A Continuous Process for the Conversion of Vegetable Oils into Methyl Esters of Fatty Acids[1]

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ABSTRACT: A continuous process for the transesterification of triglycerides to methyl esters was investigated in a pilot plant. The process was equipped with a motionless and a high-shear mixer. The experimental studies explored variations in the mixing intensity, stoichiometry, and catalyst concentration on the overall conversion. The combined as well as individual effect of mixers was examined. The developed process resulted in high conversions of vegetable oils into methyl esters. Conversion of triglycerides to methyl esters in excess of 98% was achieved. Larger excess amounts of alcohol favored higher conversions. The motionless and high-shear mixers each provided adequate mixing for the process. Higher catalyst concentrations resulted in higher conversions but increased the solubility of methyl esters in the glycerol layer. This reduced the amount of methyl esters separated by gravity settling.
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KEY WORDS: Biodiesel, continuous process, methyl esters, mixing, pilot plant, soybean oil, transesterification.

Over the last few years, fatty acid methyl esters have assumed importance as research has intensified on the utilization of vegetable oil and animal fat derivatives as liquid fuels (better known as biodiesel). Traditional batch processing has been and still is the most widely used process for this conversion. New and more efficient processing schemes for large-scale production of biodiesel for fuel purposes are the key to commercialization of biodiesel.

The idea of using vegetable oil as a substitute for diesel fuel is an old one, going back to the invention of compression ignition engines. In fact, Rudolph Diesel, the inventor of the Diesel engine, operated an engine with peanut oil in a demonstration in 1900. Vegetable-oil fuels have been examined as a possible substitute for diesel fuel by many researchers (1–3). Although the concept of vegetable-oil fuels has been introduced periodically, it has never been considered seriously. This is mostly due to the fact that although short-term tests are satisfactory (2,3), long-term use of neat vegetable oils leads to severe engine problems (4). The durability problems have been blamed on fuel degradation due to its high viscosity, chemical structure of triglyceride molecules, and incomplete combustion (5).

Esters of fatty acids have shown the greatest potential as alternative diesel fuels, due to improved viscosity relative to the triglycerides. The viscosity of vegetable oils is reduced from about 10–15 times that of No. 2 diesel fuel to about twice that of No. 2 diesel for methyl esters, which is low enough to be used as diesel fuel. Other physical properties of fatty acid methyl esters, such as cloud point and pour point, are considerably higher than No. 2 diesel fuel, which limits their use as an alternative to diesel fuel. However, up to 30 vol% of methyl esters in diesel fuel does not significantly change the cold-flow properties of the fuel (6,7). Studies have also shown that engines running on methyl esters emit slightly lower amounts of hydrocarbons and CO and significantly lower particulates (8). The NO_x emissions, however, are higher for methyl esters (8,9).

Transesterification of vegetable oils and animal fats is the most effective process for transformation of the triglyceride molecules into smaller, straight-chain molecules of fatty acid esters. Transesterification involves the reaction between an alcohol and a triglyceride molecule in the presence of a base or acid catalyst. The transesterification of vegetable oils (also known as alcoholysis) has been investigated intensively (10–13) as widening industrial uses have been found for esters (14). Variables affecting the alcoholysis of vegetable oils, such as reaction time and temperature, catalyst type and concentration, and molar ratios of the reactants, have been studied. Most of the research to date has focused on batch transesterification of vegetable oils with methanol or ethanol at or near the boiling point of the alcohol with sodium or potassium hydroxide and 50–300% excess alcohol for 1–2 h of reaction time. Nye and Southwell (15) studied the synthesis of methyl and ethyl esters of rapeseed oil in a bench-scale process and reported better than 92% conversion at room temperature. The effect of other reaction parameters, such as catalyst concentration and mixing intensity, on the yield of esters were also reported. Peterson and co-workers (16) have also reported high yields of methyl esters at room temperature for the alcoholysis of rapeseed oil. This work was on a pilot scale and was intended to develop reaction parameters and process variables. A low-waste process for the production of methyl esters of rapeseed oil has been reported recently by Ahn and co-workers (17). Based on this technology, a 15,000-tons-per-year plant is in operation in Austria, and another 30,000-tons-per-year plant is under construction in the Czech Republic.

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A factor of particular importance in the transesterification process is the degree of mixing between the alcohol and triglyceride phases. The triglyceride and alcohol phases are not miscible and form two liquid layers upon their initial introduction into the reactor. Therefore, mixing is expected to play an important role in the transesterification reaction. Although some type of mixing, mostly in the form of mechanical stirrers, has been applied in most of the research studies, the effect of mixing intensity has not been fully addressed. Better understanding of mixing effects on the transesterification process will be a valuable tool in process scale-up and design.

The objective of this study was to develop a continuous process for the production of methyl esters of soybean oil. The effect of mixing intensity on the transesterification reaction was the primary variable that was investigated. The process used two mixers/reactors, first a motionless mixer and then a high-shear mixer. The combined effect of the two reactors as well as the individual performance of each was examined. Other reaction parameters, such as reaction time, ratio of the reactants, and catalyst concentration, were also examined.

EXPERIMENTAL PROCEDURE

Materials. Refined and bleached grade soybean oil was provided by Archer Daniels Midland Company (Lincoln, NE).

The free fatty acid concentration of the oil was measured according to AOCS procedure #Ca 5a-40 (18) and was determined to be 0.09%. Anhydrous methyl alcohol was obtained from Mallinckrodt Baker, Inc. (Paris, KY). Sodium hydroxide (98.4%) was obtained from Fisher Scientific Company (Fair Lawn, NJ). The standards for the fatty acid methyl esters and glycerides were obtained from Sigma Chemical Company (St. Louis, MO). HPLC grade solvents, acetone, and acetonitrile were obtained from Mallinckrodt Baker, Inc. Catalyst solution was prepared by adding 25 g of sodium hydroxide to 1 L of methanol.

Equipment. The major sections of the pilot plant included the pump station, heaters/mixers, the residence tube, cooling system, and separatory tank. The flow diagram for the pilot plant is presented in Figure 1.

Pump station. The pump station consisted of three E Series Pulsatron Pulsafeeder (Rochester, NY) metering pumps. The in-line pumps were connected to a manifold that converged the flow into the pre-mixer. One pump was used for soybean oil, one for methanol, and one for sodium hydroxide solution in methanol. The wetted parts of the pump used for sodium hydroxide transfer were constructed with 316 stainless steel and Teflon materials, and the wetted parts of the other pumps were made with PVC and Teflon materials.

The flow rates of the pumps were varied linearly by chang-
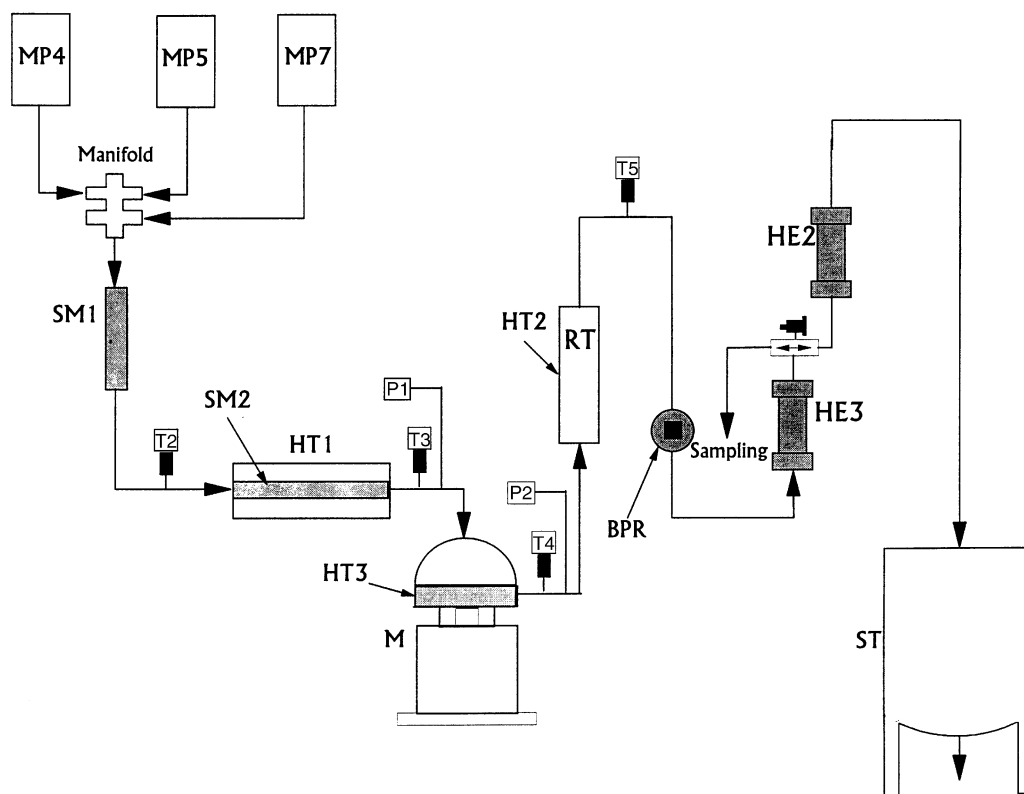
FIG. 1. Flow diagram for the continuous transesterification process. (MPn), metering pumps; (SMn), motionless mixers; (HTn), heaters; (M), high shear mixer; (Pn), pressure transducers; (Tn), thermocouples; (RT), residence tube; (BPR), back pressure regulator; (HEn), heat exchangers; (ST), separatory tank.

ing the percent stroke rate and the percent stroke length. For example, a pump with a maximum flow rate of 1000 mL/min could be adjusted to 10 mL/min by changing the percent stroke rate and stroke length to 10%. The flow accuracy decreased at very low stroke rates and lengths and the pumps were not operated below 10% stroke rate and 10% stroke length. The percent stroke rates of these pumps were controlled *via* a 4–20 mA signal, while the percent stroke length was controlled manually.

The pump station was capable of providing flows from 5.0 × 10^{-3} L/min to 0.8 L/min against a maximum pressure of 344.74 kPa (50 psi). These pumps were all calibrated and the flow rates were found to vary linearly with the percent stroke rate and stroke length.

Heaters/mixers. The reactants were converged into the pump manifold, and then were directed through two in-line motionless mixers. The first motionless mixer was made of polypropylene and was located directly past the manifold. The second motionless mixer was made of 316 stainless steel and was installed inside the heater. The heater consisted of four 0.3 kW cartridge heaters encased in an aluminum block with a flow tube in the middle. These heaters were controlled *via* a 4–20 mA signal, which set the power output from 0 to 100%. The motionless mixer inside the heater was made of stainless steel that further mixed the reactants and increased the heat transfer from the heater to the reactants. The motionless mixers were purchased from Koflo Inc. (Cary, IL) and the heaters were purchased from Watlow (St. Louis, MO).

A continuous high-shear mixer, made by Stratco Inc. (Kansas City, MO), was used to mix the reactants further. This high-shear mixer was based on a rotor-stator design and was excellent for converting input power into mechanical and hydrodynamic shear energy. This was particularly useful for mixing immiscible phases such as methanol and soybean oil. The mixer had a capacity of 600 cm^3 and could operate at pressures and temperatures as high as 10.34×10^2 kPa (150 psi) and 204.44°C (400°F), respectively. The high-shear mixer was equipped with a Watlow band heater which was used to heat the mixer during start-up. This heater was 3.81 cm (1.5 in.) wide with a 30.48 cm (12 in.) diameter, and was rated at 1000 W.

The high-shear mixer was connected to a Model UTV-2002 variable frequency drive (VFD) manufactured by Utech Systems Associates Inc. (Milwaukee, WI). The VFD controlled the power input to the mixer from 0 to 100%. A linear calibration between the percent power input and rpm was recorded. A 100% power input represented 3600 rpm. The mixing speed was controlled *via* a 4–20 mA signal.

Residence tube. The residence tube was used to increase the residence time of the transesterification reaction. The residence tube was a stainless steel 50.8 cm (20 in.) in length, 5.08 cm (2 in.) in diameter, with a volume of about 1 L. This tube was heated on the outside with a 7.62 cm (3 in.) wide, 275 W Watlow flexible silicon rubber tape heater. The tape heater was controlled by varying the power output from 0 to 100% with a 4–20 mA signal. The reactants leaving the resi-

dence tube were found to be homogeneous. The total system volume, including the residence tube and the high-shear mixer, was about 2 L.

Cooling system. Cooling of the products coming out of the process was done by two miniature shell and tube heat exchangers made in our shop. The shells of the heat exchangers were 30.48 cm (12 in.) long and 5.08 cm (2 in.) in diameter, and contained twelve 0.95 cm (3/8 in.) tubes. The heat exchangers each had 847.28 cm^2 (0.912 ft^2) of heat transfer area.

The coolant was supplied by a VWR Scientific (Philadelphia, PA) Model 1157 constant-temperature circulating bath. A 50:50 mixture of ethylene glycol and water was used as the coolant. The cooling system was closed-loop, as the coolant was constantly recycled back into the constant temperature bath. A three-way valve was installed between the two heat exchangers for sampling.

Separation. After cooling, the products were collected in a 56.78 L (15 gal) separatory tank. The separatory tank was equipped with a drainage valve on the bottom. The products were allowed to settle for 24 h, to allow the glycerol and methyl esters to separate. After settling, the glycerol and methyl ester phases were separated.

System pressure. A Tescom 26-1700 Series self-contained, spring-loaded back-pressure regulator was used to maintain system pressure. The back-pressure regulator was rated for a maximum temperature and pressure of 220°C and 34.47×10^2 kPa (500 psi), respectively. The regulator was a precision relief device that allowed the working fluid to escape at a rate appropriate for maintaining the desired system pressure. The back-pressure regulator was installed between the residence tube and the heat exchangers.

To monitor the pressure of the system, the pilot plant was equipped with two Rosemount (Eden Prairie, MN) model 1151GP gage pressure transmitters. Because of the sensitivity of these pressure transmitters to high temperatures, they were placed in a remote position to the flow and did not come in contact with the working fluid. The transmitters sent a 4–20 mA signal to the control box, which in turn transmitted real-time data to the monitor. The pressures were measured in the line before and after the high-shear mixer.

Control system. A Landis and Gyr (Buffalo Grove, IL) Model 600 control box was controlled by Procomm Plus for Windows on a personal computer. The control box had the ability to control the pumps, heaters, and mixer, and could also read various temperatures and pressures from the thermocouples and pressure transducers.

Pilot Plant Operation (i) Preparation. The control box used a control language called the Powers Process Control Language (PPCL) developed by Landis and Gyr Powers Inc. Various control options such as setting up a PID controller on the heaters, using calibration constants to calculate flow rates, and installing safety shut-offs were programmed. Meta keys were used in Procomm to make quick system changes for each run. The meta keys were macros performed a specific operation(s) when activated. The meta keys were used to

avoid the individual input of various process variables into the system.

Using PPCL, a program was written specifically for pilot plant operation. For each run, the desired flow rates and set-point temperatures were programmed into meta keys in Procomm Plus to allow for quick system changes during the run. The PID controller's gain values were optimized to obtain temperature control within ±2.5°C of the set-point temperatures.

(ii) Start-up. The high-shear mixer was initially heated for 5 min by the band heater. Then the mixer, preheater, and residence tube heaters were heated for an additional 5 min with 100% power for the preheater and 50% power for the residence tube heater. By means of the meta keys, the soybean oil flow and the temperature controllers for the high-shear mixer heater and residence tube heater were activated simultaneously. Once the temperatures before and after the high-shear mixer (T3 and T4) exceeded 70°C, and the temperature after the residence tube (T5) exceeded 65°C, the methanol and sodium hydroxide flows were started. The system temperature and pressure were set to 80°C and 172.37 kPa (25 psi), respectively. The heating process took about 20 to 30 min. The coolant for the heat exchangers was set at 15°C.

(iii) Steady-state operation. The system was operated for a period of time that allowed steady-state conditions to be reached. This was approximately equal to the time that allowed for three system volumes to pass through the system. On a series of consecutive runs, this would allow the system to completely flush out the material from the previous run and come to steady-state conditions. The duration of the pre-steady-state run time was determined by taking samples during this time. Steady-state was assumed when no more change in the composition of the product was observed. At this point run samples were collected.

Each sample was covered and allowed to stand for 24 h before the methyl esters were separated from the glycerol. The methyl esters were then separated, neutralized, and placed in a vial for further analysis.

Based on a total system volume of 2 L and a flow rate of 0.30 L/min, the total residence time for the reaction was 6.67 min. The residence time for the residence tube was 3.11 min at this flow rate. The residence time was maintained constant for all experiments except the experiments for which the change in flow rate was being investigated. In the experiments for which the high-shear mixer was at 0 rpm, this mixer was still kept in the process to maintain a consistent residence time base.

Analysis. A high-pressure liquid chromatography (HPLC) system consisting of an ISCO (Lincoln, NE) model 2350 pump and a refractive index detector (Refracto Monitor IV) made by Thermo Separation Products (Riviera Beach, FL) was used for analyzing the samples. A Spherisorb ODS 2 column, 250 × 4.6 mm with 80 micron pore size and 5 micrometer particle size, was used for the separation. Column temperature was maintained at a constant value of 35°C by a Brinkman RC 6 constant temperature bath. The mobile phase

for the system was a 50:50 volumetric ratio of acetone and acetonitrile. The mobile phase was degassed for about 20 min before use in the system. The flow rate of the mobile phase was set to 0.7 mL/min. About 6 mL of degassed HPLC mobile phase was used to dissolve about 1–2 drops of the methyl ester sample. Once the above conditions were set, the system was allowed to stabilize. Data collection and analysis were performed with Hewlett-Packard (Wilmington, DE) Chemstation Software. The components measured by the HPLC included methyl esters, monoglycerides, diglycerides, and triglycerides. The percent conversion was taken as the conversion of triglycerides to methyl esters. The relative HPLC areas and component masses were calibrated using standard samples of known compositions.

RESULTS AND DISCUSSION

Effect of mixing. The effect of mixing intensity at various catalyst concentrations was examined first. These experiments were conducted with motionless mixers in the process while the high-shear mixing speed was varied. Several experiments at catalyst concentrations of 0.1–0.4 wt% were conducted with varying mixing and molar ratios. These results are presented in Figures 2 and 3. As these figures indicate, higher mixing intensities and larger catalyst concentrations both have favorable effects on the overall conversion. There is an upper limit to both the catalyst concentration and mixing intensity where almost complete conversion of triglycerides to methyl esters is achieved. This limit is reached much faster for larger alcohol excess levels. An upper limit of 0.3 and 0.4 wt% for the catalyst concentration was identified for the alcohol to triglyceride molar ratios of 8:1 and 6:1 (methanol to soybean oil), respectively.

The next set of experiments examined the combined effect of both mixers as well as the effect of each mixer individually. At 0.4 and 0.3 wt% catalyst concentration for 6:1 and 8:1 molar ratios of the reactants, experiments were performed with and without the presence of motionless mixers in the process. The speed of the high-shear mixer was varied from 0 to 3600 rpm in both experiments. With motionless mixers in the process and 0 rpm on the high-shear mixer, motionless mixers alone were studied. While with the exclusion of motionless mixers and 0 rpm on the high shear mixer, the effect of mixing caused by fluid flow alone was examined. The results are summarized in Figures 4 and 5. The results show that both the motionless mixer and the high-shear mixer were capable of providing adequate mixing for the conversion of soybean oil to methyl esters. Conversions in excess of 97% were obtained when at least one mixer was in the process. The motionless mixer appeared to be more effective than the high-shear mixer. The results also reveal that mixing caused by the fluid flow alone results in significant conversion in the transesterification process.

Effect of catalyst concentration. Pilot plant runs were conducted to study the effect of catalyst concentration. The speed of the high-shear mixer and the flow rate were held constant
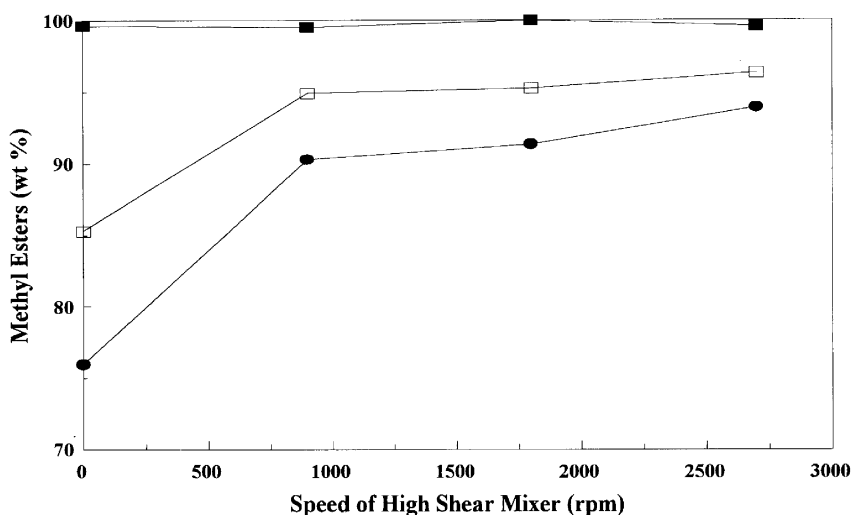
FIG. 2. The effect of variations in mixing intensity and catalyst concentration on the overall conversion subject to the reactant molar ratio of 6:1. (●) 0.1% catalyst; (□) 0.25% catalyst; (■) 0.4% catalyst.

at 900 rpm and 0.3 L/min, respectively. Figure 6 summarizes the experimental results of the effect of variations in the catalyst concentrations from 0.1–1.0 wt% (based on soybean oil) on the reaction conversion for molar ratios of 6:1 and 8:1. This figure shows that as the catalyst concentration increases, the triglyceride conversion also increases. However, at higher catalyst concentrations, this effect becomes minimal. The upper limit to the catalyst effectiveness is reached at a much lower catalyst concentration for larger alcohol excess levels.

Although higher conversions are achieved at larger catalyst concentrations under otherwise identical flow and stoichiometric conditions, there are drawbacks to the excessive use of alkaline catalyst in the transesterification reaction. Higher catalyst concentrations increase the solubility of methyl esters in the glycerol phase of the final product. As a result, a significant amount of methyl esters remains in the glycerol phase after the phase separation. Batch experiments were performed to further investigate this phenomenon. The ratio of the weight of the top phase (methyl esters) to the bottom phase was monitored as the catalyst concentration was varied. These experiments were conducted using catalyst in both aqueous (50 wt%) and solid form. The results are sum-
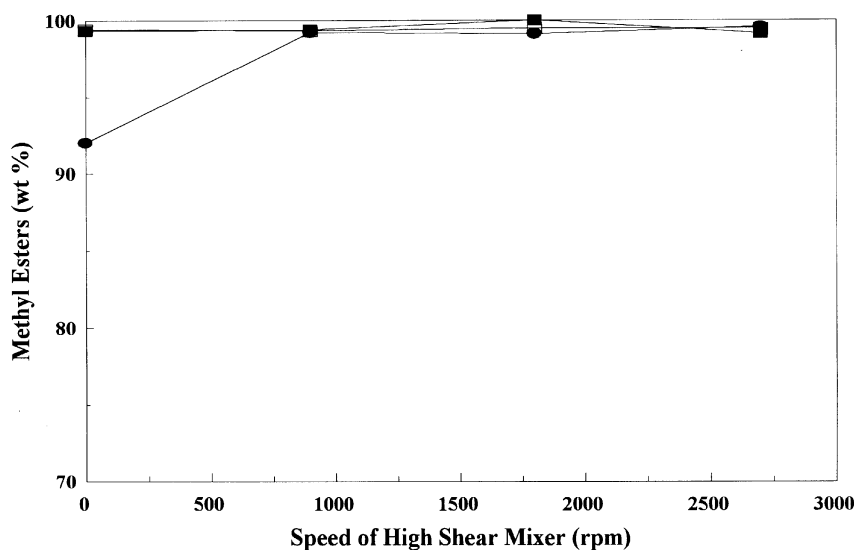

FIG. 3. The effect of variations in mixing intensity and catalyst concentration on the overall conversion subject to the reactant molar ratio of 8:1. (●) 0.1% catalyst; (□) 0.2% catalyst; (■) 0.3% catalyst.
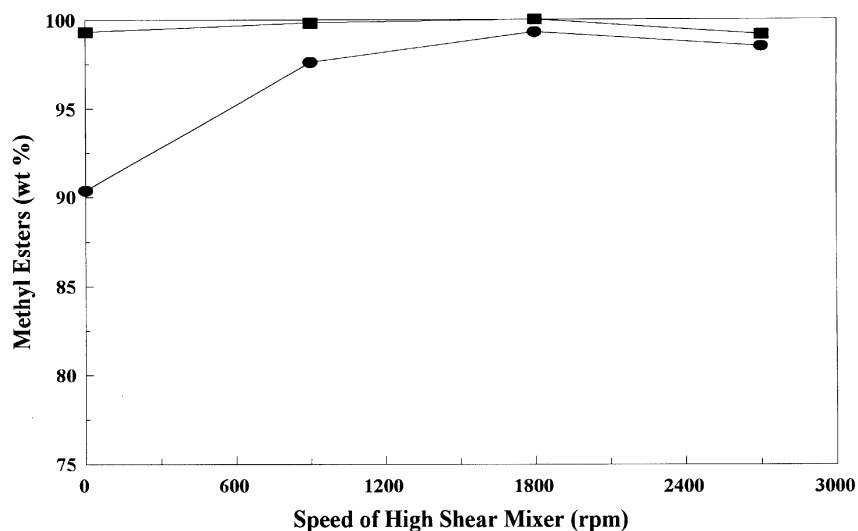
FIG. 4. The effect of variations in mixing intensity on the overall conversion subject to the reactant molar ratio of 6:1 and 0.40% catalyst. (■) with motionless mixer; (●) without motionless mixer.

marized in Figure 7, which shows that as the catalyst concentration was varied from 0.1 to 1.0 wt%, the top layer decreased from about 85 wt% to about 75 wt% of the total product. No significant reduction in the amount of methyl esters was observed in the 0.1–0.4 wt% range for solid catalyst. Moreover, use of aqueous catalyst resulted in a significantly lower methyl ester layer. The formation of soap may be responsible for this behavior.

In the transesterification process, separation of products by gravity settling is desirable. Therefore, the solid form of

the alkaline catalyst at less than 0.4 wt% was considered for the continuous pilot investigations.

Effect of molar ratio. Although the stoichiometric molar ratio of methanol to triglyceride for transesterification is 3:1, higher molar ratios are used to enhance the solubility and to increase the contact between the triglyceride and alcohol molecules. Experiments were conducted with molar ratios of 8:1 and 6:1 for mixing speed at 0 to 3600 rpm and catalyst concentration of 0.10%. Figure 8 indicates the results of these experiments. This figure shows that at all mixing levels the
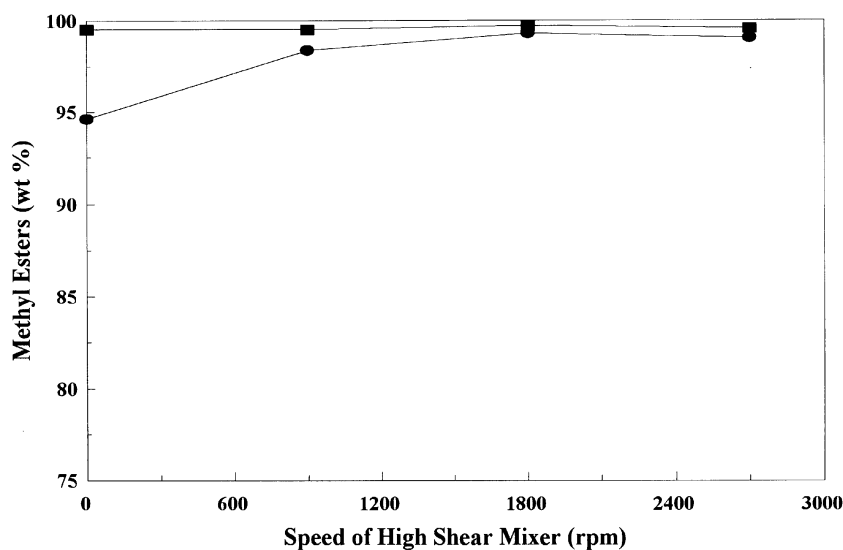

FIG. 5. The effect of variations in mixing intensity on the overall conversion subject to the reactant molar ratio of 8:1 and 0.30% catalyst. (■) with motionless mixer; (●) without motionless mixer.
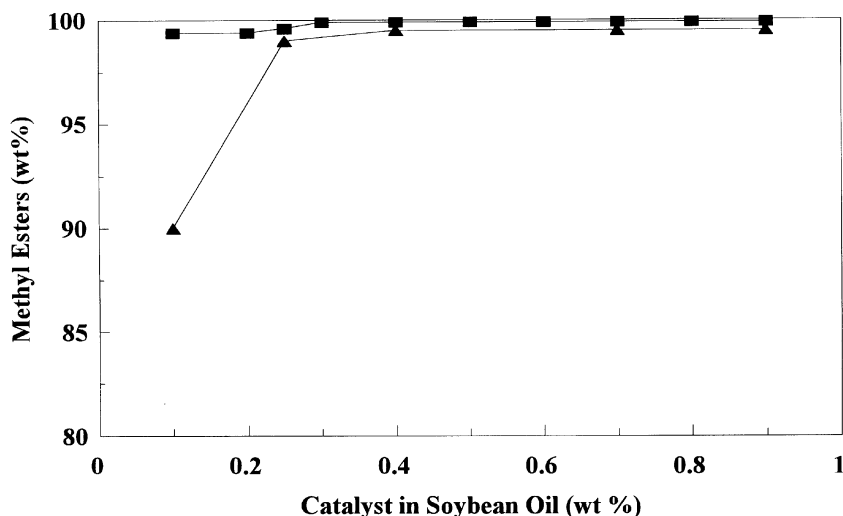
FIG. 6. The effect of variations in the catalyst concentration on the overall conversion subject to the reactant molar ratios of 6:1 and 8:1 and the high-shear mixer speed of 900 rpm. (■) 6:1 reactant molar ratio; (▲) 8:1 reactant molar ratio.
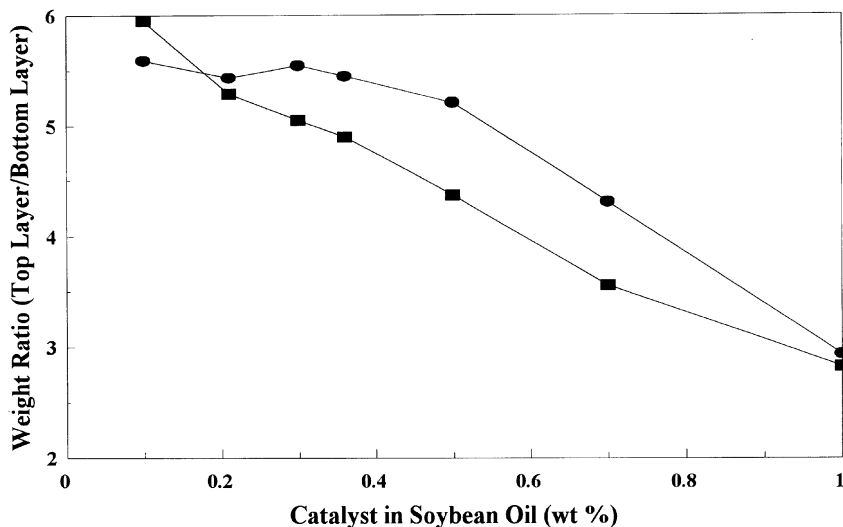

FIG. 7. The effect of variations in the catalyst concentration and form on the product distribution. (■) aqueous catalyst; (●) solid catalyst.

molar ratio of 8:1 results in significantly higher conversions than 6:1. In both cases, a decrease in conversion was observed as the high-shear mixer was operated beyond 50% of the maximum. The reasons for this are unclear, but excessive mixing appears to have created additional mass transfer resistances by admixing glycerol into the reactants, which under less intense mixing may tend to partially separate from the reactants and methyl esters.

Effect of flow rate. The pilot plant was operated at flow rates ranging from 0.250–0.350 L/min to study its effect on triglyceride conversion. This corresponded to a total reaction time of 6 to 8 min. Figure 9 shows that, in the range studied, conversion was not significantly affected by the flow rate.
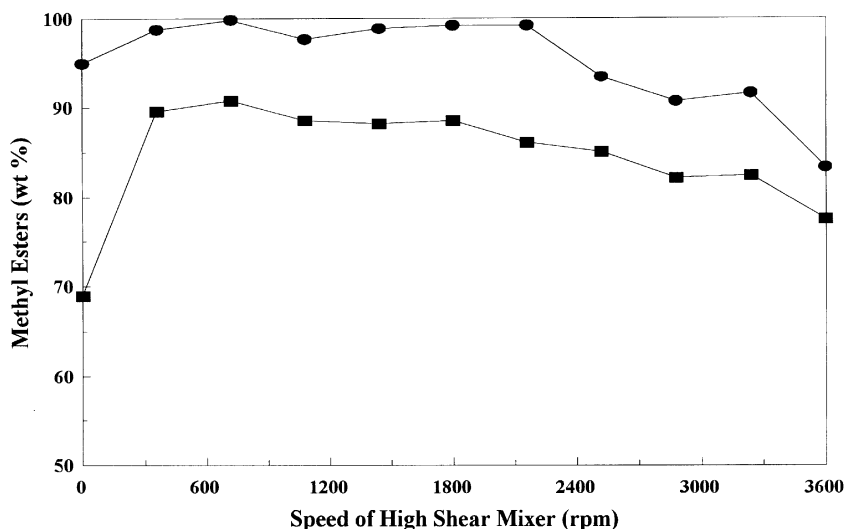
ACKNOWLEDGMENTS

FIG. 8. The effect of variations in reactant molar ratios on the overall conversion at various mixing intensities subject to 0.10% catalyst. (■) 6:1 reactant molar ratio; (●) 8:1 reactant molar ratio.
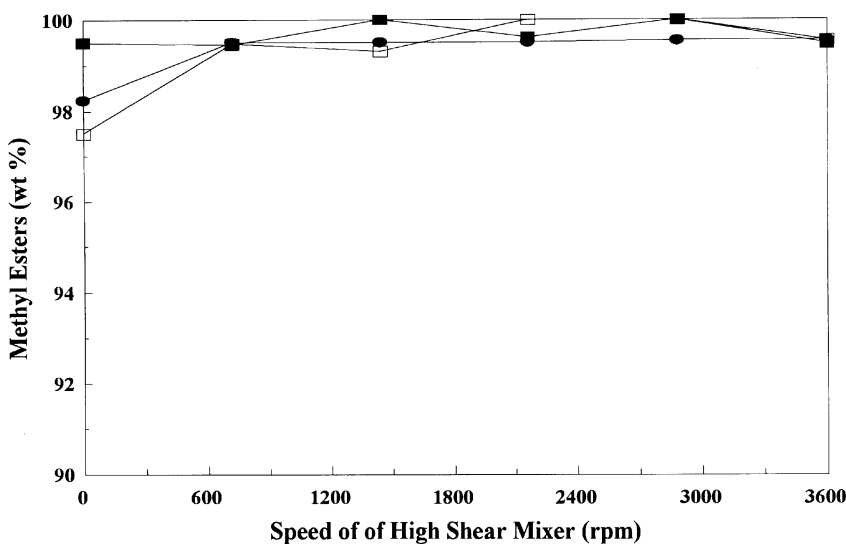

FIG. 9. The effect of variations in flow rates on the overall conversion at various mixing intensities. (□) 0.25 L/min; (■) 0.30 L/min; (●) 0.35 L/min.

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