of un-reacted oil. The bottom phase consisted of methanol, water and glycerol. Biodiesel was analyzed by gas chromatography-flame ionization detector (GC-FID) (Gas Chromatography GC-14B, Shimadzu, Japan) equipped with a HP-Innowax capillary column (30 m x 0.250 mm x 0.25 µm). The oven temperature was programmed as follow: initial temperature of 210°C was hold for 9 min, increased to 230°C at 20°C/min interval for 20 min, then increased to 250°C at 20°C/min interval for 5 min. The injector and detector temperatures were controlled at 250 and 300°C, respectively. The injection volume was 1 µl. The carrier gas was helium and the makeup gas was hydrogen. The analyses of biodiesel can be used to determine the yield % of biodiesel and the conversion of palm oil, which was defined as follows:

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\text{Yield of Biodiesel(\%)} = \frac{\text{W of biodiesel}_{\text{actual}}}{\text{W of oil}} \times 100
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Where, W of biodiesel actual and W of oil are actual weight of biodiesel from the experiment (mg) and weight of oil used in the experiment (mg), respectively.

**RESULTS AND DISCUSSION**

As mentioned in section 2, that the experiment were conducted in the batch type reaction vessel, therefore the temperature and pressure inside the reactor are different in different reaction condition (Kusdiana and Saka, 2001). Before experimenting with the variables studied, a series of experiments were conducted to measure the temperature and pressure during the reaction. In Our experiment with soybean oil, the relationship between the maximum reaction temperature and pressure inside the reactor along with the reaction occurred as shown in Figure 1. The critical point (T_c and P_c) of methanol is 239°C and 8.09, respectively.

Therefore, from Figure 1 can be determined the state of methanol. Supercritical methanol is in quadrant 1.

**Effect of Molar Ratio Oil to Methanol on Yield of Biodiesel**

The molar ratio of oil to methanol is one of the most important variables that affecting the yield of FAMEs (biodiesel) obtained. Theoretically, the stoichiometry of transesterification reaction requires three moles of methanol to react with one mole of triglyceride produced three moles of FAMEs and one mole of glycerol. Since it is an equilibrium reaction an excess of methanol will increase the yield of biodiesel by shifting the equilibrium to the right side. Generally, in the conventional process used molar ratio of oil to methanol 1:6. However, transesterification in supercritical methanol that have been done by many earlier researchers, such as Imahara et al., Minami and Saka, Kusdiana and Saka, Saka and Kusdiana used molar ratio higher than that of homogeneous catalysts, with values that varies depending on the materials and process used (Imahara et al., 2008; Kusdiana and Saka, 2001; Saka and Kusdiana, 2001). Transesterification in supercritical methanol requires molar ratio oil-methanol greater than homogeneous catalysts, because oil and methanol are the two immiscible phases, so with the higher molar ratio increased the contact area between methanol and triglyceride.

This work, therefore, the effect of molar ratio of soybean oil to methanol on the yield of biodiesel was studied in the range between 1:12 to 1:42. Reaction was carried out in the batch reactor with sub and super-critical methanol; meanwhile the reaction temperature and the reaction time were kept constant 290°C and 30 min, respectively. Figure 2 shows the influence of molar ratio soybean oil to methanol on the yield of biodiesel. The increasing molar ratio of soybean oil to methanol resulted in higher yield of biodiesel.

![Figure 1. The relationship between temperature (°C) and pressure (MPa) inside the reactor during the transesterification reaction of soybean oil in the batch type of reactor.](image-url)
biodiesel. By the increasing molar ratio from 1:12 to 1:18 the yield of biodiesel gradually increased from 22 to 26%. However, at 1:24 of molar ratio the yield biodiesel drastically increased to 73.66%. Beyond the molar ratio of 1:24 (1:30-1:42) the excessively added methanol had no significant effect on the yield of biodiesel.

Those results indicate that the optimum molar ratio oil-methanol was 1:24. For molar ratio less than 1:24, the contact area between oil-methanol was low, result low yield of biodiesel, whereas at ratio higher than 1:24 it become difficult to separate glycerol from methanol. Meanwhile, Kusdiana and Saka in their studies of transesterification of rapeseed oil in supercritical methanol obtained 95% yield of biodiesel. It should be noted that those result achieved at 350°C and 30 MPa with molar ratio 1:42 (Kusdiana and Saka, 2001).

It can be concluded that the higher molar ratio of soybean oil to methanol the higher biodiesel yield was obtained until a certain molar ratio of soybean oil to methanol. Practically, too much excess of methanol is not favorable because too much energy is needed to recover it, which is finally increasing the total production cost of biodiesel. In this work, therefore, the optimum molar ratio of soybean oil to methanol was 1:24.

On supercritical methanol the nature of a mixture of two phase’s oil and methanol easily converted into one phase because methanol is experiencing a reduction in dielectric constant. It can be explained that liquid methanol is a polar solvent and has hydrogen bonding. The degree of hydrogen bonding decrease with increasing temperature, the polarity of methanol would decrease in supercritical state. This means that supercritical methanol has a hydrophobic nature with the lower dielectric constant, resulted non polar triglyceride easily dissolved in supercritical methanol (Kusdiana and Saka, 2001; Diasakou et al., 1998)

The influence of reaction time on the yield of biodiesel on various temperature reactions of Palm oil was shown on Figure 4. For palm oil, it was seen that the yield of biodiesel rose in line with the extension of time and temperature reaction. The gradient yield of Figure 3 and Figure 4 show the effect of reaction time on yield of biodiesel at various temperature of reaction for soybean oil and palm oil, respectively. As shown in Figure 3 at 210 and 230°C, biodiesel yield (for soybean oil) rise gradually with increasing time. This is because at those temperatures methanol are on subcritical conditions (refer to Figure 1), so oil and methanol is not mixed in with perfect causing the reaction runs slowly, so that the resulting low yield. At 250°C biodiesel yield higher than both of temperature (210 and 230°C), but biodiesel yield still gradually increase along with the increase in time. This is possible because 250°C is relatively too close to critical point, so it is still affected by the stability of supercritical methanol condition. However at 270°C the yield of biodiesel drastically increases from 19 to 73% within 30 min and 60 min, respectively. Beyond the 60 min which occurred opposite, where yield of biodiesel rising gradually along the increasing time of reaction and the highest yield 77% was achieved within 90 min. At 290°C yield of biodiesel drastically increased from 6 to 73% in the shorter time (from 15 to 30 min) compared to 270°C, and the highest yield of 86% was achieved in 90 min.
biodiesel at subcritical temperature (210 and 230°C) and at near a critical point (250°C) of palm oil are much lower than soybean oil. Even at a temperature of 270°C, the biodiesel yield was still low but it gradually increases a long with the increase in reaction time. However, at 290°C the yield of biodiesel sharply increased from 0.4 to 88 at 10 min up to 90 min.

Figure 4. Yield of biodiesel (%) from palm oil as function of reaction time at various temperatures and molar ratio palm oil to methanol 1:24

Figure 5 shows, the comparison of the yield of biodiesel on various reaction times at 290°C between soybean oil and palm oil. For palm oil around 10 min to 70 min yield biodiesel gradually increase as the reaction time passed by, but the value on each time is much lower than soybean oil. Then, from 20 to 40 min the yiled increases almost linearly. A nother gradual increase of the yield is at 40-70 min.

Figure 5. Yield of biodiesel (%) as function of reaction time (min) at 290°C and molar ratio oil-to methanol 1:24 for soybean oil and palm oil.

Meanwhile, beyond 70 min (70 up to 90 min) the yields of biodiesel drastically increase from 54 to 88%. This is might be possible due to the physical properties of palm oil (viscosity, density and freezing point) higher than soybean oil. Therefore, it need much longer time than that of soybean oil for achieving the setting temperature.

CONCLUSIONS

An environmental friendly transesterification of vegetable oil (soybean oil and palm oil) without catalysts in sub and super-critical methanol was carried out in a batch type reactor system (AKICO Co., Japan). The effect of molar ratio of soybean oil to methanol, reaction time and reaction temperature were investigated. It was found that molar ratio soybean oil-methanol was greatly affected the yield of biodiesel. Reaction temperature and reaction time were significantly influence the biodiesel yield for both of oil.

The optimum molar ratio of soybean oil to methanol is 1:24. The maximum yield 86 and 88% were obtained at 90 min and 290°C for soybean oil and palm oil, respectively. At subcritical condition and near critical point the relative low yield were obtained for both of oil (soybean and palm oil). However, at supercritical methanol the yield of biodiesel drastically increased a long with the increasing the time of reaction. Therefore can be concluded, that transesterification vegetable oil with supercritical methanol is one of the potential process to overcome the drawback of conventional process.

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