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Batch (One- and Two-Stage) Production of Biodiesel Fuel From Rapeseed Oil

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Abstract

Biodiesel fuel is an alternative and renewable energy source, which may help to reduce air pollution, as well as our dependence on petroleum for energy. Several processes have already been developed for the production of biodiesel. Alkali-catalyzed transesterification with short-chain alcohols, for example, generates high yields of methyl esters in short reaction times. In this study, we have evaluated the efficacy of batch (one- and two-stage) transesterification of rapeseed oil in the production of rapeseed methyl ester. The conversion of rapeseed oil exhibited similar reaction patterns and yields in 30- and 1-L reaction systems. Approximately 98% of the rapeseed oil was converted at 400 rpm within 20 min, under the following conditions: 1% (w/w) KOH, 1:10 methanol molar ratio, and at 60°C. In the 30-L, two-stage transesterification process, approx 98.5% of the rapeseed oil was converted at a 1:4.5 molar ratio and 1% (w/w) KOH at 60°C for 30 min (first reaction condition), and at a 1:1 molar ratio and 0.2% (w/w) KOH at 60°C for 30 min (second reaction condition).

Index Entries: Biodiesel fuel; transesterification; rapeseed oil; two stage.

Introduction

The methyl esters of the higher fatty acids C_{14}–C_{22}, which can be derived from vegetable oils and animal fats via transesterification with alcohol, may be usable as an alternative fuel for diesel engines. This compound is also referred to as a biodiesel fuel. However, it also holds tremendous promise in a wide range of industrial purpose, either in direct form (e.g., paint-stripper, graffiti remover, cleaning solvent, emulsifier, and absorbent of volatile organic pollutants) or as starting materials for the

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production of other compounds (e.g., alkanolamides, isopropyl esters, fatty alcohols, fatty acid α-sulpho-esters, synthetic esters, and sugar polymers) *(1–3)*. Biodiesel fuel is a renewable alternative energy source, which may help to reduce air pollution, as well as our dependence on petroleum for energy. The ratio of fatty acid methyl ester (FAME) in mixed biodiesel fuel ranges between 5 and 30 wt%, but is usually between 20 and 30 wt%. Mixed fuels are characterized by good emissions profiles, and also tend to minimize the problems generally associated with biodiesel fuels *(3)*. Biodiesel is compatible with petrodiesel in compression–ignition engines, and mixtures of biodiesel and petrodiesel have been used without any need for engine modification *(4)*. These fuels also exhibit low viscosities, similar to those of petrodiesel. Also, many of the characteristics of biodiesel fuels, including volumetric heating value, cetane number, and flash point, are fairly similar to those of petrodiesel *(5)*. The use of biodiesel fuel is also associated with several unique advantages. It may be used as an alternative renewable energy source, or a biodegradable nontoxic fuel. Biodiesel fuels are generally associated with the generation of a low degree of air pollution from particulates, carbon monoxide, SO_x emissions, and CO_2 recycling over short periods *(6)*. Also, biodiesel exhaust gases contain a relatively low amount of polycyclic aromatic hydrocarbons, which exert proven carcinogenic and mutagenic effects *(3)*.

Despite the fact that biodiesel is being increasingly eyed as an attractive alternative fuel, problems remain regarding the costs of its production. Two factors are extremely relevant to the cost of biodiesel production: raw materials' costs (oil and alcohol), and process operation costs. The cost of raw material accounts for approx 60–75% of the total biodiesel production cost *(7)*. Whereas in the United States, soybean oil has been primarily used in the development of biodiesel, rapeseed oil has become the dominant feedstock for biodiesel production in Europe *(8)*. Several processes have been developed for the production of biodiesel fuel via acid-, alkali-, and enzyme-catalyzed transesterification reactions *(9–11)*. Alkali-catalyzed transesterification proceeds approx 4000 times faster in the presence of an alkaline catalyst than when catalyzed by an equal amount of an acid catalyst *(12)*. Transesterification, also commonly referred to as alcoholysis, is the displacement of alcohol from an ester by another alcohol, in a process which is fairly reminiscent of hydrolysis. Transesterification involves a number of consecutive and reversible reactions. During the reaction step, triglycerides are converted to diglycerides. The reaction step is followed by the conversion of diglycerides to monoglycerides, and then of monoglycerides to glyceride *(13,14)*. The main factors which affect transesterification include the molar ratio of vegetable oil to alcohol, the type and amount of catalyst, the reaction temperature and reaction time, and the contents of free fatty acid and water in the oil sources used *(10)*. In alkali-catalyzed transesterification, the constitutent oils and alcohol must be largely anhydrous, as water can cause saponification when mixed with oil. Another significant factor which

affects conversion yield is the molar ratio of alcohol to vegetable oil. The stoichiometry of the transesterification reaction requires 3 mol alcohol per mole of triglyceride, in order to yield 3 mol fatty esters and 1 mol of glycerol. Higher oil to alcohol molar ratios tend to result in greater conversion yields in a shorter reaction time. The recommended amount of alkali catalyst for effective transesterification is somewhere between 0.1% and 1% (w/w) of oils and fats. In general, the reaction temperature is set at near the boiling point of alcohol. Higher reaction temperatures tend to facilitate the reaction, and shorten reaction time *(2,10)*. The other important factor in this process is agitation speed, which plays a vital role in the transesterification process. The degree of homogeneity of alcohol with the triglyceride is critical to the success of the transesterification process *(12)*.

In this article, we have attempted to determine the optimal transesterification conditions inherent to the production of biodiesel via batch (one- and two-stage) transesterification, using rapeseed oil with methanol and potassium hydroxide.

Materials and Methods

Materials

Refined and bleached rapeseed oil was obtained from the Onbio Co., Ltd. (Pucheon-Si, Korea). Table 1 illustrates the fatty acid composition and characteristics of the rapeseed oil. Reference standards of FAMEs, including palmitic, stearic, linolenic, linoleic, and oleic methyl ester, all of >99% purity, were purchased from the Sigma Chemical Co. (St. Louis, MO). Methanol and potassium hydroxide were analytical grade.

Apparatus

1-, 5-, and 30-L reaction systems were applied to the transesterification process. The 1-L reactor system was composed of a 1-L four-necked reactor, which was equipped with a reflux condenser, a thermometer, and a sampling port. The reactor was immersed in a constant-temperature water bath which was controlled by a PID temperature controller, capable of controlling the temperature to within ±0.2°C of the set point. Mixing was done by an electrical motor equipped with a propeller-type impeller *(2)*. The 5-L reaction system consisted of a 5-L reactor, and an impeller with six flat blades. The 30-L reaction system (KobioTec, Korea) consisted of a 30-L reactor and three impellers with six flat blades. During the experiments, samples were withdrawn at preset time intervals with a 1-mL glass pipet through a sampling port in the reactor.

Reaction Procedures and Conditions

For the batch transesterification of the rapeseed oil, the reactor was initially charged with a given amount (400 g in the 1-L reaction system, 3.5 L

Table 1
Fatty Acid Composition and Characteristics of Rapeseed Oil

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

in the 5-L system, and 18 L in the 30-L system) of rapeseed oil, and then heated to the set temperature along with agitation. The catalyst was prepared by dissolution in the required amount of methanol. After the set temperature of oil and methanol was achieved, a methanolic catalyst was added to the base of the reactor, in order to prevent the methanol from evaporating. The reaction was timed, beginning immediately after the addition of the methanol and the catalyst.

For the two-stage transesterification of the rapeseed oil, the first reaction was performed under the following conditions: 1:4.5 molar ratio, 1% (w/w) potassium hydroxide, and at 60°C. After the first reaction ceased, the supernatant was rereacted by adding potassium hydroxide and methanol.

Sample Preparation and Analysis

Samples were drawn at preset time intervals. Approximately 1 mL of the sample mixtures were collected in 10-mL test tubes, to which 1 *N* hydrochloric acid was immediately added and vortexed, in order to neutralize the catalyst and halt the reaction. The pretreated samples were evaporated in order to remove any nonreacted methanol, and then centrifuged at low temperature to remove the glycerin. The supernatant was then evaporated under a vacuum, and diluted with methanol for high-performance liquid chromatography (HPLC) analysis.

Prepared samples were analyzed for FAMEs, using HPLC. An HPLC (Waters Korea Ltd., Korea) was equipped with a model Waters 1525 binary HPLC pump and a ultraviolet detector (Waters 2487 dual λ absorbance detector, 205 nm). A Waters Spherisorb ODS2 column (4.6×250 mm^2 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 1 h. The pump was operated

at a 1 mL/min constant flow rate, and column temperature was maintained in the column chamber at 35°C. The sampling injection volume used was 20 μL, and peak identification was conducted by comparing retention times between the sample and the standard materials. The conversion yields were finally calculated using calibration curves for FAMEs.

Results and Discussion

In order to perform the alkali-catalyzed transesterification process with the rapeseed oil, we applied several reaction systems. In the alkali-catalyzed transesterification, the amount of free fatty acid was proposed to be less than 0.5% on the basis of oil weight, in order to ensure a high conversion yield *(15)*. As it exhibits a high acid value, the activity of the catalyst was diminished during the transesterification reaction. As reported in Table 1, the fatty acid content of the rapeseed oil used in this experiment was 0.018%, which was lower than the proposed value (below 0.5%). In our previous report *(2)*, we optimized rapeseed FAME (biodiesel) production by the alkali-catalyzed transesterification reaction, using anhydrous methanol and potassium hydroxide. The optimized conditions for alkali-catalyzed transesterification using KOH were determined to be the following: 1:8 to 1:10 molar proportion of oil to methanol, 1% (w/w) by oil weight of KOH catalyst; 60°C reaction temperature, and 30 min reaction time. Under the given conditions, the conversion yield was approx 98%. From the refined product (rapeseed FAME, biodiesel), the purity of the product was found to be more than 99% through posttreatment, which included washing and centrifugation.

Batch Production System of Rapeseed Methyl Ester

Agitation speed appears to play a vital role in the transesterification process. The degree to which the alcohol is homogeneous with the triglycerides is also relevant to the transesterification process *(12)*. We assessed the effects of agitation speed on the biodiesel conversion yield in the 1-L reaction system. In this reaction system, the agitation was provided by an electrical motor, which was equipped with a propeller-type impeller with a diameter of 50 mm, and three blades. As shown in Fig. 1, we compared conversion yields at different agitation speeds, from 400 to 1800 rpm, under the following conditions: 1% (w/w) potassium hydroxide, a methanol molar ratio of 1:6, and 60°C after a reaction time of 20 min. Below 600 rpm, the rapeseed oil and methanol were visually confirmed to mix rather poorly. The conversion yields occurring at 600 and 1800 rpm were approx 75% and 90%, respectively. Above 1400 rpm, production yield was unaffected by agitation speed.

We also attempted to determine the effects of agitation speed on the production of FAME in the 5-L reaction system. We organized the 5-L reaction system, which consisted of an impeller with six flat blades. The conversion

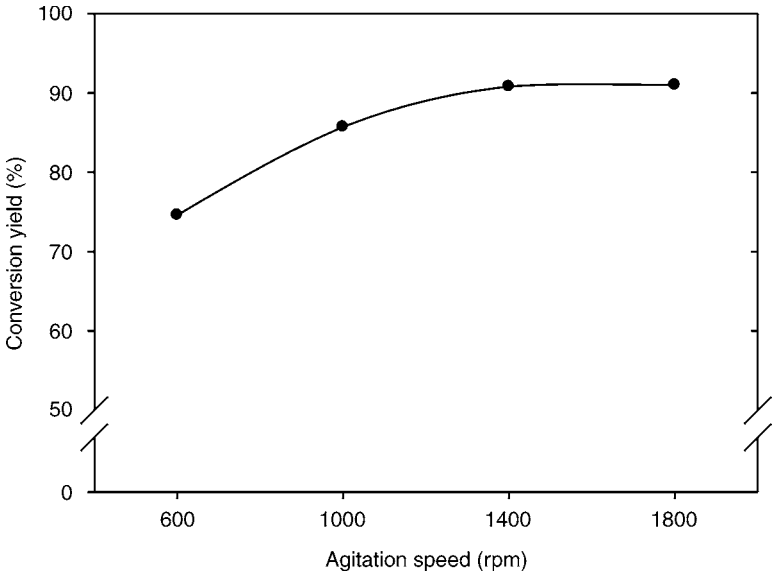

Fig. 1. Effect of agitation speed on conversion yield at 1% (w/w) of potassium hydroxide (1:6 methanol molar ratio and 60°C) after 20 min in 1-L reaction system.

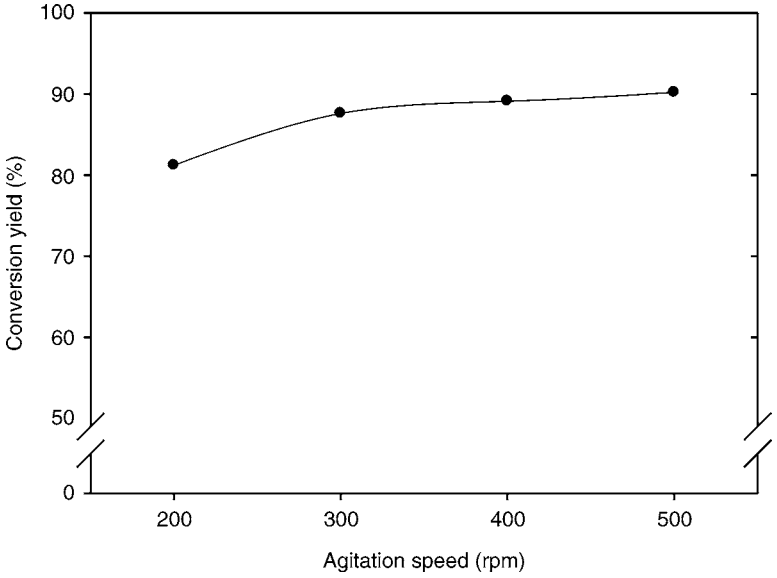

Fig. 2. Effect of agitation speed on conversion yield at 1% (w/w) of potassium hydroxide (1:6 methanol molar ratio and 60°C) after 30 min in 5-L reaction system.

yields were compared at different agitation speeds from 200 to 500 rpm, under the following conditions: 1% (w/w) KOH, a methanol molar ratio of 1:6, and a temperature of 60°C after 30-min reaction. Figure 2 shows the effects of agitation speed on the conversion of rapeseed oil to biodiesel.

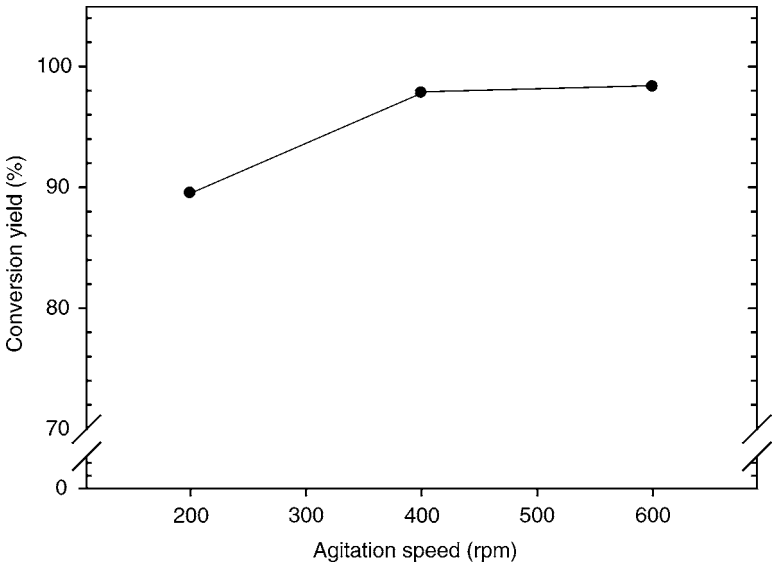

Fig. 3. Effect of agitation speed on conversion yield at 1% (w/w) of potassium hydroxide (1:10 methanol molar ratio and 60°C) after 30 min in 30-L reaction system.

The rapeseed oil and methanol were observed to mix poorly at less than 200 rpm. The conversion yields at 200 and 600 rpm were approx 80% and 90%, respectively. Above 400 rpm, the production yields of rapeseed FAME were unaffected by agitation speed.

We also organized a 30-L reaction system, which consisted of a 30-L reactor and three impellers with six flat blades, which were used to agitate the reactants. Figure 3 shows the effects of agitation speed on the conversion of rapeseed oil to biodiesel at different agitation speeds, ranging from 200 to 600 rpm, in 1% (w/w) KOH, at a methanol molar ratio of 1:10, and at 60°C, after reacting for 30 min. At less than 200 rpm, the rapeseed oil and methanol did not mix well. Approximately 89% of the rapeseed oil was converted at 200 rpm within 20 min, and approx 98% was converted at 400 rpm under the same conditions. Above 400 rpm, the production yield of the rapeseed FAME was unaffected by agitation speed.

Regarding the operating parameters for this process, reaction time constitutes one of the most important factors in the determination of production cost. Shorter reaction times with stable conversion are associated with less costly operation processes. Figure 4 shows the time-course of rapeseed oil transesterification in the 30-L reaction system, using different methanol-to-oil molar ratios. The conversion yield of the rapeseed oil in the 30-L reaction system provided a similar reaction pattern and yield, as was obtained in the 1-L reaction system *(2)*. Within 30 min, approx 91.2% of the rapeseed oil was converted, at a methanol molar ratio of 1:6. Approximately 98.5% of the rapeseed oil was converted in 30 min at a molar ratio of 1:10. However, both conversions achieved equilibrium after 5 min.

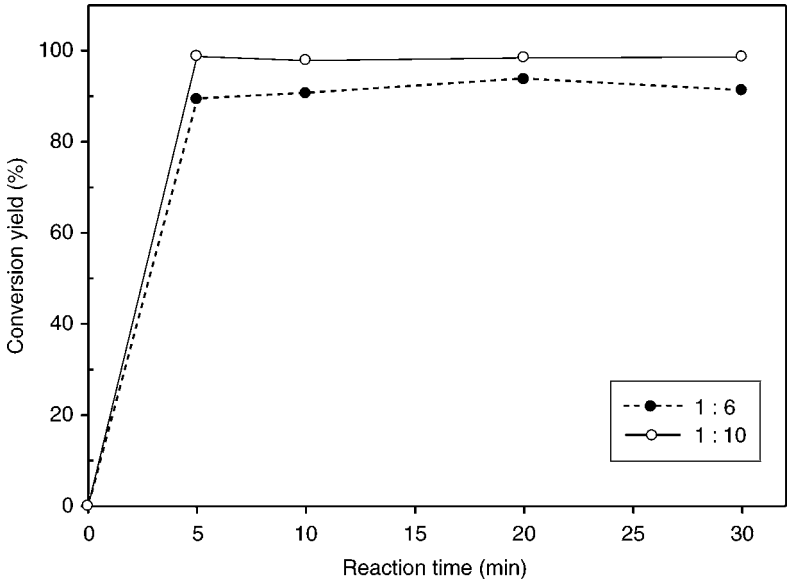

Fig. 4. Effect of methanol molar ratio on rapeseed oil transesterification in 30-L reaction system.

Several researchers have reported that the conversion of vegetable oils to FAME was above 80% within 5 min when a sufficient molar ratio was used *(2,16,17)*. Kim and Kang *(16)* reported that the optimum molar ratio was 1:6 at a reaction temperature of more than 60°C, in an experiment involving soybean oil with high unsaturated fatty acid content. However, rapeseed oil with high oleic acid content was found to have an optimal molar proportion of 1:6 to 1:8, and a reaction temperature below 60°C. Zmudzinska-Zurek and Buzdygan *(17)* reported that the complete factorial design of the KOH-catalyzed transesterification of refined rapeseed oil could be optimized at 50°C, 0.9% KOH, and 6:1 MeOH to oil ratio; the conversion yield was 80.3%.

Two-Stage Transesterification of Rapeseed Oil

Several processes have been developed for the production of biodiesel fuel via two-step transesterification *(9,18–20)*. Tanaka et al. *(18)* performed two-step transesterification using 6:1 to 30:1 molar ratios with alkali catalysis, in order to achieve a 99.5% conversion yield in his two-step reaction of oils and fats, including tallow, coconut oil, and palm oil. The first reaction was conducted at or near the boiling temperature of the lower alcohol, for a period of 0.5–2 h. The crude ester layer was then employed in a second reaction, which used 8–20% alcohol and 0.2–0.5% alkali catalyst, and was conducted for 5–60 min. Zhong *(19)* conducted a conversion with edible beef tallow containing 0.27% free fatty acids, using a 6:1 molar ratio of methanol to tallow, 1% NaOH, and a temperature of 60°C, for approx 30 min. After the separation of glycerol, the ester layer

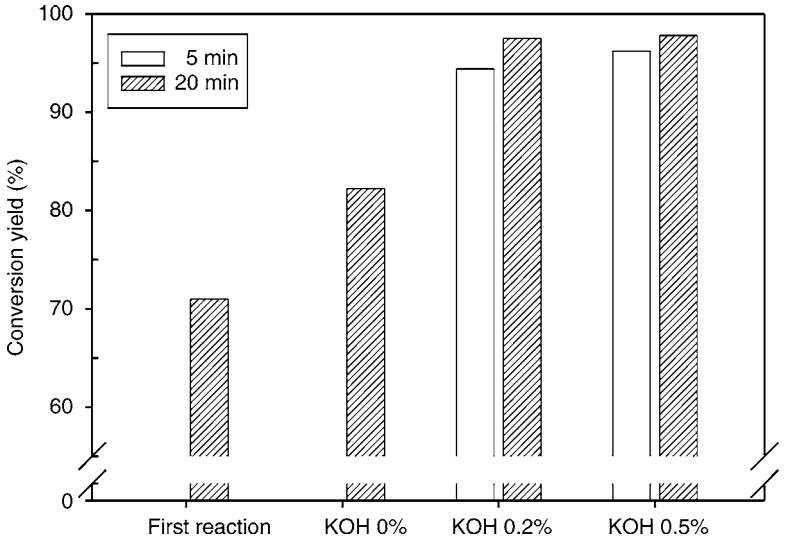

Fig. 5. Effect of reaction time and KOH concentration on second transesterification with addition of 1:1 molar ratio in 1-L reaction system.

was rereacted using 0.2% NaOH and 20% methanol at 60°C, for approx 1 h. Cvengroš and Cvengrošová *(20)* conducted a two-step reaction in one reactor, in which the oil to MeOH molar ratio was 1:3.5 for step I, and 1:0.95 for step II, with each step lasting 1.5–2 h. Also, Ahn et al. *(9)* carried out the transesterification of two steps in the VN process for the production of biodiesel, resulting in a reported 99% conversion rate.

In our previously mentioned trials, successful yields for the batch transesterification process of rapeseed oil were achieved under the following conditions: methanol molar ratio of 1:10, potassium hydroxide concentration of 1% (w/w), reaction temperature of 60°C, and a reaction time of within 30 min. This process consumed a large amount of methanol, which increased the manufacturing cost of the biodiesel, and also required a great deal of energy to recover the nonreacted methanol. To save the required amount of methanol and obtain a high conversion yield, we conducted two-stage transesterification of rapeseed oil with different methanol molar ratios and KOH concentrations. Figure 5 shows the effects of reaction time in the second reaction, using a molar ratio of 1:1 and different KOH concentrations (0–0.5% [w/w]). The first reaction was performed for 20 min with a 1:4.5 molar ratio and 1% (w/w) KOH, and resulted in a conversion yield of approx 71%. The second reaction was conducted with a 1:1 molar ratio and different KOH concentrations (0–0.5% [w/w]). The conversion yields were 82%, 97%, and 98% in 0%, 0.2%, and 0.5% (w/w) KOH after a reaction time of 20 min, respectively. Within 5–20 min, rapeseed FAME was produced at a concentration of 94.4–97.5%.

Figure 6 shows the effects of added KOH and methanol amounts on the conversion yields of rapeseed oil under the second transesterification

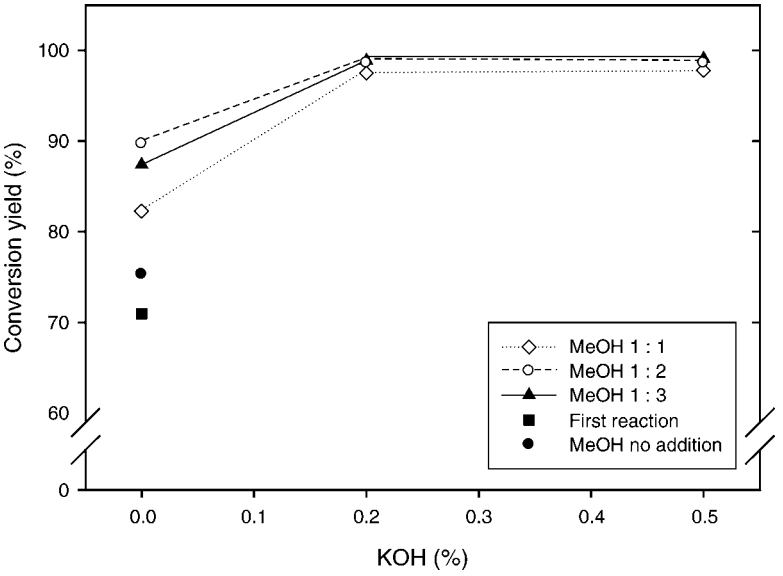

Fig. 6. Effect of added KOH on added MeOH molar ratio in second transesterification in 1-L reactor system.

conditions. The first reaction was performed with a 1:4.5 molar ratio and 1% (w/w) KOH, and achieved a conversion yield of approx 71%. In the second reaction without added KOH, the enhanced conversion of the rapeseed oil was observed to added amount of 1:2 molar ratio. Conversion yields were not significantly affected by amounts of added KOH of more than 0.2% (w/w) with different methanol molar ratios. Above 0.2% (w/w) addition of KOH, more than 98% of the rapeseed oil was converted, at methanol molar proportion of 1:1 to 1:3. According to our results, the second reaction scale-up condition in the two-stage transesterification of rapeseed oil was set to a methanol molar ratio of 1:1, and a 0.2% (w/w) amount of added KOH.

Figure 7 shows the conversion yields associated with the two-stage transesterification of rapeseed oil in the 30-L reaction system. In this system, the first reaction was characterized by a 1:4.5 molar ratio and 1% (w/w) of added KOH, and the second reaction was characterized by a 1:1 molar ratio and 0.2% (w/w) of added KOH. In the first reaction, approx 72% of the rapeseed oil was converted within 5 min, and was equilibrated to approx 73% for 30 min. After 30 min, during the first reaction, the reaction was discontinued and the upper product (mixture of FAME, nonreacted rapeseed oil, and methanol) was separated. The nonfinished product was then rereacted with methanol at a 1:1 molar ratio with 0.2% (w/w) added KOH at 60°C for 30 min. The conversion of rapeseed oil ultimately generated a yield of approx 98.5% under the second reaction conditions.

From our analysis of the refined products (rapeseed FAME; biodiesel) of the batch (one- and two-stage) transesterifications, we found that the

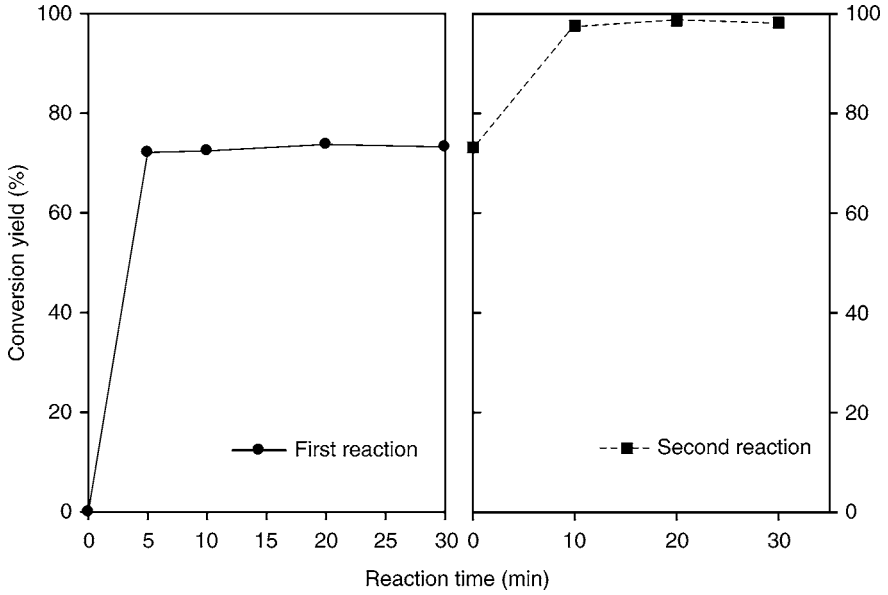

Fig. 7. Time-course of two-stage transesterification of rapeseed oil in 30-L reaction system. First reaction: 1:4.5 molar ratio and 1% (w/w) KOH; second reaction: 1:1 molar ratio and 0.2% (w/w) KOH.

purity of the products obtained was more than 99% after posttreatment, which included washing and centrifugation.

Conclusions

In this article, we have attempted to evaluate the efficacy of a method for the production of methyl ester of rapeseed oil via alkali-catalyzed batch (one- and two-stage) transesterifications. Approximately 89% and 98% of the rapeseed oil was converted at 200 and 400 rpm within 20 min, respectively, under the following conditions: 1% (w/w) potassium hydroxide, a methanol molar ratio of 1:10, and a reaction temperature of 60°C after 30 min of reaction in a 30-L reaction system. The rapeseed oil conversion yield showed a similar reaction pattern and yield in the 30-L reaction system, as was seen in the 1-L reaction system. For the two-stage transesterification of rapeseed oil in the 1-L reaction system, the first reaction was performed using a 1:4.5 molar ratio and 1% (w/w) of added KOH, and a conversion yield of 71% was achieved. In the second reaction, the conversion yield was not significantly affected by the amounts of added KOH of more than 0.2% (w/w) with different methanol molar ratios. With the addition of 0.2% (w/w) KOH, over 98% of the rapeseed oil was converted using methanol molar proportion of 1:1 to 1:3. In the 30-L, two-stage transesterification reaction system, 72% of the rapeseed oil was converted within 5 min, and was equilibrated to approx 73% for 30 min in the first reaction. The conversion of rapeseed oil was discontinued at a yield of above

98.5% in the second reaction condition, involving a 1:1 methanol molar ratio and 0.2% (w/w) of added KOH at 60°C for 30 min. According to our analysis of the final refined FAME product (biodiesel), the purity obtained was found to be more than 99% after posttreatment, which involved washing, centrifugation, and drying.

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