

Production of Biodiesel Fuel by Transesterification of Rapeseed Oil

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Abstract

Fatty acid methyl esters (FAMES) show large potential applications as diesel substitutes, also known as biodiesel fuel. Biodiesel fuel as renewable energy is an alternative that can reduce energy dependence on petroleum as well as air pollution. Several processes for the production of biodiesel fuel have been developed. Transesterification processes under alkali catalysis with short-chain alcohols give high yields of methyl esters in short reaction times. We investigated transesterification of rapeseed oil to produce the FAMES. Experimental reaction conditions were molar ratio of oil to alcohol, concentration of catalyst, type of catalyst, reaction time, and temperature. The conversion ratio of rapeseed oil was enhanced by the alcohol:oil mixing ratio and the reaction temperature.

Index Entries: Biodiesel fuel; transesterification; rapeseed oil; molar ratio; fatty acid methyl ester.

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Introduction

Fatty acid methyl esters (FAMES), which can be derived from vegetable oil and animal fats by transesterification reaction with alcohol, show large potential applications as diesel substitutes, also known as biodiesel fuel (1–3). Biodiesel fuel as a renewable energy is an alternative that can reduce both energy dependence on petroleum and air pollution. Biodiesel fuels produced from various vegetable oils and animal fats have low viscosities similar to those of petrodiesel. In addition, characteristics of biodiesel fuels such as volumetric heating value, cetane number, and flash point are generally similar to those of petrodiesel (4,5). The several advantages of using biodiesel fuel are that it may be an alternative renewable energy or a biodegradable nontoxic fuel; and that there is a reduction in air pollution from particulates, CO₂, SO_x emissions, and recycling of CO₂ in short periods (6).

Several processes for the production of biodiesel fuel have been developed by acid-, alkali-, and enzyme-catalyzed transesterification reactions (7–10). Transesterification, called alcoholysis, is the displacement of alcohol from an ester by another alcohol in a process similar to hydrolysis. Transesterification is represented by a number of consecutive and reversible reactions. The reaction step is the conversion of triglycerides to diglycerides, followed by the conversion of diglycerides to monoglycerides and of monoglycerides to glyceride at each step (11,12).

The transesterification process under alkali catalyst and short-chain alcohol gives a high level of conversion in short reaction times. At present, the most developed process using transesterification reactions employs an alkali-catalysis system. The main parameters affecting transesterification are molar ratio of vegetable oil to alcohol, catalysts, reaction temperature and time, contents of free fatty acids, and water in oils and fats (8). Several alcohols were used for this process, including methanol, ethanol, propanol, butanol, and amyl alcohol. Methanol was utilized most broadly owing to low cost and its physical and chemical advantages such as polar and shorter-chain alcohol (3). The bases used for the transesterification reaction include NaOH; KOH; carbonates; and alkoxides such as sodium methoxide, sodium ethoxide, sodium propoxide, and sodium butoxide. Sodium methoxide has been found to be more effective than NaOH, which produces a small amount of water by mixing NaOH and MeOH. However, NaOH and KOH are widely used in the industrial biodiesel production process owing to its low cost. For alkali-catalyzed transesterification, the oils and alcohol must be substantially anhydrous because water causes saponification with oil (2,8). Ma et al. (13) suggested that the free fatty acid content of the refined oil should be as low as possible, below 0.5%. Another significant parameter affecting the conversion yield is the molar ratio of alcohol to vegetable oil. The stoichiometry of the transesterification reaction requires 3 mol of alcohol/mol of triglyceride to yield 3 mol of fatty esters and 1 mol of glycerol. Higher molar ratios result in greater conversion yields in a shorter reaction time (8,14). The commonly used molar

Table 1
Fatty Acid Composition
and Characteristics of Rapeseed Oil

Characteristic	Content
Specific gravity	0.917
Moisture content (%)	0.01
Free fatty acid (%)	0.018
Unsaponifiable matter (%)	0.39
Fatty acid (%) [w/w]	
Palmitic (C _{16:0})	5.7
Stearic (C _{18:0})	2.2
Oleic (C _{18:1})	58.5
Linoleic (C _{18:2})	24.5
Linolenic (C _{18:3})	9.1

ratio of alcohol to glycerides is 6:1 (8,9). The recommended amount of alkali catalyst for transesterification is between 0.1 and 1% (w/w) of oils and fats. Generally, reaction temperature was set at near the boiling point of alcohol. Higher reaction temperatures facilitate the reaction and shorten the reaction time (14). Freedman et al. (8) reported the transesterification reaction of soybean oil and other vegetable oils in their investigation of the effects of the type of alcohol, molar ratio, type and amount of catalyst, and reaction temperature and time.

Biodiesel has become an attractive fuel but one problem remains: its production costs. There are two aspects of the cost of biodiesel production: the cost of raw materials (oil and alcohol) and the cost of process operation. The cost of raw materials accounts for approx 60–75% of the total biodiesel production cost (15).

In the present study, we investigated the transesterification reaction of rapeseed oil with alcohol, examining the effects of the molar ratio of oil to alcohol, concentration of catalyst, type of catalyst, reaction time, and reaction temperature.

Materials and Methods

Rapeseed Oil, FAMES, and Chemicals

Refined and bleached rapeseed oil were obtained from Onbio Co. Ltd. (Pucheon-Si, Korea). Table 1 presents the fatty acid composition and characteristics of rapeseed oil. Reference standards of FAMES such as palmitic, stearic, linolenic, linoleic, and oleic methyl ester of >99% purity were purchased from Sigma (St. Louis, MO). Methanol and catalysts such as KOH, NaOH, and sodium methoxide were analytical-grade chemicals.

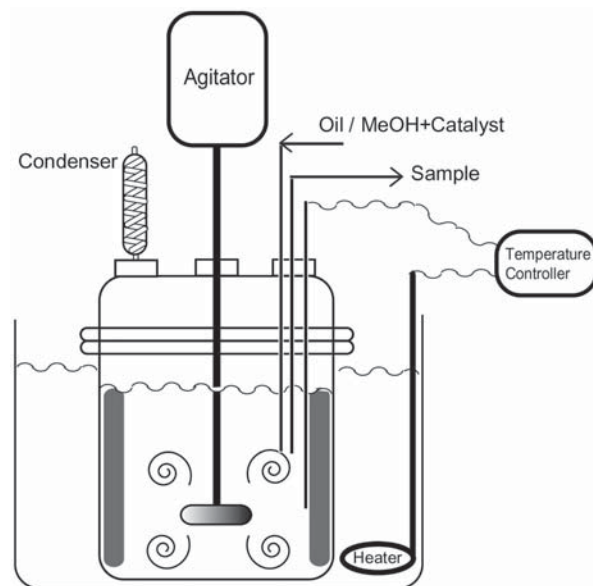


Fig. 1. Reactor setup for transesterification of rapeseed oil.

Apparatus

Transesterification reactions were performed in a 1-L four-necked reactor equipped with a reflux condenser, a thermometer, and a sampling port (Fig. 1). The reactor was immersed in a constant-temperature water bath controlled by a PID temperature controller, which was capable of controlling the temperature to within $\pm 0.2^\circ\text{C}$ of the setting point. Mixing was provided by an electric motor with a propeller-type impeller. During the experiments, samples were withdrawn with a 1-mL glass pipet through a sampling port of the reactor at various times.

Reaction Procedures and Conditions

Initially, the reactor was charged with 400 g of rapeseed oil and heated to the set temperature with agitation. Catalyst was dissolved in the required amount of methanol and heated to the set temperature. After reaching the set temperature of reactant and catalyst, methanolic catalyst was added to the base of the reactor to prevent evaporation of methanol. The reaction was timed immediately after the addition of catalyst and methanol. Reaction experiment parameters were designed to determine the conversion yield of rapeseed oil (Table 2).

Preparation and Analysis of Samples

Samples were drawn at preset time intervals. About 1 mL of sample mixture was collected in 10-mL test tubes, and 1 N HCl was added and vortexed immediately to neutralize the catalyst and stop the reaction.

Table 2
Proposed Operating Conditions
of Alkali-Catalyzed Transesterification

Process	Base-catalyzed alcoholysis
Fatty glyceride	Vegetable oil (rapeseed oil)
Alcohol	Methyl alcohol (above 99.8%)
Catalyst	Sodium methoxide, KOH, NaOH (0.1–1.2% [w/w])
Reaction condition	Reaction temperature: 30–65°C; oil:MeOH molar ratio:1:3–1:20
Purification and recovery	Distillation, centrifugation, washing

Pretreated samples were evaporated to remove nonreacted methanol and extracted by solvents (chloroform:*n*-hexane = 1:2) and centrifuged at low temperature to remove glycerin. One milliliter of supernatant was evaporated under vacuum and diluted with methanol (high-performance liquid chromatography [HPLC] grade) for HPLC analysis.

Samples were analyzed for FAMES using HPLC. An HPLC (Younglin) was equipped with a model 930D pump and an ultraviolet detector (M720, 205 nm). A Waters Spherisorb ODS2 column (4.6 × 250 mm with 5-μm particle size) was used for the separation. The mobile phase consisted of a 48:48:4 volumetric mixture of acetonitrile, acetone, and water. The mobile phase was degassed by sonication for 30 min. The pump was operated at a constant 1.0 mL/min flow rate, and the column temperature was maintained in a column chamber at 35°C. The sampling injection volume was 20 μL, and peak identification was made by comparing the retention time between the sample and the standard materials. Using calibration curves of FAMES, the conversion yields were calculated.

Results and Discussion

For the alkali-catalyzed transesterification reaction of rapeseed oil, we investigated several operating conditions: reaction temperature, type and amount of catalyst, molar ratio of methanol to oil, and reaction time. In alkali-catalyzed transesterification, the amount of free fatty acid was assumed to be below 0.5% on the basis of oil weight, in order to obtain high conversion yield (13). The conversion yield or percentage of conversion was calculated by dividing the amount of product by the maximum theoretical product. Because it has a high acid value, the activity of catalyst was diminished in the transesterification reaction. As reported in Table 1, the fatty acid content of rapeseed oil used for this experiment was 0.018%, which was lower than the proposed value (below 0.5%).

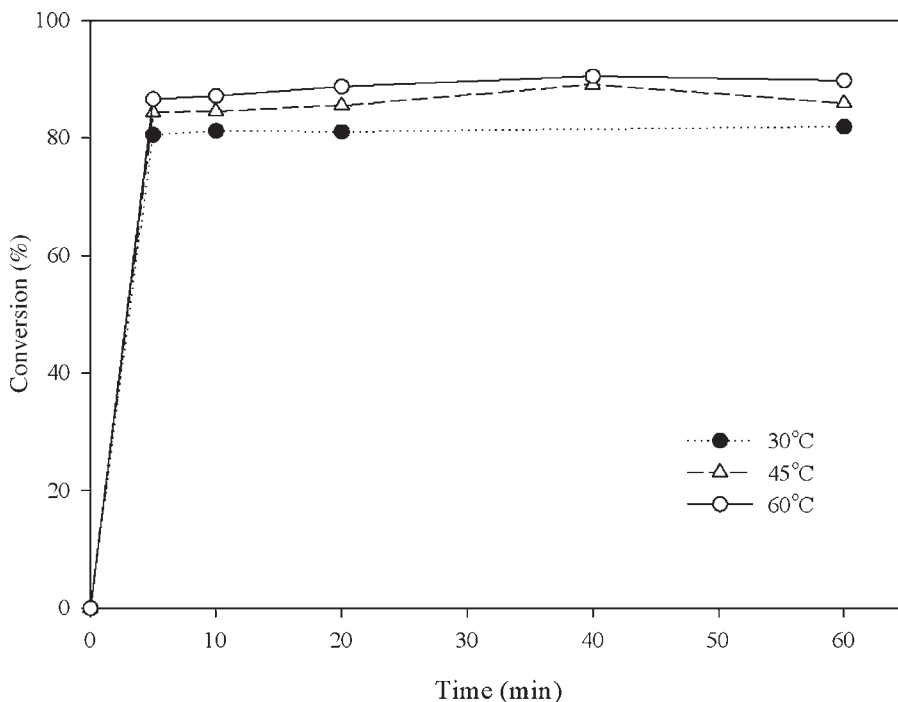


Fig. 2. Effect of reaction temperature on conversion at 1.0% (w/w) KOH at molar ratio of 1:6.

Effect of Temperature

Generally, alkali-catalyzed transesterification is performed near the boiling point of the alcohol, but several researchers have reported high conversion yield at room temperature (8,14). Low reaction temperature was desirable, since reaction temperature was closely related to the energy cost of the biodiesel production process.

The effect of temperature on rapeseed oil transesterification reaction was investigated at 60, 45, and 30°C using the conditions of 1% (w/w), KOH as a catalyst and a methanol:oil molar ratio of 6:1 (Fig. 2). Reaction equilibrium was reached within 10 min at each temperature studied. After 10 min of reaction, the conversion yields were 87.1, 84.5, and 81.2% at 60, 45, and 30°C, respectively. The conversion yield of rapeseed oil had only a small difference at lower temperatures. Freedman et al. (8) reported the effect of temperature on transesterification of refined soybean oil using a molar ratio of 1:6 and 1% NaOH. After 0.1 h, conversion yields were 94, 87, and 64% at 60, 45, and 32°C, respectively (8). Another study showed that the conversion of rapeseed oil at different temperature conditions (65, 50, and 40°C) with an oil:MeOH molar ratio of 1:6, and 1.7% NaOH began at 40, 20, and 5 min, respectively (9). This study used longer reaction times than our experiments.

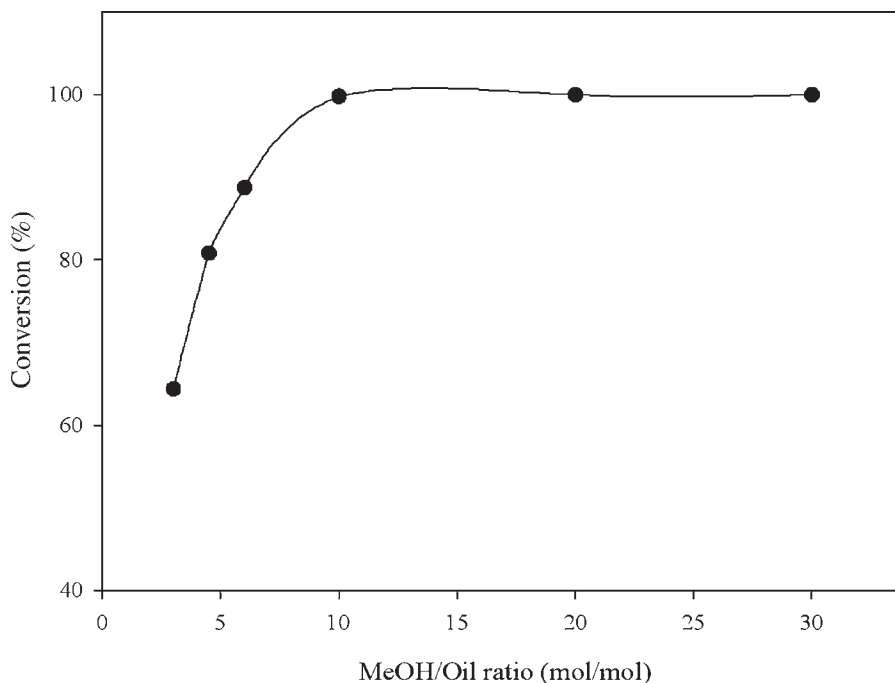


Fig. 3. Effect of methanol molar ratio on conversion at 1.0% (w/w) KOH, 60°C, and 60 min.

Effect of Molar Ratio

The most significant factor of alkali-catalyzed transesterification was the molar ratio of the alcohol and oil. The stoichiometry of alkali-catalyzed transesterification requires 3 mol of alcohol/1 mol of triglyceride to generate 3 mol of FAME and 1 mol of glycerol. Since the transesterification is composed of reversible and consecutive reactions, the increase in molar ratio of methanol will result in high conversion yields.

In this experiment, the effect of molar ratio was studied by varying it from 1:3 to 1:20 with a reaction temperature of 60°C, and 1% KOH on the basis of oil weight as catalyst for 60 min; the results are shown in Fig. 3. High conversion yield was obtained in a short period of reaction time for every molar ratio condition. After 20 min, conversion yields were equilibrated at 64~99%. Below a 1:10 molar ratio, conversion yields sharply increased with an increase in molar ratio. The increase in conversion yield was not noticed at a molar ratio higher than 1:10. In the alkali-catalyzed transesterification process, the conversion yield increased with added methanol, and total production costs increased when using high amounts of methanol. Despite high energy consumption by the addition of a large amount of methanol, it was concluded that a molar ratio of 1:6 to 1:10 was more suitable. Kim and Kang (14) reported an optimum molar ratio of 1:6 in an experiment using

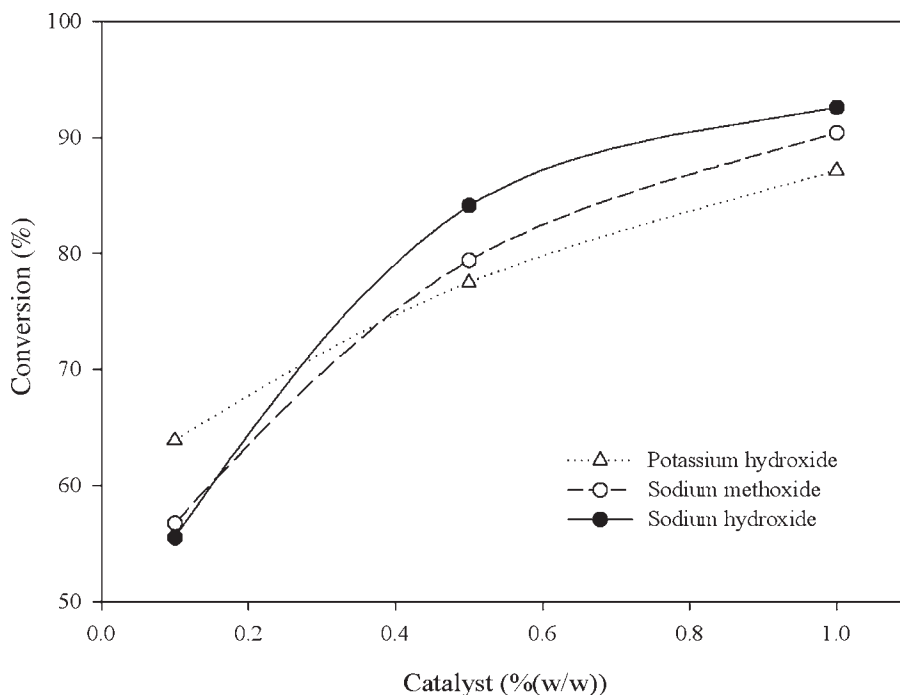


Fig. 4. Effect of catalyst type and concentration on conversion at molar ratio of 1:6, 60°C, and 20 min.

soybean oil with a high unsaturated fatty acid content and a reaction temperature above 60°C, whereas rapeseed oil with a high oleic acid content had an optimum molar ratio of 1:6 to 1:8 below 60°C.

Comparison of Alkali and Alkoxide

Alkali metal alkoxides such as KOH, NaOH, and CH_3ONa are the most effective catalysts in alkali-catalyst transesterification. When using KOH, NaOH, and CH_3ONa alkali-catalyst for FAME conversion, the active catalytic species were the methoxide anion (CH_3O^-), formed by the reaction between methanol and hydroxide ions of KOH and NaOH. In addition, the methoxide anion was formed by dissolution of sodium methoxide. Sodium methoxide causes the formation of several byproducts, mainly sodium salts, that have to be treated as waste and additionally require high-quality oil (16). However, KOH has an advantage because it can be converted into KOH by reaction with phosphoric acid, which can serve as a fertilizer. Since KOH is more economical than sodium methoxide, it is the preferred choice for large-scale FAME production process.

Figure 4 compared the conversion yields of three different alkali catalysts at a molar ratio of 1:6, 60°C, and a reaction time of 20 min. All three alkali catalysts caused some difference in conversion yields. NaOH

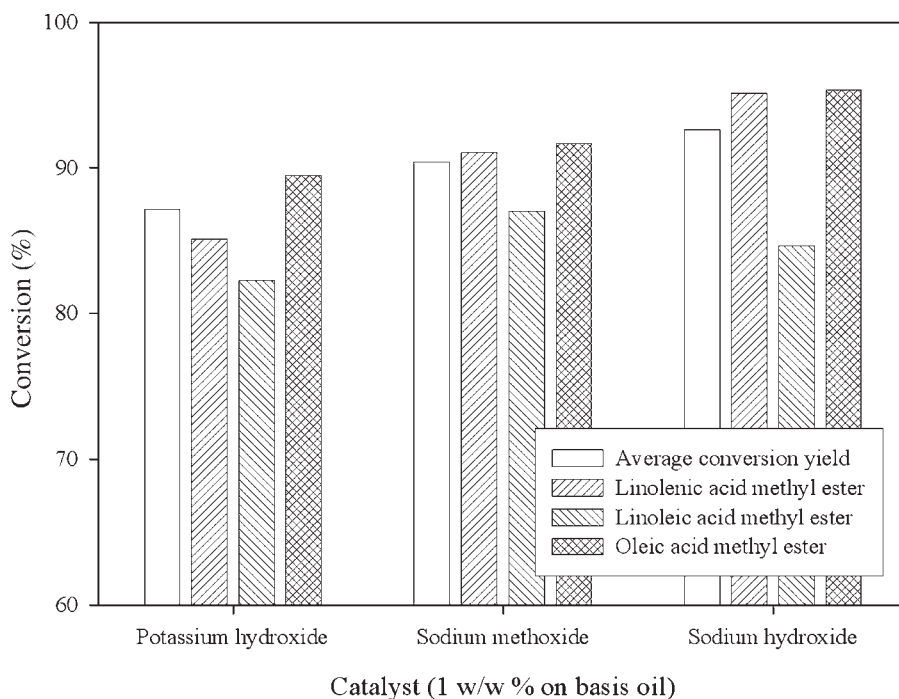


Fig. 5. Effect of catalyst type on FAME content after 10-min reaction with a catalyst of 1.0% (w/w) at a effect of molar ratio of 1:6, 60°C, and 10 min.

showed the best conversion yield, above 0.5% (w/w). NaOH has a lower molecular weight than KOH, so a smaller concentration (w/w) is required to achieve the same effect. In addition, its salts are less soluble in FAME solution than those of KOH. KOH was less effective than NaOH as a catalyst for FAME production from rapeseed oil. Freedman et al. (8) reported that methyl ester conversion yields were very similar to those of 1% NaOH and 0.5% NaOCH₃ used as catalyst in soybean oil with a 1:6 molar ratio. In our following experiments, KOH was used as alkali catalyst because of transesterification catalyzed by NaOH and CH₃ONa resulted in byproducts, as previously described.

Figure 5 compares the conversion yields of each FAME, transesterified from rapeseed oil, after a 10-min reaction with a 1.0%(w/w) catalyst at a molar ratio of 1:6 and 60°C. In all the catalysts studied, oleic acid was best converted to methyl oleate.

Effect of Catalyst Concentration

In alkali-catalyzed transesterification, the optimal catalyst and the amounts used were collected by optimal concentration instead of high conversion conditions, because a high catalyst concentration at a high conversion yield was decreased by a reverse hydrolysis reaction. Figure 6

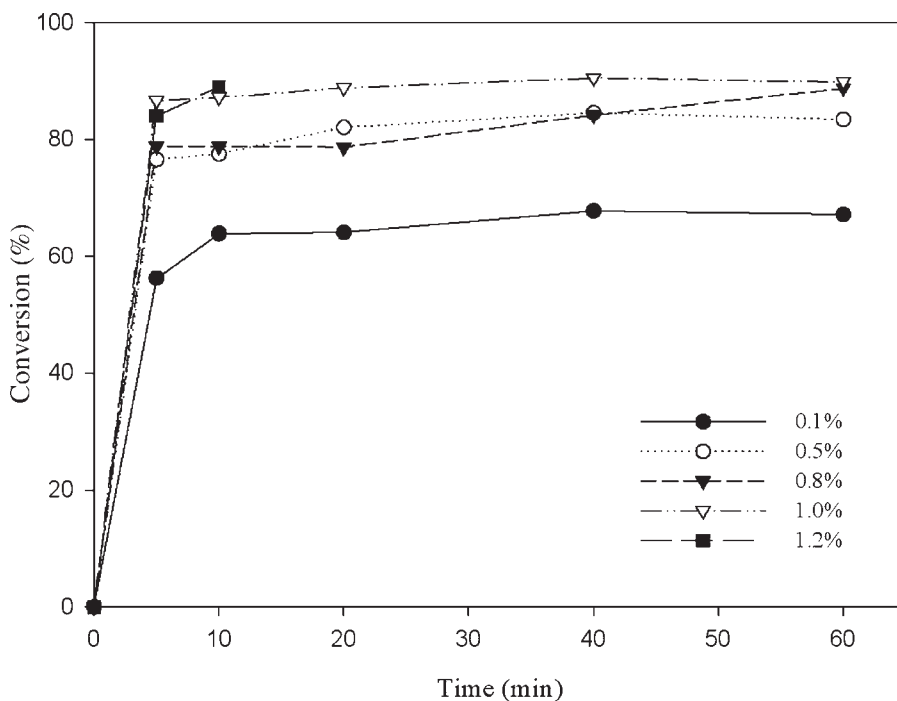


Fig. 6. Effect of KOH concentration on conversion at molar ratio of 1:6 and 60°C.

shows the effect of the concentration of KOH catalyst on the basis of oil weight at 60°C and a molar ratio of 1:6. The conversion yield was enhanced by increasing KOH concentration. The conversion rate increased rapidly within 5 min, and slowly after 10 min. At a low catalyst concentration (0.1%), the conversion rate was low. A small difference in FAME was shown at a conversion yield above 1.0% KOH. Some studies have shown that 1% KOH was optimum for transesterification of rapeseed oil (17).

Effect of Reaction Time

Reaction temperature and time were significant operating parameters, which are closely related to the energy costs, of the biodiesel production process. Figure 7 shows the effect of reaction time on the transesterification of rapeseed oil at a catalyst concentration of 1%, molar ratio of 1:6, and 60°C. Within 5 min, the reaction was rapid. Rapeseed oil was converted to above 85% within 5 min and reached equilibrium state after about 10 min. Several researchers reported that the conversion of vegetable oils to FAME was achieved above 80% within 5 min with a sufficient molar ratio (8,11). For a reaction time of 60 min, linoleic acid methyl ester was produced at a low conversion rate, whereas oleic and linolenic methyl ester were rapidly produced.

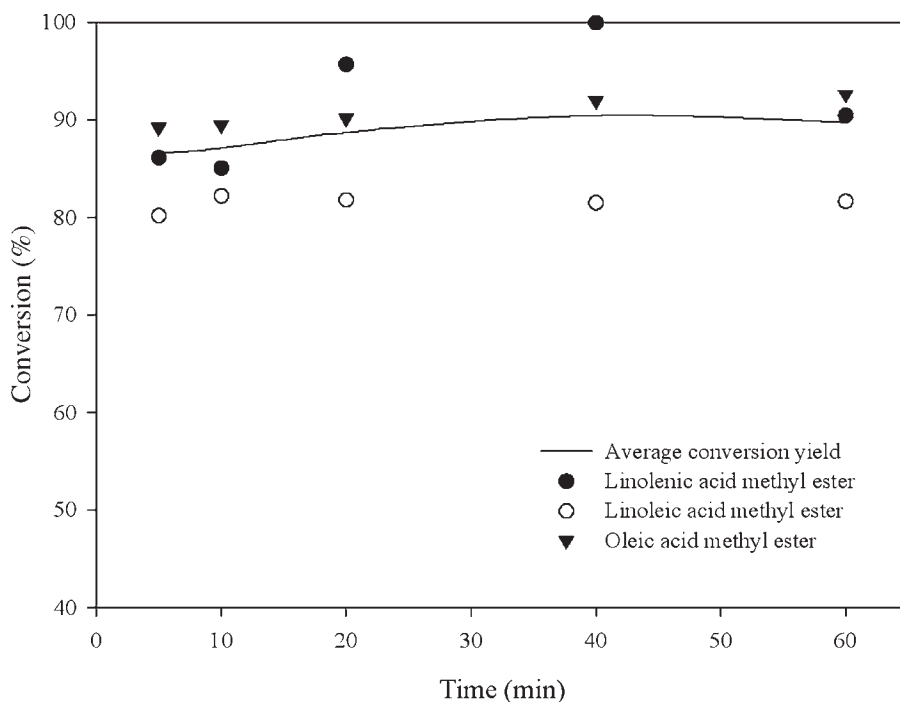


Fig. 7. Effect of reaction time on conversion and composition at 1.0% (w/w) KOH, molar ratio of 1:6 and 60°C.

Some studies have shown that the complete factorial design of KOH-catalyzed transesterification of refined rapeseed oil could be optimized at 50°C, 0.9% KOH, and an MeOH/oil ratio of 6:1; conversion was 80.3% (18).

Conclusion

FAME production of rapeseed oil by alkali-catalyzed transesterification reaction was investigated. To obtain optimum conversion yield, anhydrous methanol and rapeseed oil with a free fatty acid content of <0.5% were used. The optimum conditions for alkali-catalyzed transesterification using KOH were determined as follows: an oil to methanol molar ratio of 1:8 to 1:10; KOH, 1.0% (w/w) on the basis of oil weight, as catalyst; a reaction temperature of 60°C; and reaction time of 30 min. At these conditions, the FAME conversion yield was approx above 98%. From the refined FAME product (biodiesel), the FAME purity was obtained above 99% through posttreatment such as washing and centrifugation.

Acknowledgment

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