Korean J. Chem. Eng., 32(11), 2290-2294 (2015)
DOI: 10.1007/s11814-015-0203-y

pISSN: 0256-1115
eISSN: 1975-7220

Biodiesel production from palm oil using a non-catalyzed supercritical process

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(*Received 9 May 2015 • accepted 24 September 2015*)

Abstract−The effects of free fatty acid (FFA) and moisture contents in palm oil, as well as working volume ratio on the production of biodiesel (fatty acid methyl esters; FAMEs), were investigated using palm oil and a non-catalytic supercritical process. FAME content obtained using anhydrous palm oil was 95.8% during the non-catalytic supercritical process. FAME content produced with 15% moisture content and 15% FFA content was 94.4% and 95.1% respectively, which was similar to that of anhydrous palm oil with no FFA. The non-catalytic supercritical process was not affected by FFA or moisture content in oil. By increasing working volume ratio, reaction temperature decreased from 340 °C to 260 °C at the same pressure, whereas FAME content increased from 69.9% to 95.5%.

Keywords: Biodiesel Production, Non-catalytic Supercritical Process, Palm Oil

INTRODUCTION

Inexpensive and convenient use of fossil fuels is expected to decrease in the near future. Additionally, high oil press, energy supply, and demand are very unstable caused by the unstable political environment in the Middle East. Countries are trying to establish long-term strategies using reliable and environmentally friendly biodiesel as an alternative energy source [1-3]. Biodiesel is fatty acid methyl ester (FAME) manufactured through a transesterification reaction between vegetable oil and alcohol. It can be used directly in a diesel engine without any special modifications. Unlike fossil fuels, biodiesel has many advantages such as a significant reduction in CO_2 emissions [1,2].

The reasons for replacing fossil fuels with biodiesel are due to sustainable supply of inexpensive raw materials and the cheap cost of the biodiesel synthetic process compared to fossil fuels. The price of raw materials for biodiesel production is approximately 70% of fossil fuels, which is an absolute factor [4]. Therefore, the problem of securing inexpensive raw materials is directly related to the competitiveness of the production process. Vegetable oils such as soybean, corn, and rapeseed oil were used as raw materials for primary biodiesel production. The use of edible grains and oil feed as biodiesel feedstock for biodiesel production caused soaring prices, which were sparked by triggering side effects in the international market [5]. Therefore, researchers began to use cheaper oils such as palm oil, jatropha oil, waste vegetable oil, and animal fat to reduce production costs [2,6-8]. In addition, studies using wood fiber, marine resources, and microalgae have actively progressed [9-12].

The biodiesel manufacturing process is divided into catalytic processes and non-catalytic supercritical processes. The main commercial manufacturing processes use a basic transesterification catalyst. However, low-grade feedstocks with high moisture and free fatty acids (FFA) content cause saponification reactions and decrease catalytic activity. The catalyst must be able to be removed after the reaction, but in glycerin, it remains. To overcome these disadvantages, applications with solid acid catalysts or lipase have progressed, but a significantly lower reaction rate than that of the base-catalyzed reaction has become a stumbling block [6,13].

Supercritical methods are being studied to solve this problem of using a catalyst. These methods use supercritical methanol transesterification methods without a catalyst. The supercritical state is the state at which temperature and pressure are over the critical point, and substances exist in a shared gas and liquid form. Therefore, the density of the material close to a liquid state causes an increase in solute solubility. This is similar to the diffusion rate of gases, which have low surface tension and viscosity. Studies have been actively progressing using non-catalyzed reaction conditions in which methanol is converted to supercritical methanol to apply the solvent and reactant to biodiesel production [14-17]. The polarity of methanol is very low when it is in a supercritical state, and solvency to oil increases. These properties are easily synthesized biodiesel using oil without a catalyst. Because the reaction mixture exists in two phases, the reaction only occurs at the interface when using a catalyst. Thus, the mass transfer rate of reactants in contact with the interface determines the overall reaction rate, but the resistance

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to mass transfer vanishes due to disappearance of the interface between oil and methanol when using supercritical methanol. A supercritical reaction is significantly faster and achieves higher productivity compared with that using an alkali catalyst. In addition, because the supercritical reaction does not use a catalyst, it greatly simplifies the separation process, and glycerin can be recovered easily as a by-product [5,16].

In this study, we investigated the effects of FFA and moisture content in palm oil on transesterification for production of biodiesel in a supercritical state. The effect of working volume in a supercritical state was also investigated.

MATERIAL AND METHODS

1. Materials

Refined and bleached palm oil was obtained from the Samyang Well Food, Co. (Incheon, Korea). FAMEs and heptadecanoic methyl ester reference standards (>99% purity) were purchased from Sigma Chemical Co. Ltd. (St. Louis, MO, USA). Methanol (>99.8%, Duksan Chemical, Co., Ansan, Korea) and all other chemicals were of analytical grade.

2. Experimental Apparatus

A reactor made of Hastelloy C-278 (Reaction Engineering Co., Ltd., Korea, limited temperature of 400 °C, 500 bar pressure and a 300 mL reaction capacity) was used to achieve the supercritical reaction. The temperatures and pressures outside the reactor and inside the furnace were controlled by a PID control system, which can be used to build a dual system. Agitation under certain conditions (high temperature and pressure) was maintained by circulating coolant into a gasket stirring device.

3. Experimental Procedures

3-1. Non-catalytic Supercritical Reaction

The reactor was charged with palm oil and heated to the set temperature using a PID temperature controller with a heating rate of 15 °C/min under agitation. Experiments were at 270-340 °C, which is over the critical temperature of methanol (T_c=240 °C), and 300-415 bar, which is over the critical pressure of P_c=80 bar. Samples were harvested at 0-15 min intervals for analysis. Biodiesel produced by the supercritical reaction was used to analyze FAME content. The working volume ratio is defined as the ratio of working volume per total reactor volume.

3-2. Alkali-catalyzed Transesterification

Alkali-catalyzed transesterification was conducted using a 1-L reactor system, composed of a 1-L four-necked glass reactor equipped with a reflux condenser, a thermometer, and a sampling port. The reactor was heated by a heating jacket which was controlled by a PID temperature controller [2]. Experiments were perfomed under conditions of a palm oil-to-methanol molar ratio of 1 : 10, reaction temperature of 65 °C, reaction time of 10 min, agitation speed of 2,000 rpm, and 1 wt% potassium hydroxide based on oil weight. Samples were harvested at 0-10 min intervals and used to analyze FAME content.

4. Analytical Methods

Samples were obtained at predetermined time intervals. Approximately 1 mL of sample mixture was collected in a 10 mL test tube, and the samples were evaporated to remove non-reacted methanol and eliminate glycerin. The treated samples were diluted with hexane, and an internal standard (methyl heptadecanoate) was added for gas chromatography analysis [2]. FAME content was measured according to KS H ISO 5508 (Animal and vegetable fats and oils analysis by gas chromatography of methyl esters of fatty acids; Korean Standard Association, [18]). The analyses were conducted on a gas chromatograph (iGC7200, DS Science, Seoul, Korea) using a fused silica capillary column (HP-INNOWAX, Agilent Technologies, Santa Clara, CA, USA) and a flame-ionization detector with an injector temperature of 250 °C, oven temperature of 210 °C, and a detector temperature of 250 °C [2].

Approximately 250 mg of sample for analysis was added to a 10 mL vial and dissolved with 5 mL of internal standard solution (methyl heptadecanoate dissolved in hexane). FAME content was calculated with Eq. (1).

$$C = \frac{\sum A - A_{SI}}{A_{SI}} \times \frac{C_{SI} \times V_{SI}}{m} \times 100\% \qquad (1)$$

where C is FAME content (wt%), $\sum A$ is the peak area of the C_{14}-$C_{24:1}$ methyl esters, A_{EI} is the peak area of methyl heptadecanoate, C_{EI} is the concentration of methyl heptadecanoate in the solution

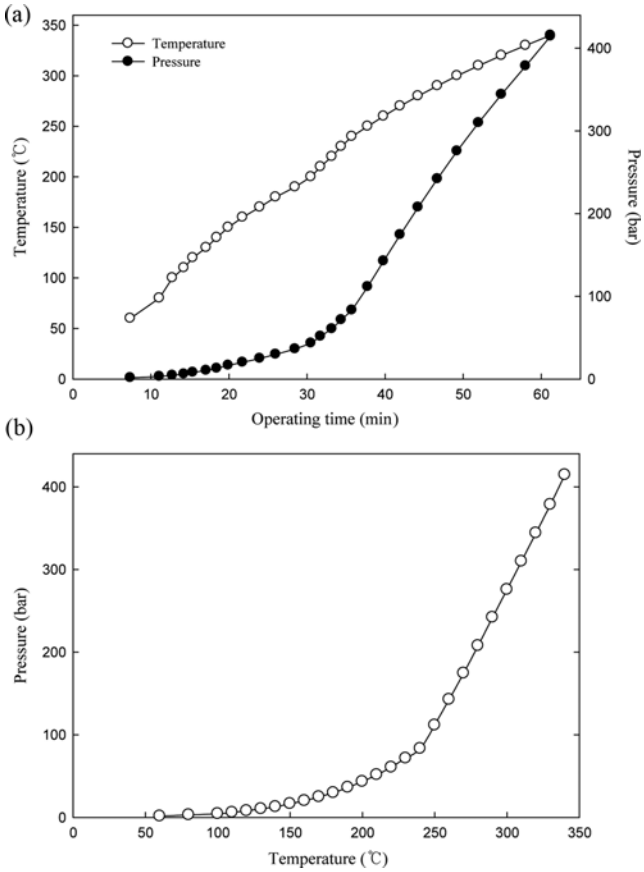

Fig. 1. Changes of reaction temperature and pressure during biodiesel production from palm oil in the non-catalytic supercritical reaction (0.815 working volume ratio, 0.02 mol oil/mol methanol). (a) Changing pressure and temperature with respect to operating time, (b) characteristic of increasing pressure with respect to temperature.

(mg/mL) used, V_{EI} is the volume of the methyl heptadecanoate solution (mL) used, and m is sample weight (g) [2,18]. The results of analysis were repeated three times and were stated as average value ± standard deviation.

RESULTS AND DISCUSSION

1. Changes of Reaction Temperature and Pressure During Supercritical Reaction

Palm oil and methanol were introduced into the supercritical reactor at molar ratio of 1 : 50 to develop the supercritical biodiesel production process. Fig. 1(a) shows the changes in pressure at 340 °C with respect to time. After 32 min of reaction, the temperature and pressure of the reactor reached 240 °C and 83.2 bar, respectively. The reaction temperature increased linearly with respect to time, but reactor pressure increased sharply. This phenomenon indicated that the supercritical condition of methanol was 240 °C and 80 bar, where the liquid methanol phase changed to gas, and then inflated the volume, which caused the pressure increase [5,19]. Fig. 1(b) shows the characteristic of increasing pressure with respect to temperature during FAME production from palm oil in a non-catalytic supercritical reaction under a working volume ratio of 0.815 and a 0.02 mol oil/mol methanol molar ratio. As shown in Fig. 1(b), reactor pressure was 83 bar when the reaction temperature reached 240 °C. Reactor pressure increased sharply by increasing reaction temperature. Finally, the reactor pressure was 414.5 bars when 340 °C was reached.

2. Biodiesel Production Using Non-catalytic Supercritical Process

2-1. Effect of Reaction Temperature

Fig. 2 shows the effect of temperature on FAME content in the non-catalytic supercritical reaction under a working volume ratio of 0.723 and 0.02 mol palm oil/mol methanol. FAME content was approximately 70% when reaction temperature was 260 °C. FAME content was 88.7% and 95.5% when temperature was 270 °C and 340 °C, respectively. We conclude that FAME content increased linearly by increasing reaction temperature. In the reaction time experiment, FAME content under conditions of 340 °C and 300 bar was 94.37, 95.28, and 95.83% at 0, 5, and 10 min, respectively. FAME content decreased slightly to 94.41% when reaction time was extended to 15 min. These FAME production patterns were similar to those of previous studies [5,14,19] based on reaction time. Table 1 shows the results of composition analysis of palm oil FAMEs obtained from the non-catalytic supercritical reaction. Similar amounts of palmitic acid and oleic acid were detected.

Table 1. Composition of palm oil fatty acid methyl esters

Fatty acid	Content (%)	Reference [20]
Palmitic acid (C16:0)	41.52	37-40
Stearic acid (C18:0)	5.06	5-6
Oleic acid (C18:1)	40.7	43-45
Linoleic acid (C18:2)	10.28	9-11
Linolenic acid (C18:3)	0.22	1-2
Other (C14:0, C24:0)	0.48	-

2-2. Effect of Moisture Content in Palm Oil

There is a limitation on the catalytic process of biodiesel production using low cost, low-grade feedstocks that contain high moisture and FFA content [2,6,20]. We wanted to determine the proper process to enhance biodiesel quality and yield using the non-catalytic supercritical reaction, despite using low cost and low-grade feedstocks. Fig. 3 shows the effect of moisture content on FAME production during the alkali-catalyzed and non-catalytic supercritical processes. FAME content reached 98.24% during biodiesel production by using the alkali-catalytic process with anhydrous palm oil. FAME content decreased to 93.26 and 92.45%, respectively, in the case of using 1 and 2% moisture content. Only 24.63% FAME content was observed when moisture content increased to 10%. In conclusion, FAME content decreased sharply by increasing palm oil moisture content. This phenomenon occurred due to methoxide ion, which acts catalytically, and was inhibited by moisture in the oil. Additionally, saponification occurred due to the FFAs in

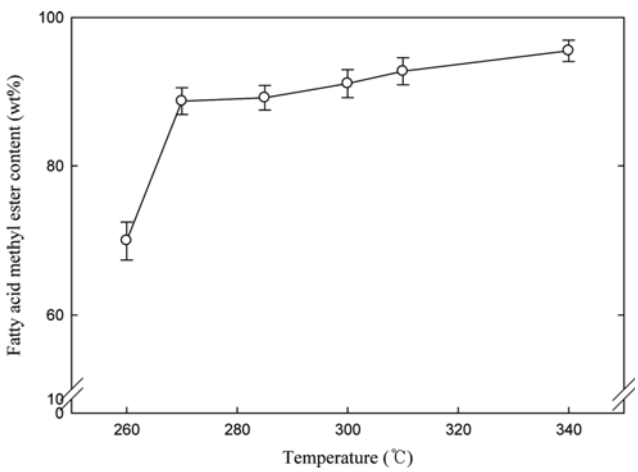

Fig. 2. Effect of temperature variations on fatty acid methyl ester content during the non-catalytic supercritical reaction (0.723 working volume ratio, 0.02 mol palm oil/mol methanol).

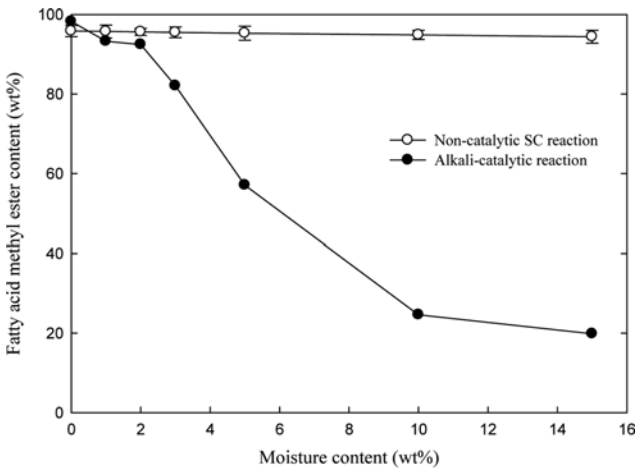

Fig. 3. Effect of palm oil moisture content on the fatty acid methyl ester production process (0.723 working volume ratio, temperature 340 °C, gauge pressure 300 bar, 0.02 mol palm oil/mol methanol).

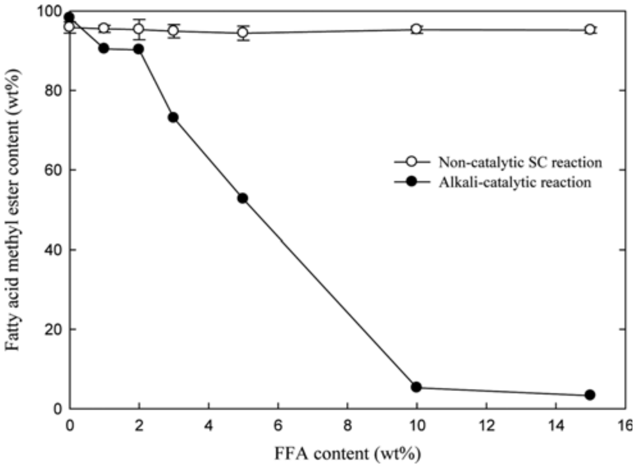

Fig. 4. Effect of palm oil free fatty acids on the fatty acid methyl ester production process (0.723 working volume ratio, temperature 340 °C, gauge pressure 300 bar, 0.02 mol palm oil/mol methanol).

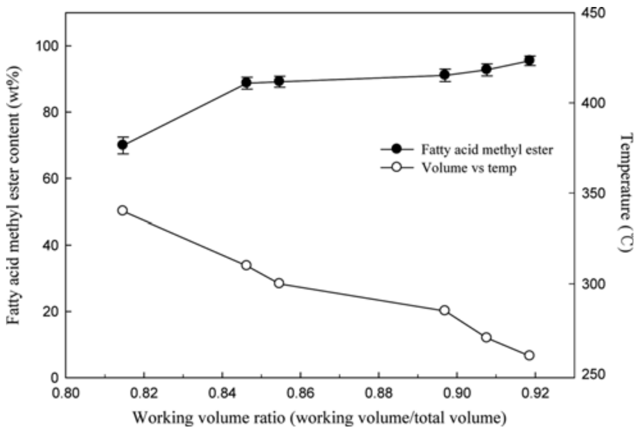

Fig. 5. Relationship between fatty acid methyl ester content and temperature with working volume ratio during the non-catalytic supercritical reaction (gauge pressure 415 bar, 0.02 mol oil/mol methanol).

the oil and the alkali metal in the alkali catalysts [1,2,20]. FAME content of 95.8% was obtained during the non-catalytic supercritical process using anhydrous palm oil as the substrate. Palm oil with 15% moisture content was used to obtain 94.4% FAME content. As a result, the moisture content in the oil had a limited effect on FAME production during the non-catalytic supercritical process. The non-catalytic supercritical process can be applied at low cost using low-grade feedstocks compared to the alkali-catalytic process.

2-3. Effect of FFA Content in Palm Oil

Fig. 4 shows the effect of FFA content in palm oil on FAME production during the alkali-catalyzed and non-catalytic supercritical processes. The alkali-catalyzed process using anhydrous palm oil reached 98.24% FAME content. FAME content decreased with palm oil containing 1% or 2% FFAs to 90.41 and 90.23%, respectively. FAME content decreased sharply to 72.99 and 52.64% with 3% and 5% FFA content. Furthermore, only 5.2% of FAME was observed with palm oil containing 10% FFA content. This was a result of saponification, which occurred due to the FFAs in the oil and alkali metal in the alkali catalysts during the alkali-catalytic biodiesel process. The shortage of alkali-catalyst causes a decrease of FAME conversion in oils containing high FFAs [1,20]. Additionally, water is formed when FFAs react with an alkali catalyst. This water inhibits the formation of methoxide ion, which acts as catalyst [1,2,20]. The non-catalytic supercritical reaction resulted in similar FAME content produced by oil containing FFAs or no FFAs. As a result, FAME production during the non-catalytic supercritical process was not affected by FFA content in the oils. This result indicates that FFAs can be converted to FAME without a catalyst under supercritical conditions. As a similar result, Saka et al. [16] reported a 98.9% ester yield from palm oil containing 5.3% FFA and 2.1% water using the supercritical methanol method under conditions of 350 °C, 20 MPa, 9 min, and a molar ratio of methanol to oil of 42.

2-4. Effect of Working Volume Ratio

The relationships between temperature and pressure were investigated during FAME conversion to determine the optimum temperature at constant pressure for obtaining the highest FAME yield. The reaction temperature was changed to 260-340 °C using a 300 mL-scale supercritical reactor to find the optimal working volume ratio at constant pressure of 415 bar. The change in temperature and pressure similarly progressed to 180 °C in all tested reaction temperature ranges. However, pressure increased proportionally to working volume ratio at temperatures >180 °C. Therefore, constant pressure was reached rapidly at a low temperature with a high working volume ratio [S1].

To investigate the effect of working volume ratio (0.815-0.919) on the non-catalytic supercritical reaction for biodiesel production, the reaction was conducted for 10 min at 260-340 °C under conditions of palm oil-to-methanol molar ratio of 1 : 50 (0.02 mol oil/mol methanol), reaction pressure of 415 bar, and mixing speed of 500 rpm using a 300 mL-scale supercritical reactor (Fig. 5). The highest FAME content of 95.5% was obtained with palm oil, a working volume ratio of 0.919, and reaction time of 10 min. Reaction temperature decreased from 340 °C to 260 °C by increasing working volume ratio, and FAME content increased from 69.9% to 95.5%. This result is similar to previous results [5,14,21]. Although, those previous studies conducted the supercritical reaction in a small scale reactor (<44 mL) to obtain high FAME content in 10, 20, and 60 min [5,14,21]. In contrast, our results were obtained for a larger scale system. The possibility of scale-up was properly confirmed for the supercritical reaction.

The non-catalyzed supercritical process is economically feasible because it does not require pretreatment of raw materials, neutralization, washing, drying and wastewater treatment operations, which is essential during the catalyzed process. Additionally, the non-catalyzed supercritical process requires very short reaction times, so productivity was higher than that of the catalyzed process. Therefore, it is a more economical process than catalytic processes of biodiesel production.

CONCLUSIONS

The supercritical characteristics of methanol without catalyst were applied to develop the optimal non-catalytic supercritical biodiesel process. When reaction temperature increased during the non-catalytic supercritical process, reactor pressure increased sharply. FAME content produced using anhydrous palm oil was 95.8%. This result was similar to the reaction using palm oil containing 15% moisture content and 15% FFAs, which was 94.4% and 95.1%, respectively. The non-catalytic supercritical process can be applied at low cost with low-grade feedstocks containing high FFA and moisture content. Working volume ratio during the supercritical reaction affected temperature and pressure. Constant pressure was achieved rapidly at low temperature, when the working volume ratio of the reaction increased. The highest FAME content of 95.5% was obtained under a 0.919 working volume ratio. The reaction temperature decreased by increasing working volume ratio; however, FAME content increased to 95.5%. Our results suggest that a supercritical biodiesel production process could be highly competitive for industrialization.

ACKNOWLEDGEMENTS

This research was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT, and Future Planning (2013R1A1A2011230).

SUPPORTING INFORMATION

Additional information as noted in the text. This information is available via the Internet at http://www.springer.com/chemistry/journal/11814.

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Supporting Information

Biodiesel production from palm oil using a non-catalyzed supercritical process

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(*Received 9 May 2015 • accepted 24 September 2015*)

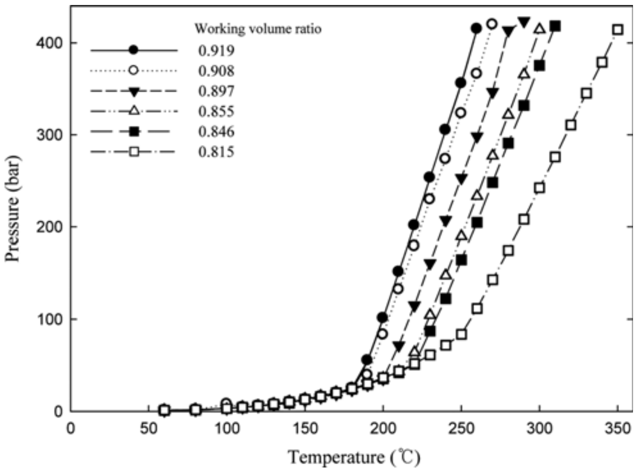

Fig. S1. Characteristics of pressure and temperature with various working volumes during fatty acid methyl ester production in the non-catalytic supercritical reaction (0.02 mol palm oil/mol methanol).