A NOVEL CONTINUOUS-FLOW REACTOR USING A REACTIVE DISTILLATION TECHNIQUE FOR BIODIESEL PRODUCTION

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EXECUTIVE SUMMARY

Biodiesel from seed oils has attracted increasing interests and shown to be the best substitute for fossil-based fuels due to its environmental advantages and renewable resource availability from vegetable oils. Several studies have showed that biodiesel is a better fuel than fossil-based diesel in terms of engine performance, emissions reduction, lubricity and environmental benefits.

Increasing popularity of biodiesel has generated great demand for its commercial production methods, which in turn calls for a technically and economically sound reactor technology. Most of the existing biodiesel processes requires at least 100 percent excess alcohol for complete transesterification of seed oils into alkyl esters (biodiesel) and glycerol (by-product), which has to be recovered and purified through rectification and distillation for reuse. This project explores the applicability of homogenous reactive distillation (RD) technique for transesterification of seed oils for biodiesel preparation.

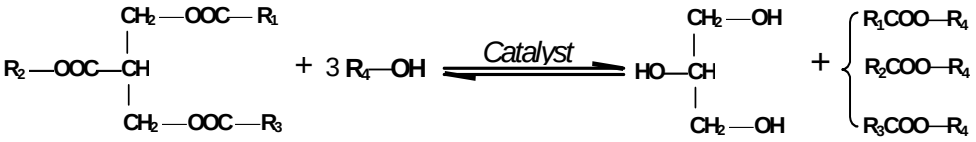
Reactive distillation is a chemical unit operation in which chemical reaction and product separation occur simultaneously in one unit. In this research, a RD reactor reacts vegetable oil and alcohol in a ratio close to stoichiometric while excess alcohol is created by internal alcohol recycling. The RD reactor consists of perforated plates. Each plate holds certain amount of reacting liquid on it, forming a sequential mini-reactor series. Unreacted alcohol is vaporized from the reboiler, flows upward constantly, and bubbles through the liquid on each plate, which provides a uniform mixing. The thru-vapor is condensed at the top of the RD column and refluxes partially back to the column and the rest combines with the feeding stream. It is this portion of the recycled alcohol that creates a locally excess alcohol to oil ratio, which drives the reactions in the series of mini-reactors to a completion. Therefore, the excess alcohol needed at the input stream is considerably reduced. Combined with elevated operating temperature, the RD technique shortens the reaction significantly from that of a conventional process, and greatly increases the productivity.

To summarize, the RD reactor system has the following major advantages over the traditional processes:

1. RD reactor system requires much less feeding alcohol. Compared to other systems, the alcohol feed input can be reduced by 66 percent.
2. Elevated temperatures enhance high reaction rates, thus require short reaction time and provide high productivity. Experimental results showed that the overall reaction time was reduced to 10 to15 min and productivity was increased 6 to9 times.
3. The RD reactor system greatly reduces the load of downstream alcohol recovery processes, which significantly reduces initial capital and also operating costs.The use of reactor/mixer prior to the reactive column is found to be very effective to increase the overall productivity. High reaction rates at initial stage in the pre-reactor significantly reduce the reaction duty on the reactive column.

DESCRIPTION OF PROBLEM

Transesterification of vegetable oils or animal fats with simple alcohols has long been the preferred method for producing biodiesel. The overall transesterification reaction is given by:



Seed oil Alcohol Glycerol Esters
(Triglycerides)

The transesterification is reversible reaction in which excess alcohol is required to drive the reaction close to completion. Almost 100 percent excess alcohol is needed to achieve an ester yield of 95-98 percent. The excess alcohol then has to be recovered and reused to reduce cost per unit of production. The recovery is generally done through rectification or distillation, an energy-consuming processes that increases the operating cost of production.

Most existing biodiesel production technologies are batch-type in nature, which are labor-intensive, time-consuming and less cost-effective than a continuous process. A continuous transesterification process is preferred over batch processes to lower the cost for quantity production. In order to achieve this, a shorter reaction time and/or greater production capacity are desirable. In this research, a novel transesterification process using reactive distillation technique is proposed to produce biodiesel from seed oils using less alcohol and thus less energy.

The ultimate goal of this research is to explore a technically and economically sound reactor technology for biodiesel production, which applies the reactive distillation technique. The hypothesis is to reduce the amount of alcohol in the input stream close to its stoichiometric ratio with oil (3:1 molar). The objectives of the first stage of this project were to

1. Construct and test a lab-scale continuous-flow reactive distillation process system.

2. Determine and evaluate the process parameters affecting ester yields, including the operating temperatures, feeding positions, loading rate or reactor capacity, and operating pressures.
3. Determine and evaluate the effect of recycled alcohol, which indicates the oil to alcohol ratio on a fixed feeding rate, on the fatty ester yields by targeting a close to theoretical feeding ratio of 1:3 (molar).

The functioning of reactive distillation is basically based on two chemical aspects—reaction kinetics and vapor-liquid phase thermodynamics. As there is a large difference in the boiling points of alcohol (either methanol or ethanol) and the seed oils or their fatty acid esters involved in the transesterification reaction. During the RD operation, the vapor phase is mainly consisting of methanol while the reaction takes place in liquid phase. In our case, vapor-liquid thermodynamics has less effect on the process; main focus was given to reaction kinetics.

APPROACH AND METHODOLOGY

MATERIALS USED

Canola oil and methanol were used as the reactant materials, and potassium hydroxide was the catalyst in this research. The crude canola oil was obtained from the oil seed processing plant at the Department of Biological and Agricultural Engineering of the University of Idaho, and its fatty acid profile is listed in Table 1. Analytical grade methanol and potassium hydroxide were obtained from J. T. Baker (Phillipsburg, NJ). GPO-trinder Reagent and reference standards such as triolien, diolien, methyl olieate and glycerol were purchased from Sigma-Aldrich Co. (St. Louis, MO).

Table 1. Fatty Acid Profile of Canola Oil Used in This Research

Fatty Acid	Composition (percent wt.)
Palmitic (16:0)	3.9
Stearic (18:0)	2.1
Oleic (18:1)	59.3
Linoleic (18:2)	18.4
Linolenic (18:3)	7.8
Eicosic (20:1)	2.1
Erucic (22:1)	4.4

RD REACTOR SYSTEM SET-UP

During the first stage of this research, a laboratory-scale continuous-flow RD system (Fig. 1) was constructed and tested on various process parameters. The key component in the system is the vacuum jacketed, perforated plate Oldershaw column (Chemglass, Vineland, NJ). This ten-plate column has an inner diameter of 23 mm, a weir height of 4 mm and a distance of 25 mm between plates.

Figure 1. Experimental setup of the laboratory-scale continuous-flow RD reactor system.

A 150-mm in-line static mixer (Cole-Parmer, IL) was used as a feed mixer and heat exchanger. It serves as a pre-reactor prior to the RD column as well. The lower end of the column was fitted to a 500 ml three-neck flat-bottom flask, which was used as a reboiler. A water-cooled condenser was fitted to the top of the column to recover alcohol, which is combined with reactants and pumped back into the column. The product mixture was withdrawn from the reboiler and send to a separation decanter. Biodiesel/glycerol separation was carried out by gravity in the continuous separation decanter ($\phi 70 \times 300$ mm) with an adjustable feed-in point. The input and output streams of methanol/KOH solution, oil, and product mixture were handled simultaneously with three Masterflex peristaltic pumps (Cole-Parmer, IL) that were calibrated and adjusted to achieve the desired flow rates ranging from 0.5ml/min to 8.0ml/min. Temperature monitoring and feedback controls were accomplished with Fuji PXR3 and PXR4 PID/feedback controllers (distributed by TTI Inc., VT).

EXPERIMENTAL PROCEDURES

Experiments were conducted on important process parameters: oil-to-alcohol ratio, flow rates, reaction time and temperature. In preparation for each trial, stock alcoholic KOH was prepared on a stirring plate at a ratio that corresponds to one percent wt. KOH of oil for each

given methanol-to-oil molar ratio and placed in a holding reservoir. Canola oil was held in a separate reservoir. The reactants were fed through separate pre-calibrated peristaltic pumps into the in-line mixer/pre-reactor or directly into the column. The methanol-to-oil molar ratios used were 3.0, 3.5, 4.0 and 4.5 (molar). These various ratios were achieved by adjusting the alcohol/catalyst flow rate relative to the flow rate of the oil.

From several trials, it is found that column can be operated without any significant operational difficulties at an overall flow rate of 5-6 ml/min and column temperature of 65°C. Excess methanol vapor was condensed and recycled back to the column while the product mixture was continuously drawn from the bottom flask, the reboiler. The product mixture was separated into biodiesel and glycerol layers in the continuous gravity decanter with feed-point at the middle of the column. Temperatures were monitored and controlled at various strategic locations, as shown in Fig. 2.

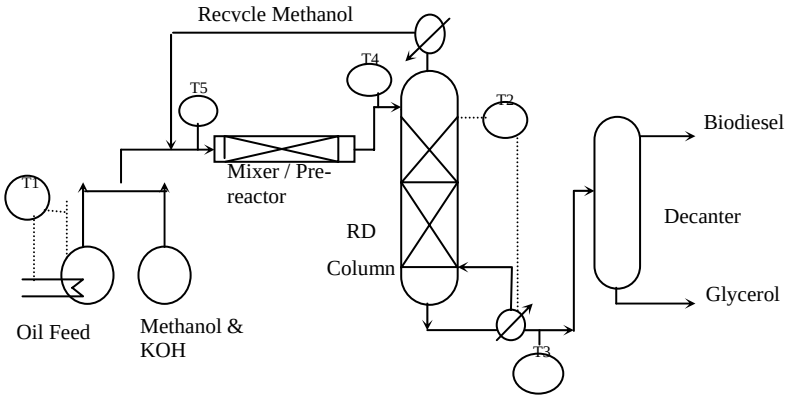


Figure 2. Schematic diagram of the RD reactor system.

KINETICS EXPERIMENTS

Batch transesterification reactions were performed in a vigorously mixed 500-ml three-necked flask equipped a reflux condenser, a thermocouple, and a sampling port. A given quantity of oil was first heated to the reaction temperature of 60°C, which is close to column operating temperature, and then premixed methanol/KOH was injected. After the completion of the injection, the time was to be recorded as the beginning of reaction time. Samples were

taken in pre-determined intervals by means of a syringe from the reacting mixture until the reaction of the mixture was stopped, and then the samples were analyzed by HPLC.

ANALYTICAL METHODS

Chemical Analysis

Compositions of the reaction mixtures were analyzed by HP 1090 HPLC with ELSD (Altech2000). The column used is C18, 7µm SGX. The column temperature was maintained at 40°C while the temperature of ELSD was kept at 60°C. The flow rate of the carrying Nitrogen gas was at 1.5 L/min.

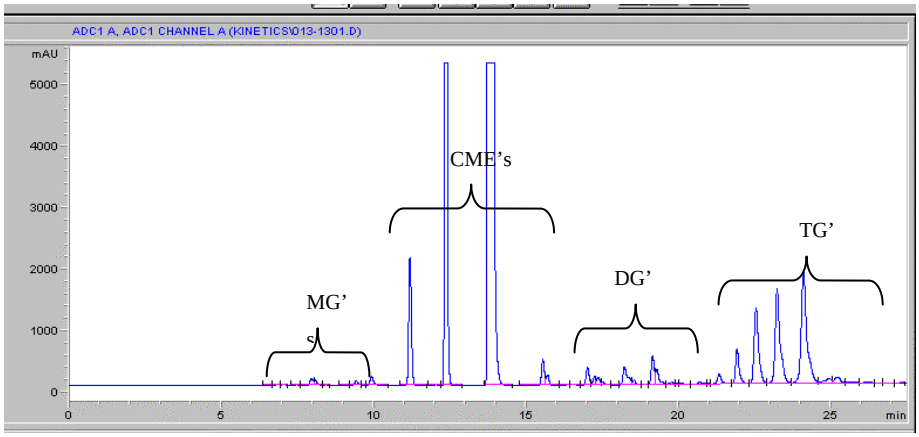


Figure 3: Determination of triglycerides (TG), diglycerides (DG), monoglycerides (MG) and canola methyl esters (CME).

The method uses gradient elution with aqueous-organic and non-aqueous mobile phase steps: 70 percent acetonitrile plus 30 percent water in 0 min, 100 percent acetonitrile in 10 min, 50 percent acetonitrile plus 50 percent 2-propanol- hexane (5:4 v/v) in 20 min and 7.5 min final hold up. Figure 3 shows typical chromatogram obtained for canola methyl ester (CME) phase containing small amounts of triglycerides (TG), diglycerides (DG) and monoglycerides (MG).

The reaction mixture obtained from the transesterification of canola oil with a basic catalyst KOH in methanol was immediately diluted with small amount of 0.1N HCL in order to stop

further reaction. Then methanol in the sample was removed by heating it under vacuum. The mixture was then converted into two-phases: The upper phase contains MEs and unconverted TG, DG and MG, while lower layer contains glycerol, catalyst, residual methanol and acidic water. The upper layer was carefully separated and analyzed for its chemical composition.

Determination of TG

The mass of all triglycerides present in the sample was calculating the areas of peaks obtained between 22 min to 27.5 min in Fig. 4 into the calibration curve – peaks area vs. (TG) mg in the sample. This calibration curve was constructed by measuring a series of 5 standard solutions of the canola oil used in the mobile phase C. The concentration of TG in the ester phase (wt. percent) was then calculated from the mass of the sample and the determined TG value.

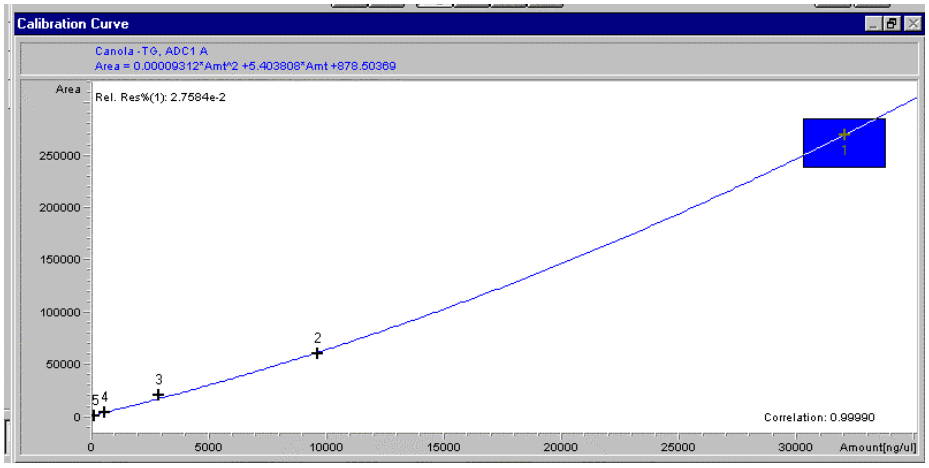


Figure 4. HPLC calibration curve, peak area vs. amount of TG, obtained for triglycerides of canola oil.

Determination of DG

The reaction mixture includes 12 isomers of DG with various combinations of pairs of the Oleic (O), linoleic (L) and linolenic (Ln) acid and couples of positions 1,2 and 1,3 in the molecule of glycerol (see peaks between 16 min and 22 min). The calibration curve (Fig. 5) was constructed by means of seven standard solutions of Diolien (Nu-check Prep, NN), and thus peak area of DO vs mass of the DO in the sample. The mass of all DG in ester phase

was calculated under the assumption that the mass ratio O:L:Ln = 60:19:8, valid for canola oil (see Table 1) is not changed in total DG during the reaction course.

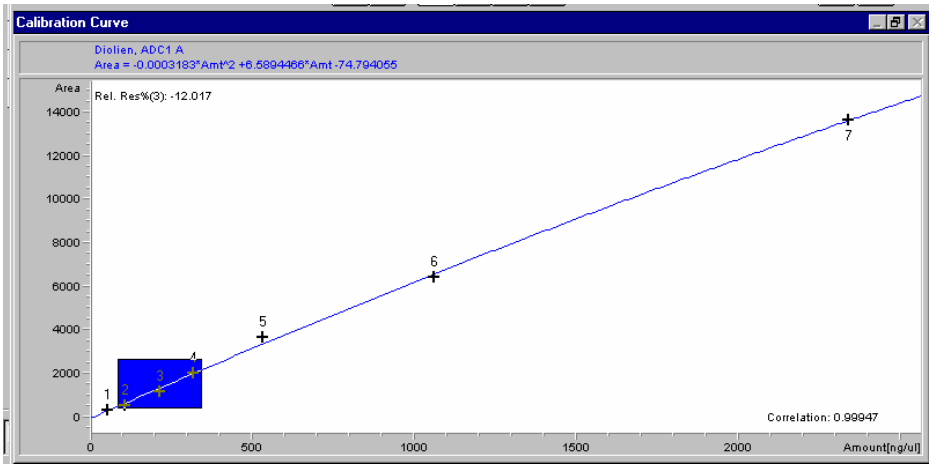


Figure 5. HPLC calibration curve, peak area vs. amount of DO, obtained for Diolien..

The relative mass representation of the combinations of pairs of the same acids can be expressed with the sum (60 + 19 + 8) = 87 and combinations of pairs of various acids with combinatory number C (87,2) = 3741. Thus, the total quantity of all DG, identified in the Fig. 5 is represented by the number 3741 + 87 = 3828. In a similar manner, the numeral expressions of the relative mass representation of single combinations of pairs O, L and Ln can be calculated:

Combination O/O:	C (60,2) + 60 = 1830
Combination O/L:	C (79,2) – 1770 – 171 = 1140
Combination O/Ln:	C (68,2) – 1770 – 28 = 480
Combination Ln/Ln:	C (8, 2) + 8 = 36
Combination L/L :	C (19,2) + 19 = 190
Combination L/Ln :	C(27,2) + 27-36-190 = 152

Thus, the single DG isomers are represented by the mass ratios

O/O: O/L: O/Ln: Ln/Ln: L/L: L/Ln = 1830:1140:480:36:190:152

The total mass of DG was calculated from the formula: DG = DO × (3828/1830). From the known mass of the ester phase and the calculated DG, the value of the concentration of DG in ester phase was expressed.

Determination of MG

The reaction mixture includes 6 MG isomers of the O, L and Ln acid in the positions 1 and 2 in the glycerol molecule. The calibration curve (Fig. 6) was constructed by means of 8 standard solutions of monolien (MO), thus peak area of MO vs. mass of the MO in the sample. The mass of all monoglycerides, assuming that in the reaction course the ratio of masses O:L:Ln = 60:19:8 would not change, was calculated as follows:

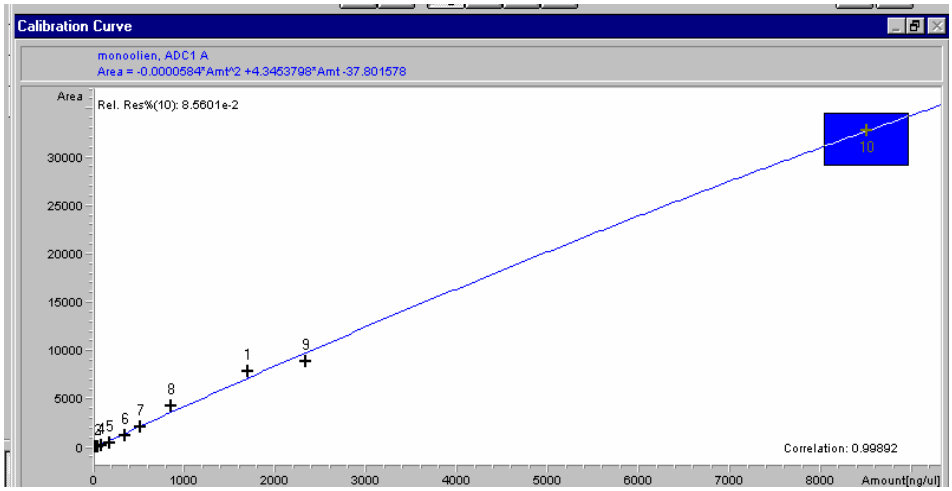


Figure 6. HPLC calibration curve, peak area (MO) vs. amount of MO, obtained for monoloien.

The relative mass representation of all MG can be expressed by the sum (60+19+8) = 87. The total mass MG = MO × 97/60

Determination of CME

The mass of all isomers of fatty acid methyl esters in the sample (E) was calculated from the sum of the peaks obtained between 10.5 min and 16.0 min, using the calibration curve peak area of E vs. amount of E in the sample. The calibration curve (Fig. 7) was obtained by means of the same measurement for the series of seven standard solutions with various concentration of so-called E-standard in the mobile phase C. From the total known mass of the EP sample and the (E) value calculated from the calibration curve, the concentration of E in EP (percent wt.) was expressed.

The preparation of E-standard was performed as follows. KOH/Methanol solution (1.5 percent wt. KOH):Oil molar ratio was set to 10:1. The reaction mixture was mixed for about six hours and then separated after settling time for another 24 hours. The EP was taken out, then washed, heated and filtered in order to obtain high quality methyl esters. Such a filtrate was taken as the E- standard relevant to the biodiesel produced from the canola oil.

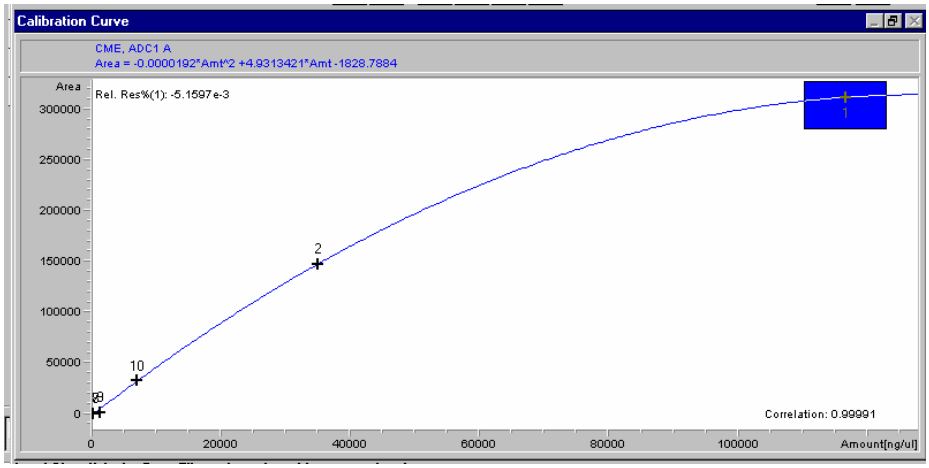


Figure 7. HPLC calibration curve, peak area (E) vs. amount of E, obtained for canola methyl esters.

Other Testing Methods:

The Greenhill method issued by National Biodiesel Accreditation Commission, BQP–02(03), was used to measure total glycerol content in biodiesel samples. It is a spectroscopic determination and was set up as an alternative to ASTM D 6584, which is specified under the standard specification for biodiesel fuel (ASTM D 6751).

The specific gravity was measured using a 20-ml Bingham Pycnometer (Fischer Scientific, PA) at 20ºC under the guidelines of ASTM Method D1217. Viscosity measurements were performed using a #100 Cannon-Fenske viscometer (Fischer Scientific, PA) at 40ºC maintained in a Koehler Model K-23300 oil bath (Koehler, Bohemia, NY). The methanol content in biodiesel samples was determined by the mass difference of a sample before and after being heated at 70ºC under vacuum for 30 min.

FINDINGS, SUMMARIES, AND RECOMMENDATIONS

KINETIC STUDY

Three experimental runs were conducted with different feed molar ratios in order to understand the trend of reaction rates and equilibrium conversion at various levels in the reactive column. The results are summarized in Fig. 8.

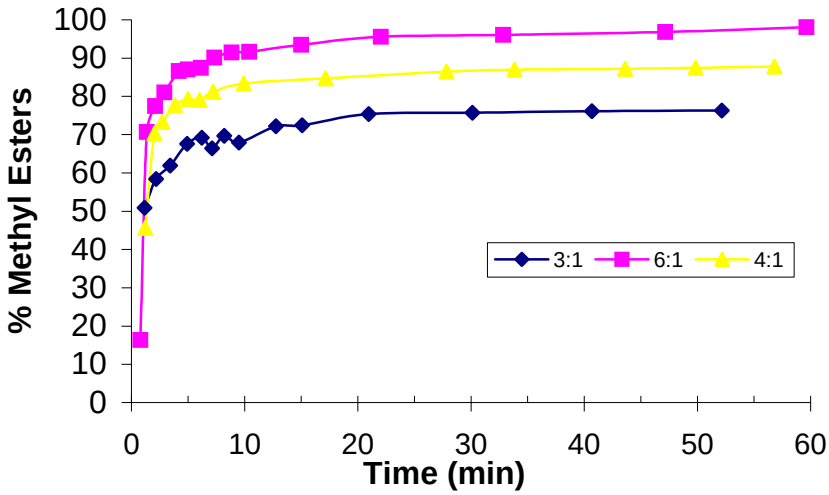


Figure 8. Effect of methanol/ oil ratio, temperature = 60°C, KOH = 1.0 wt.. percent.

It can be seen that at initial stages of reaction, production of ME is rapid. After the very first minute, the ME concentrations in the mixture reached 45.1 percent wt., 51.1 percent wt., and 71.2 percent wt., respectively for the three molar ratios. In five minutes, reaction showered down considerably. The ME concentrations were 67.8 percent wt., 79.4 percent wt., and 87.2 percent wt., respectively. The reaction rate then diminished and finally reached equilibriums of 76.4 percent wt., 87.8 percent wt., and 91.1 percent wt., respectively, in about 60 min. Also the equilibrium methyl esters (EM) yield increases with the increase of the feed ratio of methanol and triglycerides. Inside the reactive column, there is a wide variation of methanol concentration usually higher than feeding ratio. And, for optimum design, pre-reactor should achieve this part of reaction and further reaction duty is accomplished. The in-situ trend of

methanol concentration throughout the column will be studied during Stage 2 on a bench scale pilot plant.

EXPERIMENTAL RESULTS OF RD REACTOR SYSTEM

The process integration was studied and important process parameters were evaluated through experiments and logical hypothesis test, which are discussed respectively below.

Use of Pre-Reactor

From the kinetic experiments, it is evident that the initial reaction rate is high. For such cases, use of pre-reactor prior to the reactive column is wise option to handle a substantial portion of the reaction separately from RD reactor till reaction rates drops drastically. Experimental results confirmed the benefit of using a pre-reactor. Fig. 9 shows the comparison of methyl esters yields with and without use of a pre-reactor. It is of importance economically to provide the same residence time in a pre-reactor than on the trays of the RD column in practice.

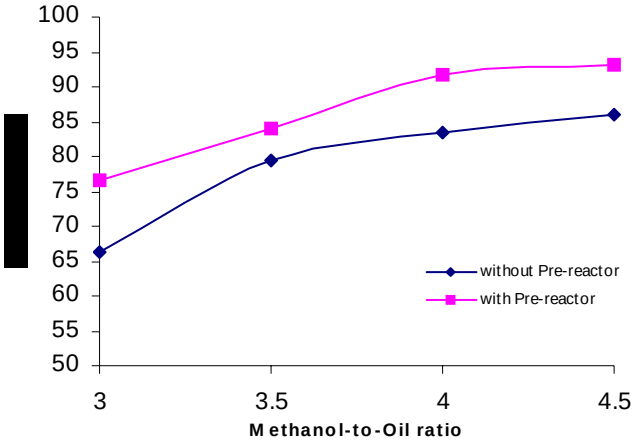


Figure 9. Comparison of methyl esters yields with and without use of a pre-reactor.

Column Feed Location

The feed point location depends upon feed composition and on the reactive zone location. As there is very large difference in the volatility (boiling points) of methanol and all other

reaction components, there is no need to provide any stripping trays for distillation performance than a condenser. And the inlet feed has to be in liquid phase, because the reaction will takes place in the liquid phase only. Therefore, feed inlet into the top plate can be optimum for performance as well as plant economics.

Reactive Zone

Although all trays below the feed point act as reactors, there may not be a uniform reaction rate throughout the column because the oil concentrations at lower stages is much lower and become the limiting agent. Some of the lower trays act as both reaction zone and rectification zone .The complete study of variation of reaction rates throughout the column was not conducted on the lab scale column because of the difficulties of sampling on the small quantity of liquid held on each plate. But it will be studied on the bench-scale system in Stage 2 research.

Column Temperature

The temperature inside column is a function of the dew point of vapor phase, which can be maintained by reboiler duty. For methanol it is about 65°C. The goal of this study is to maintain high methanol concentration in the reaction zone, i.e., the liquid phase. Therefore, the constant column temperature works without problem. Higher temperature will increase energy consumption and lower temperature will decrease the liquid holdup on each plate.

Reflux Ratios

The amount of methanol collected in the condenser was in small amounts under current experimental condition. The primary function of reflux is to improve separation efficiency of the stripping section of a distillation column. In our case, it is not an important process parameter because there is essentially the pure methanol on the plates above feeding point. Therefore, instead of refluxing the condensed methanol back into the top of column it was beneficial to recycle it to the pre-reactor, where it causes higher alcohol to oil ratio thus increases the conversion rate.

Reactor Capacity

This term can be related to residence time or the throughput of the given reactor system. From batch kinetic experiments at 60°C, major part of the reaction occurs in initial 20 min. With higher methanol concentration in the column, this value can be further reduced to about 10-15 minutes. From the experiments conducted, residence time achieved was about 5 min each in the pre-reactor and RD column with a total residence time about 10 min. Varying residence time or reaction time on the lab-scale column was difficult because of operational ability. Studies will be further performed at bench scale in Stage 2.

Feeding Ratio

As kinetic study shows feed ratios can very affect the rate of reaction and equilibrium reaction conversion. Table 2 shows the quality of product obtained using different feed molar ratio. The methyl esters shown may not indicate the equilibrium concentration; surely these are higher than for batch process with residence time of about 10 min.

Effect of Methanol-to-oil Ratio on Product Parameters

The process sensitive characteristics, such as total methyl esters, total glycerin, methanol, and viscosity, of samples obtained under different experimental runs were summarized in Table 2.

Table 2. Effect of Methanol-to-Oil Ratio on the Product Parameters

Trials	Molar Ratio	Methyl esters (percent wt.)	Total Glycerol (percent wt.)	Methanol (percent wt.)	Viscosity (cst)	Specific gravity
1) With Pre-reactor						
Run 1	3.0:1	76.5	0.26	1.99	6.18	0.85
Run 2	3.5:1	84.0	0.33	1.38	5.01	0.85
Run 3	4.0:1	91.7	0.15	0.90	4.63	0.82
Run 4	4.5:1	93.2	0.30	1.51	4.23	0.87
2) Without Pre-reactor						
Run 5	3.0:1	66.2	0.11	3.74	8.44	0.82
Run 6	3.5:1	79.5	0.19	2.19	6.32	0.83
Run 7	4.0:1	83.3	0.18	1.98	5.96	0.81
Run 8	4.5:1	85.9	0.28	4.84	5.50	0.82

A significant amount (approx. 10 percent) of unreacted methanol flowed out of the column with the products. About 30 percent of this methanol ended up in the biodiesel layer while the remainder was found in the glycerol layer. Figure 10 shows the trend followed by methanol content in the biodiesel layer. Biodiesel obtained without the pre-reactor had higher methanol content. This was most likely due to incomplete reaction due to less residence time. At a 4:1 molar ratio, methanol content in the product was found to be the lowest for both experimental setups under the tested conditions. The methanol content rose if the ratio was increased to 4.5:1 due to a greater excess of methanol and its incomplete vaporization from the reboiler.

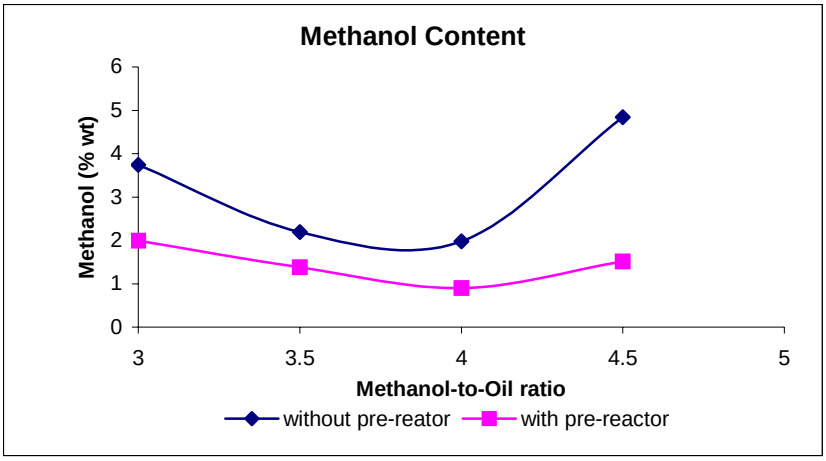


Figure 10. Effect of methanol-to-oil ratio on methanol content in product.

Effect of Methanol-to-Oil Ratio on Product Viscosity

There is a correlation between the viscosity and the amount of unreacted glycerides present in the biodiesel. It can be seen in table 3 that as the molar ratio increased, the percent ester increased while the unreacted glycerides correspondingly decreased. This is reflected in Fig. 11 which illustrates a decrease in viscosity with a higher molar ratio. Additionally, samples obtained with the pre-reactor setup have higher ester percentages and hence lower viscosity as compared to corresponding runs without the pre-reactor.

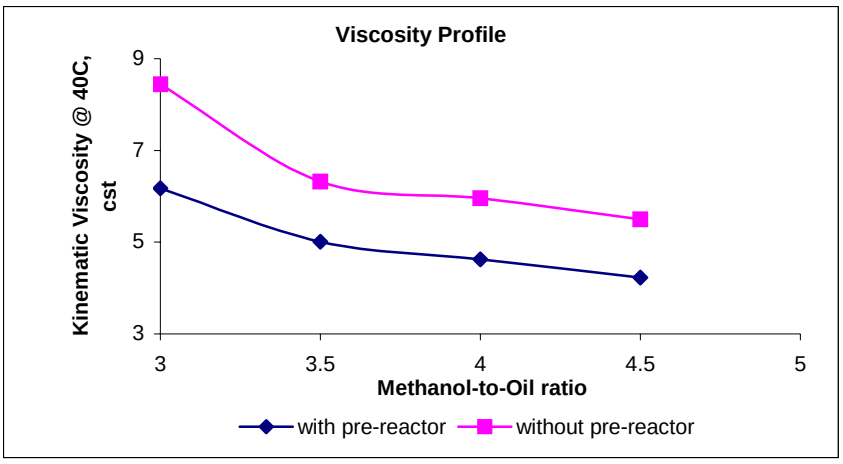


Figure 11. Effect of methanol-to-oil ratio on product viscosity.

SUMMARY

The RD reactor process has been found to be feasible for the continuous production of biodiesel from seed oils. The original objective of making the process more efficient by reducing the alcohol-to-oil molar ratio was realized. A 66 percent reduction to the industrial standard of 6:1 alcohol to oil molar ratio was achieved with good results. It is concluded based on the experimental results that the operating the RD system at 65ºC with a 4:1 molar ratio and a pre-reactor was the optimum point for producing biodiesel from among the parameters examined in this study. There are other parameters such as residence time and methanol distribution in the column will be studied in the next phase on the bench-scale.

RECOMMENDATIONS

Most of the process parameters have been studied with lab-scale RD system. However, some operating parameters, such as temperature profile and concentration profile inside the column which are valuable in understanding the operation of RD system, would be studied on a bench-scale setup. It is recommended that temperature monitoring and sampling ports be located at each plate of the bench-scale column. Meanwhile, the reboiler is very crucial in the whole reactive distillation process. It should be effective enough to vaporize at least 90

percent of residual to provide sufficient methanol vapor flow in the column. Heat transfer and mixing should be considered in designing reboiler system for the bench-scale setup. The objectives in Stage 2 of this project include also the development of RD process on bench-scale and fuel quality test. SpecificallyL

1. Scale-up of the process to a bench-scale reactor system of continuous-flow with automation based on lab-scale results,
2. Optimization of the operating conditions for bench-scale biodiesel production,
3. Production of biodiesel with the bench-scale RD reactor on a continuous basis for 150~300 hours. Fuel quality will be monitored for consistency. Tests will be conducted on representative fuel properties for quality control,
4. Chassis dynamometer testing on a 1999 Dodge pickup to compare horsepower and torque using the RD biodiesel versus petroleum diesel, and
5. Measurement of injector coking with the RD biodiesel vs diesel on a 1.9 L Yanmar engine coupled to a stationary dynamometer. This data will be compared to historical data.

APPENDIX

Arvinder Singh, biological and agricultural engineering graduate student, along with Joseph Thompson and Dr. Brian He presented a paper based on this research at the 2004 ASAE/CSAE International Annual Conference held at Westin Conference Centre, Ottawa, Ontario, Canada, Aug.1–4, 2004: Singh, A., J. Thompson, and B. He. 2004. "A Continuous-Flow Reactive Distillation Column for Biodiesel Preparation from Seed Oils." ASAE Paper No: 04-6071. ASAE, St. Joseph, Mich..