Transesterification of soybean oil with methanol and acetic acid at lower reaction severity under subcritical conditions

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ABSTRACT

Soybean oil (56–80 g) was reacted with methanol (40–106 mL) to produce fatty acid methyl ester in the presence of 1–6% acetic acid under subcritical condition at 250 °C. Stirring and loading of the reaction system affected the yield and severity of the process. The presence of acetic acid improved the yield of FAME from 32.1% to 89.5% at a methanol to oil molar ratio of 20 mL/g. Acetic acid was found to act strongly as an acid catalyst and to some extent improved the solubility between oil and methanol. Reaction pressure higher than the supercritical pressure of methanol (7.85 MPa) was not required to achieve high FAME yield (89.5–94.8%) in short time (30–60 min).

1. Introduction

After Saka and Kusdiana [1] introduced supercritical methanol technology to produce biodiesel in 2001, many authors have since then studied biodiesel production by utilizing the unique properties exhibited by methanol under sub and supercritical conditions. Its main advantages include the fact that it requires a relatively shorter time (4–30 min) to produce high purity (>95%) fatty acid methyl esters (FAME) and its tolerance to impurities like water and free fatty acids (FFA), without the use of any catalysts [1–6].

Despite its many advantages over conventional acid and base catalyzed reactions, it has been greatly criticized for the high temperature (>300 °C) and high pressure (>20 MPa) required. Operating at severe temperature and pressure conditions require a well engineered process that can efficiently recover the spent energy [7], which would need high capital cost and for the moment not feasible to commercialize. Another concern is thermal degradation of the product at elevated temperatures. Imahara et al. [8] suggested that the supercritical methanol method should be carried out at temperature below 300 °C, preferably at 270 °C, with a pressure higher than 8.09 MPa. Shin et al. [9] reported that degradation of

unsaturated fatty acids, in the presence of water, was observed at temperatures above 250 °C with an operating pressure of 20 MPa.

In order to decrease the severity of the process, a two-step approach was introduced by Kusdiana and Saka [10] in which hydrolysis was followed by esterification. Fatty acids (FA) and glycerol were firstly produced during hydrolysis at 270 °C for 1 h. After that FAs were separated from glycerol and then esterified with methanol at 270 °C for 40 min to achieve an FAME yield of 94% [11]. This approach seems to use less severe operating conditions but required a long reaction time, resulting in a lower overall productivity and is less energy efficient due to cooling and heating in between steps. Later Minami and Saka [11] introduced an important concept of the catalytic activity of FAs during hydrolysis and esterification. This idea was accepted by some researchers and applied it in the hydrolysis of sunflower oil [12] and *Jatropha* oil [13]. Chen et al. [13] added acetic acid in hydrolysis reaction as a catalyst instead of the common FAs found in vegetable oils. Some researchers disagree with this idea since there is certain limitation for FFA to act as an acid catalyst due to its lower extent of ionization and its large steric hindrance to form an active intermediate with triglyceride [14]. The use of supercritical methanol with acetic acid addition has been investigated by Wei et al. [15] in which high amount of methanol (up to 60 mol per mole of oil) and long reaction time (90 min) were required even with the addition of carbon dioxide as a co-solvent. However the use of acetic acid as both a catalyst and a co-solvent has not been explored.

This study aimed to investigate the production of FAME from soybean oil at 250 °C and attempted to utilize acetic acid as a catalyst and a co-solvent to reduce the amount of methanol required. The effects of reactor loading, pressure and stirring on FAME yield were also studied.

2. Materials and methods

2.1. Materials

Refined soybean oil used in this study was obtained from local supermarket. Standards of FA, acylglycerides such as monoolein, diolein and triolein and FAMEs were obtained from Supelco (Bellefonte, PA). All solvents and reagents used were either high performance liquid chromatography (HPLC) or analytical reagent grade, obtained from commercial sources.

2.2. Transesterification reactions

Soybean oil (56.6–80.0 g), acetic acid (0.1–40.0 mL) and methanol (40.0–106 mL) were weighed and added into a glass chamber (190 mL) and placed in a high-pressure reactor (290 mL). Unless otherwise specified, the reactions were carried out with a fix total volume of ∼170 mL, which is about ∼87% of the glass chamber capacity. A detailed reactor description is given elsewhere [16]. The reactor is equipped with an external electric heater and a magnetic stirrer. Temperature in the reactor was controlled to within ±2 °C. After the sample was put in the reaction chamber, the reactor was sealed and the chamber was purged with N_2.

The reaction was carried out with constant stirring (∼300 rpm) at 250 °C to avoid thermal degradation for a predetermined time. Heating rate of the reactor was kept at ∼5 °C/min with a heating time of 40–45 min. The moment the reactor reached the desired temperature was counted as time zero. After the reaction, the reactor was rapidly cooled, pressure inside the reactor was released and product in the reactor was collected at room temperature.

Methanol and acetic acid in the product were removed and recovered using a rotary evaporator (BUCHI Labortechnik AG in Flawil, Switzerland) operated at 40 °C and 13.3 kPa. The residual acetic acid and water were further removed by heating the mixture to 80 °C at 13.3 kPa. The collected product containing FAME was washed three times, each using 20 mL 5% NaCl solution, in a separation funnel to remove glycerol and residual acetic acid. The solution was allowed to clarify in between washings. The upper FAME rich phase was withdrawn and dried using a rotary evaporator. The recovered product was weighed and analyzed for its FAME, FA and acylglyceride contents. Results of the reaction were evaluated in terms of FAME yield, conversion and productivity.

FAME yield is defined as the mass of FAME (M_{FAME}) produced per mass of oil (M_{Oil}) used in the reaction. This was calculated using Eq. (1), where A_{FAME} is the area calculated from the GC analysis and f_c is the external calibration factor (slope of the calibration curve) while C_s and V_s are the concentrations and volumes of the samples prepared and injected to the GC for analysis, respectively.

$$\text{FAME yield } (\%) = \frac{M_{FAME}}{M_{Oil}} \times 100\%$$
$$= \frac{M_{product}}{M_{Oil}} \times \frac{\Sigma A_{FAME} \cdot f_c}{C_s V_s} \times 100\% \qquad (1)$$

Conversion of FAME was calculated using Eq. (2). The theoretical FAME yield based on stoichiometry where 1 mol of triacylglyceride produces 3 mol of FAME was used as reference to incorporate the un-reacted partial glycerides and FFAs.

$$\text{Conversion } (\%) = \frac{\text{FAME yield}}{\text{Theoretical FAME yield}} \times 100\% \qquad (2)$$

Productivity is an important parameter in chemical processes but is often overlooked. Eq. (3) was utilized to calculate the productivity, which is defined as the amount of FAME (M_{FAME}) produced per reactor volume (V_r = 240 mL) per reaction time (t).

$$\text{Productivity}\left(\frac{\text{kg}}{\text{L h}}\right) = \frac{M_{FAME}}{V_r t} \qquad (3)$$

Experiments were carried out in triplicates and values reported are average values of the triplicate trials.

2.3. Gas chromatography analysis

A 20 mg aliquot of the lipid sample was dissolved in ethyl acetate and filtered through a 0.2 μm PTFE hydrophobic membrane to remove moisture. From this prepared solution, a 1.0 μL sample was injected into a high temperature gas chromatography (HTGC) for analysis. External calibration curve was generated using 0.2–20 mg of a pure standard dissolved in ethyl acetate. The calibration curve was generated by fitting a straight line with the y-intercept passing through zero ($R^2 > 0.99$).

Qualitative and quantitative analyses of FAME and un-reacted FFA in each sample were performed using a Shimadzu GC2010 (Kyoto, Japan) equipped with a split-injector and a FID. Separation was carried out on a ZB-5HT (5% phenyl)-methylpolysiloxane non-polar column (15 m × 0.32 mm i.d., 0.1 mm film thickness) (Zebron, Phenomenex, Torrance, CA, USA). Both injector and detector temperatures were set at 370 °C. The column temperature was programmed to increase at a rate of 15.0 °C/min from 80 °C to 365 °C and held at 365 °C for 48 s. N_2 was used as the carrier gas with a linear velocity of 30 cm/s at 80 °C. Data analyses were carried out by the software "GC Solution version 2.3", Shimadzu.

3. Results and discussion

3.1. Effects of reactor loading and pressure

In principle the effect of pressure can only be accurately investigated using a tubular flow reactor where pressure can be controlled via a backpressure regulator. For a batch reactor altering the initial amounts of oil and methanol could change the reactor pressure. However there have been various interpretations with regards to initial amount of reactants charged into a batch reactor. Some authors chose to carry out reactions with fixed amount of oil and varying the amount of methanol to investigate the effects of methanol to oil ratio and used an inert gas like nitrogen to maintain a given final pressure [13,15]. Fig. 1 shows the effects of solvent to oil ratio at a fixed amount of soybean oil. Apparently the increase in solvent to oil ratio (SOR) resulted in an increase in FAME yield since forward reaction during transesterification was favored in the presence of excess methanol.

Some researchers varied the amounts of reactant but used only a fixed percentage of the total reactor volume [17,18]. Fig. 2 shows the effects of the reactor loading at a fixed SOR on FAME yield and reactor pressure. It is evident that FAME yield and reactor pressure both increased with increasing reactor loading. A higher reactor loading corresponds to a smaller void volume, which serves as space for expansion of reactants. Since methanol has much lower boiling point (68 °C) than oil or any of the reaction products, it is safe to assume that part of methanol occupies the void space as vapor. If smaller space is available for the vapor at a fixed temperature, it results in higher system pressure. It was also observed that reactor pressure decreased as reaction proceeded. In batch reaction, pressure changes in the course of reaction due to changing amounts of reactants and products [19]. Nevertheless, it can be observed from the results that it is not necessary to reach the