

Performance of a Bubble Column Reactor for the Non-Catalytic Methyl Esterification of Free Fatty Acids at Atmospheric Pressure

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A bubble column reactor has been developed to produce fatty acids methyl esters (biodiesel) by blowing superheated methanol continuously into vegetable oils without using any catalysts at atmospheric pressure. Two types of reactions exist in this method for methyl esters formation; transesterification of triglycerides and esterification of fatty acids. A kinetic study for the transesterification of triglyceride has been studied at 250–290°C. However, performance of the bubble column reactor for methyl esterification of free fatty acids has not yet been revealed. Therefore, we studied effects of reaction temperatures (200, 225, and 250°C) on the composition of reaction product, conversion of the reaction and the reaction rate constant under a semi-batch mode of operation with oleic acids as free fatty acids. The activation energy and the frequency factor values of the methyl esterification reaction obtained in this experiment were 24.8 kJ/mol and 2.9, respectively. Compared with the obtained results of the transesterification of triglycerides, the reaction rate of methyl esterification of free fatty acids at the same reaction temperature (250°C) was higher than the former, but the quality of the product (the methyl ester content in the gaseous product) was lower.

Introduction

Biodiesel, an alternative diesel fuel, is made from renewable biological sources such as vegetable oils and animal fats. It is biodegradable and nontoxic, has low emission profiles, and so is environmentally beneficial (Krawczyk, 1996). Biodiesel, consisting of fatty acids methyl esters (FAME) can be produced by transesterification of triglycerides or esterification of fatty acids with short-chain alcohol, mainly methanol (MeOH).

In a catalytic process, alkali-catalyzed transesterification is much faster than acid-catalyzed transesterification and is most often used commercially (Ma and Hanna, 1999). Alkali-catalyzed

transesterification is suitable only for biodiesel production from feedstocks containing low levels of free fatty acids (FFA). Special processes are required if the oil or fat contains significant amounts of FFA. Used cooking oils typically contain 2–7% FFA, and animal fats contain 5–30% FFA. Some very low-quality feedstock, such as trap grease, can approach 100% FFA (Van Gerpen and Knothe, 2005). When an alkali catalyst is added to these feedstocks, the FFA reacts with the catalyst to form soap and water. If the FFA level is over 5%, the soap inhibits separation of the glycerol from the methyl esters after the reaction and contributes to emulsion formation during the water wash. For these cases, an acid catalyst such as sulfuric acid can be used to esterify the FFA to FAME. Acid-catalyzed esterification process can be used as a pretreatment to convert the FFA to FAME, thereby reduce the FFA level (Jeromin *et al.*, 1987). Then, the low-FFA pretreated oil can be transesterified with an alkali catalyst to convert the triglycerides to FAME.

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Saka and Kusdiana (2001) and Demirbas (2002) have developed a method for biodiesel production with supercritical MeOH. Two types of reactions exist in this method for methyl esters formation; transesterification of triglycerides and methyl esterification of fatty acids. As a result, the reaction was found to complete in a very short time (4–15 min). However, the reaction requires temperatures of 350–577°C and pressures of 43–105 MPa, which are not easily viable for application in industry. Han *et al.* (2005) used CO₂ as co-solvent to decrease the operating temperature, pressure and molar ratio of alcohol to vegetable oil. It was demonstrated that, with an optimal reaction temperature of 280°C, MeOH to oil molar ratio of 24 and CO₂ to methanol molar ratio 0.1, a 98% yield of methyl esters was observed in 10 min at a reaction pressure of 14.3 MPa. Kusdiana and Saka (2001) had studied methyl esterification of free fatty acids of rapeseed oil treated in supercritical MeOH. Warabi *et al.* (2004) have reported about alkyl esterification of fatty acids in various supercritical alcohols (300°C, 6–20 MPa). The reaction temperature could be decreased but the reaction pressure was still high. The reactor costs will be expensive for their pressurized reactions.

Yamazaki *et al.* (2007) have developed a bubble column reactor to produce FAME under around atmospheric pressure by blowing bubbles of superheated MeOH vapor into oil (triglycerides) without using any catalysts. Bubble columns are widely used for conducting gas–liquid reactions in variety of practical applications in industry such as absorption, fermentation, bio-reactions, coal liquefaction and waste water treatment, but it has not yet been used for biodiesel production. Due to their simple construction, low operating cost, high energy efficiency and good mass and heat transfer, bubble columns offer many advantages when used as gas–liquid contactors (Mouza *et al.*, 2004). Kinetics of the non-catalytic transesterification of palm oil at atmospheric pressure has been reported by Joelianingsih *et al.* (2007). However, performance of the bubble column reactor for the non-catalytic methyl esterification of FFA has not yet been known very well. Therefore, in this study the non-catalytic methyl esterification of FFA in a bubble column reactor was investigated. Oleic acid which is commonly found at high concentration in vegetable oil was chosen as a substrate (Demirbas, 2003). The effects of reaction temperatures on the composition of the gaseous product, conversion of the reaction and the rate constant are investigated.

1. Experimental

1.1 Materials

Oleic acid, technical grade 90% w/w, as a substrate was obtained from Sigma-Aldrich Inc. Methanol HPLC (High Performance Liquid Chromatography) grade as

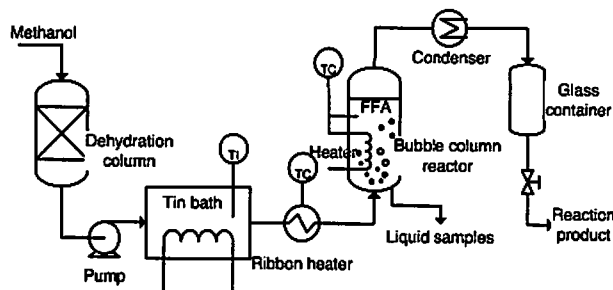


Fig. 1 Schematic flow diagram of the reactor used in non-catalytic esterification experiment

a substrate was purchased from Wako Pure Chemical Industries, Ltd.

Benzene and hexane (all HPLC grade) used in the thin layer chromatography/flame ionization detection (TLC/FID) analysis were purchased from Wako Pure Chemical Industries, Ltd. Benzene was used as developing solution, and hexane as solvent. Squalane (C₃₀H₆₂) as internal standard was purchased from Sigma-Aldrich Japan K. K. Oleic acid and methyl oleate used as standards were purchased from Sigma Chemical Co.

1.2 Reactor for the non-catalytic methyl esterification

A schematic flow diagram of a reactor used in this experiment is shown in Figure 1. This system has been used in our previous work for non-catalytic methyl transesterification (Joelianingsih *et al.*, 2007).

The bubble column reactor was a four-necked flask (capacity, 500 mL) equipped with a condenser, a pipe for methanol vapor feed and a temperature controller (TC). The reactor was placed in a mantle heater. The glass dehydration column was filled with molecular sieves. A pump with a variable speed motor (model NPD-461, Nihon Seimitsu Kagaku Co., Ltd.) was used to control the charging rate of MeOH. A tin bath was placed on an electric heater. Temperature of the tin bath was monitored by a temperature indicator (TI). Temperatures of the superheated methanol supplied to the reactor and liquid in the reactor were controlled with the TC.

1.3 Methyl esterification procedure and conditions

The reactor was initially charged with 200 g of oleic acid and heated to the desired temperature. Reactions were conducted at 200, 225, and 250°C under atmospheric pressure. Liquid MeOH was pumped out of the dehydration column to the tin bath for vaporization. The Methanol vapor was passed through a ribbon heater and the reaction started by blowing superheated methanol bubbles continuously into the reactor at 4 g/min of liquid methanol. The temperature of superheated methanol feed was set up to the reaction temperature. Reacted products in the gas phase were condensed and collected in the glass container. The reaction products were taken from the glass container every

Table 1 The composition of total MO in the samples B (gaseous product)

| <i>t</i> [min] | Total MO composition in the samples B [% w/w] | | | | | |
|----------------|---|-------|------------------|-------|------------------|-------|
| | <i>T</i> = 200°C | | <i>T</i> = 225°C | | <i>T</i> = 250°C | |
| | Mass [g] | MO | Mass [g] | MO | Mass [g] | MO |
| 20 | 2.73 | 62.70 | 10.95 | 19.41 | 25.07 | 12.41 |
| 40 | 6.28 | 69.95 | 24.47 | 32.07 | 56.05 | 43.59 |
| 60 | 10.83 | 72.14 | 39.89 | 41.52 | 90.00 | 51.84 |
| 80 | 15.77 | 73.55 | 56.33 | 48.68 | 124.59 | 57.57 |
| 100 | 20.98 | 74.18 | 74.08 | 54.85 | 159.96 | 60.59 |

Table 2 The composition of total MO in liquid in the reactor

| <i>t</i> [min] | Total MO composition in the liquid [% w/w] | | | | | |
|----------------|--|-------|------------------|-------|------------------|-------|
| | <i>T</i> = 200°C | | <i>T</i> = 225°C | | <i>T</i> = 250°C | |
| | Mass [g] | MO | Mass [g] | MO | Mass [g] | MO |
| 0 | 199.98 | 0.00 | 200.04 | 0.00 | 199.82 | 0.00 |
| 20 | 197.25 | 10.39 | 189.09 | 12.81 | 174.75 | 14.41 |
| 40 | 193.70 | 16.89 | 175.57 | 22.27 | 143.77 | 34.42 |
| 60 | 189.15 | 24.74 | 160.15 | 38.14 | 109.82 | 46.47 |
| 80 | 184.21 | 32.13 | 143.71 | 46.41 | 75.23 | 51.16 |
| 100 | 179.00 | 38.47 | 125.96 | 49.08 | 39.86 | 56.00 |

20 min and then weighed (samples A). During the reaction course (100 min), 5 samples were collected. Liquid samples in the reactor were taken every 20 min to analyze methyl oleate and oleic acid contents using TLC/FID.

1.4 Analysis

Methanol and water contents in the gaseous products (samples A) were evaporated using a rotary evaporator and then the gaseous products without methanol and water were obtained (samples B). Samples B were weighed and their methyl oleate and oleic acid content were analyzed using TLC/FID.

TLC/FID was used to analyze the contents of methyl oleate and oleic acid in the samples B and the liquid samples in the reactor. Analyses were performed with an Iatroscan MK-5 Analyzer (Iatron Laboratories, Inc.). The flame ionization detector used hydrogen and air with flow rates of 160 and 2000 mL/min, respectively. Type SIII Chromarods were used as thin layers. Before being spotted, rods were scanned as blank on the instrument to obtain the proper degree of hydration. The samples B and the liquid samples (20–30 mg) were diluted with 1 mL solvent (hexane containing 5 mg/mL of squalane) and 1 μ L of the solution was spotted on each rod. Five replicates were used for each solution. The rods were developed for 30 min (they were stored in a glass chamber in which the atmosphere was saturated with benzene vapor), oven dried at 60–65°C for 5 min and then analyzed by the Iatroscan. The mass fraction of methyl oleate and oleic acid in the samples B and the liquid samples taken from

the reactor was calculated based on the concentration of an internal standard.

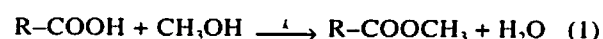
2. Results and Discussion

2.1 The effects of reaction temperatures on the composition of the reaction product and conversion of the reaction

The composition [% w/w] of total methyl oleate (MO) in the samples B (gaseous product) and liquid in the reactor and the total mass of each fraction at 200, 225, and 250°C are shown in Tables 1 and 2, respectively.

Based on the results presented in the Tables 1 and 2, concentration expressed in % mol/mol of OA and MO in the total system (samples B and liquid in the reactor) at 200, 225, and 250°C are presented in Table 3.

Oleic acid reacts with MeOH to form FAME by the following esterification reaction:



where R is an alkyl group with chain length $C_{18:1}$.

Conversion of the reaction (α) is defined by Eq. (2).

$$\alpha = \frac{C_{\text{OA},0} - C_{\text{OA},t}}{C_{\text{OA},0}} \times 100 \quad (2)$$

Table 3 The concentration of OA and MO in the total system

| t [min] | OA and MO concentrations in the total system [% mol/mol] | | | | | |
|-----------|--|-------|-------------------------|-------|-------------------------|-------|
| | $T = 200^\circ\text{C}$ | | $T = 225^\circ\text{C}$ | | $T = 250^\circ\text{C}$ | |
| | OA | MO | OA | MO | OA | MO |
| 0 | 100 | 0.00 | 100 | 0.00 | 100 | 0.00 |
| 20 | 89.37 | 10.63 | 87.37 | 12.63 | 86.42 | 13.58 |
| 40 | 82.16 | 17.84 | 77.39 | 22.61 | 64.13 | 35.87 |
| 60 | 73.65 | 26.35 | 62.33 | 37.67 | 52.32 | 47.68 |
| 80 | 65.71 | 34.29 | 54.15 | 45.85 | 46.04 | 53.96 |
| 100 | 58.96 | 41.04 | 49.99 | 50.01 | 41.50 | 58.50 |

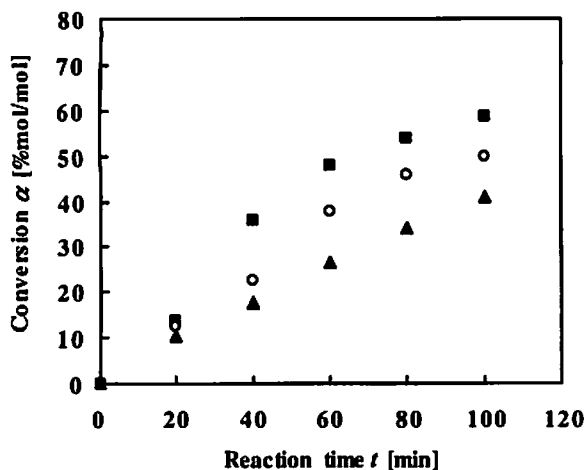


Fig. 2 Conversion of the reaction at various temperatures: (▲) 200°C; (○) 225°C; (■) 250°C

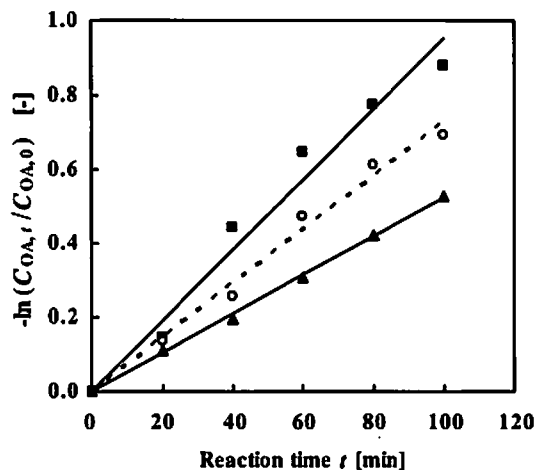


Fig. 3 First order reaction model of OA esterification at various temperatures: (▲) 200°C; (○) 225°C; (■) 250°C

where $C_{OA,0}$ and $C_{OA,t}$ are concentrations of oleic acid in the total system at the initial point of the reaction and after the reaction time of t , respectively. Effects of the reaction temperatures on the conversion can be seen in **Figure 2**.

As can be seen in **Figure 2**, conversion of the reaction increased with reaction temperature. After 100 min of reaction time, conversion of the reaction at 200, 225, and 250°C was 41.04, 50.01, and 58.50 [% mol/mol], respectively. However, compositions of MO in the gaseous product (sample B) at 200, 225, and 250°C are 74.18, 54.85, and 60.59 [% w/w], respectively. Conversion of the reaction could not achieve 100% because OA can be obtained in the gaseous product. The volatility of MO and OA at atmospheric pressure is almost the same, so the compositions of MO and OA in the liquid and gaseous product have little differences.

2.2 The effect of the reaction temperature on the rate constant

In a semi-batch mode of operation where MeOH is continuously passed through a reactor containing OA, the concentration of MeOH in the gas does not

change appreciably. With the passage of reaction time (t) the concentration of OA (C_{OA}) will fall, but the concentration of MeOH (C_M) will remain unchanged. If the kinetics is a first order with respect to both OA and MeOH, the reaction rate based on the decreased concentration of OA can be given by Eq. (3) (Levenspiel, 1972).

$$-r_{OA} = -\frac{dC_{OA}}{dt} = kC_{OA}C_M \quad (3)$$

Rearranging and integrating, noting that C_M is constant, the equation will be:

$$-\ln(C_{OA,t}/C_{OA,0}) = k't \quad (4)$$

where

$$k' = kC_M \quad (5)$$

Figure 3 shows the relationship between the normalized concentration of OA ($C_{OA,t}/C_{OA,0}$) and reaction

Table 4 The rate constant of OA methyl esterification

| T [°C] | k' [min ⁻¹] | R^2 |
|----------|---------------------------|--------|
| 200 | 0.0052 | 0.9984 |
| 225 | 0.0073 | 0.9874 |
| 250 | 0.0095 | 0.9720 |

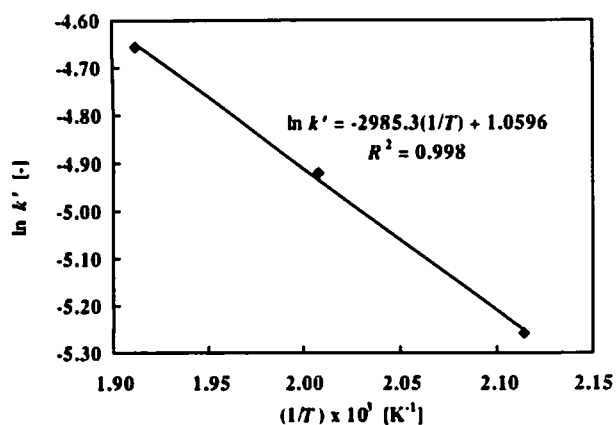


Fig. 4 First order reaction rate constant in the Arrhenius plot during OA methyl esterification

times at different temperatures. The gradient of the linear regression of the $-\ln(C_{OA,t}/C_{OA,0})$ curve with respect to the reaction time is regarded as the rate constant (k') according to Eq. (4).

Summary of the rate constant (k') for each reaction temperature is given in Table 4. The coefficient of determination (R^2) is computed from the quantities that are available in the analysis of variance.

As shown in Table 4, the R^2 value decreased with reaction temperature, because the evaporation rate of oleic acid as a substrate increased with the reaction temperature so that the quantity of oleic acid in the gaseous product increased. As a consequence the reaction rate constant at higher temperature can not be obtained by using Eq. (4). The k' value increased with the reaction temperature, according to the Arrhenius equation (Perry and Green, 1984).

$$\ln k' = \ln A - \frac{E_a}{RT} \quad (6)$$

The data in Table 4 were used to determine the activation energy (E_a) and the frequency factor (A) from a plot of the reaction rate constant (k') versus the reciprocal of absolute temperature ($1/T$) as shown in Figure 4.

According to Eq. (6), the activation energy was found to be 24.8 kJ/mol and the frequency factor was 2.9.

Table 5 Comparison of methyl esterification and transesterification results

| Reaction type | ME content [% w/w] | α [% mol/mol] | Y [% w/w] |
|----------------------|--------------------|----------------------|-------------|
| Esterification: | | | |
| 200°C | 74.18 | 41.04 | 7.78 |
| 225°C | 54.85 | 50.01 | 20.31 |
| 250°C | 60.59 | 58.50 | 48.50 |
| Transesterification: | | | |
| 250°C | 88.70 | 11.11 | 3.85 |
| 270°C | 87.56 | 14.78 | 4.98 |
| 290°C | 85.64 | 21.15 | 7.12 |

2.3 Methyl esterification and transesterification in a bubble column reactor

In our previous work, the non-catalytic transesterification of triglycerides (TG) from palm oil in a bubble column reactor have been studied at reaction temperatures of 250, 270, and 290°C under atmospheric pressure (Joelianingsih *et al.*, 2007). In the transesterification reaction, TG reacts with MeOH to form methyl esters (ME) for biodiesel fuel and glycerol (GL) as a co-product. Monoglyceride (MG) and diglyceride (DG) are formed as intermediate products. Evaluation on the reaction kinetic was based on the overall reaction:



The reaction rate constant obtained at 250, 270, and 290°C was 0.0034, 0.0051, and 0.0056 min⁻¹, respectively. As can be seen in Table 4, the rate constant of methyl esterification at 250°C was 0.0095 min⁻¹. The rate constant of methyl esterification at the same reaction temperature (250°C) was about 3 times higher than methyl transesterification.

The reaction product in the gas phase for methyl esterification after evaporation of unreacted MeOH and water as co-product contains only FFA and methyl ester, while in the transesterification, the reaction product in the gas phase after evaporation of unreacted MeOH contains ME, TG, DG, MG, and GL. The volatility of each component in the reaction mixture in the reactor has an effect on the ME content in the gaseous product. The volatility of ME was higher than TG, therefore the ME could be obtained in the gaseous product, while the TG as a substrate was obtained only in the liquid product. Table 5 shows the ME content in the gaseous product, conversion of the reaction and yield of ME (Y) for methyl esterification and transesterification after 100 min reaction times. Yield of ME is the mass ratio of ME in the gaseous product to the mass of the initial substrate (oil or FFA).

These results show that methyl esterification of FFA and transesterification of TG can be conducted

simultaneously in a bubble column reactor. The reaction temperatures in the esterification of FFA are lower than those in the transesterification of TG because volatility of FFA is higher than TG. The optimum reaction temperature for esterification is not same with transesterification. Comparing the obtained results of the transesterification of TG and the methyl esterification of FFA at the same reaction temperature (250°C), a higher reaction rate constant can be obtained with the latter, but the quality of the product (the methyl ester content in the gaseous product) was better in the former, as shown in Table 5. Therefore, FFA content in vegetable oil can give effect on the reaction rate and the quality of the product if the oil which contains significant amounts of FFA is used as a feedstock for biodiesel production via the non-catalytic process in a bubble column reactor. To obtain the better quality of biodiesel, the reaction temperature should be adjusted to the quality of oil or fat (FFA content). According to the European Union standards for biodiesel, the minimum acceptable purity of methyl esters is 96.5% [w/w]. The reactions should be conducted by utilizing the multistage non-uniform reaction method for obtaining the best quality biodiesel.

Conclusions

Free fatty acids of vegetable oil could be methyl esterified in a bubble column reactor under atmospheric pressure in the absence of a catalyst. Evaluation on the reaction kinetic based on changes in the FFA concentration shows that the reaction rate constants at 200, 225, and 250°C were 0.0052, 0.0073, 0.0095 min⁻¹, respectively, activation energy was 24.8 kJ/mol, and the frequency factor was 2.9. The experimental results showed that methyl esterification reaction of FFA takes place simultaneously with the transesterification reaction of TG to form FAME for biodiesel fuels. The reaction rate of methyl esterification was faster than that of methyl transesterification, but the ME content in the gaseous product was lower.

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Nomenclature

| | | |
|-----------|---|-------------|
| A | = frequency factor | [—] |
| C_{OAO} | = oleic acid concentration at initial point of the reaction | [% mol/mol] |

| | | |
|------------|---|--|
| C_{OAt} | = oleic acid concentration at t reaction time | [% mol/mol] |
| C_M | = methanol concentration | [% mol/mol] |
| dC_{OAt} | = change in oleic concentration | [% mol/mol] |
| dt | = change in reaction time | [min] |
| E_a | = activation energy | [kJ mol ⁻¹] |
| k | = reaction rate constant defined by Eq. (3) | [min(mol/mol) ⁻¹] |
| k' | = reaction rate constant defined by Eqs. (4), (5) and (6) | [min ⁻¹] |
| R | = universal gas constant defined by Eq. (6) | [J mol ⁻¹ K ⁻¹] |
| R^2 | = coefficient of determination | [—] |
| r_{OA} | = reaction rate of oleic acid | [(mol/mol) min ⁻¹] |
| T | = reaction temperature | [°C or K] |
| t | = reaction time | [min] |
| Y | = yield of methyl ester | [% w/w] |
| α | = conversion of the reaction | [% mol/mol] |

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