A NOVEL CONTINUOUS-FLOW REACTOR USING

A REACTIVE DISTILLATION TECHNIQUE FOR

BIODIESEL PRODUCTION

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16.   Abstract

Biodiesel is a fuel comprised of mono-alkyl esters of long-chain fatty acids produced from vegetable oils through a transesterification process. In existing continuous-flow biodiesel production processes, 100 percent excess alcohol is typically used in order to drive the reaction to completion. The excess alcohol must be recovered in a separate process, which involves additional operating and energy costs. In the first stage of this study, a novel reactor system using a manufactured (glass) reactive distillation (RD) column was developed and studied. The concept to dramatically reduce the use of excess alcohol and still produce a quality fuel was proven. The next step, and the focus of this part of the study, was to scale-up the system to a production rate of 80 to 100 ml/min and measure its effectiveness. A 20 sieve-tray RD reactor system was designed by the author and fabricated at the University of Idaho machine shop. This model was used to produce biodiesel and product parameters such as methyl ester content and total glycerol were analyzed. Preliminary results showed that process parameters of methanol-to-oil ratio of 4:1 (molar) and a column temperature of 65°C produced a biodiesel that was 90.71 percent converted in five minutes.

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TABLE OF CONTENTS

INTRODUCTION

Biodiesel from seed oils has attracted increasing interests and has been shown to be the best supplement to fossil-based fuels due to its environmental advantages and renewable resource availability. Seed oils of rapeseed, canola, and yellow mustard have certain advantages for biodiesel production over other vegetable oils, among them are better cold-flow properties. There is a great demand for the commercialization of biodiesel production, which in turn calls for a technically and economically sound reactor technology. Reactive distillation (RD) is a chemical unit operation in which chemical reactions and separations occur simultaneously in one unit. It is an effective alternative to the traditional combination of reactor and separation units especially when involving in reversible reactions, such as vegetable oil transesterification, or consecutive chemical reactions. The significant advantages of the RD over the conventional sequential process are the high chemical conversion rate and low capital and operational cost. The performance of a reactive distillation column is influenced by several parameters, e.g. operating temperatures, size of reactive and separation zones, reflux ratio, feed rate and location, etc, which were thoroughly investigated.

The ultimate goal of this research was to explore a technically and economically sound reactor technology for economical biodiesel production. RD technique was applied to the transesterification of seed oils including rapeseed, canola, and yellow mustard. The hypothesis was that by employing the RD technique, biodiesel preparation and product concentration can be accomplished in one single unit. The use of excess alcohol was greatly reduced, but a high alcohol to oil ratio was achieved locally in the reaction zone by recycling a small quantity of alcohol. This ensured a higher conversion of oil to biodiesel. The recovery of alcohol is integrated into the RD reactor, which reduces capital and operating costs. Combining this lower alcohol requirement with elevated operating temperature, the RD technique significantly shortened the reaction time from that of conventional processes and greatly increased the productivity.
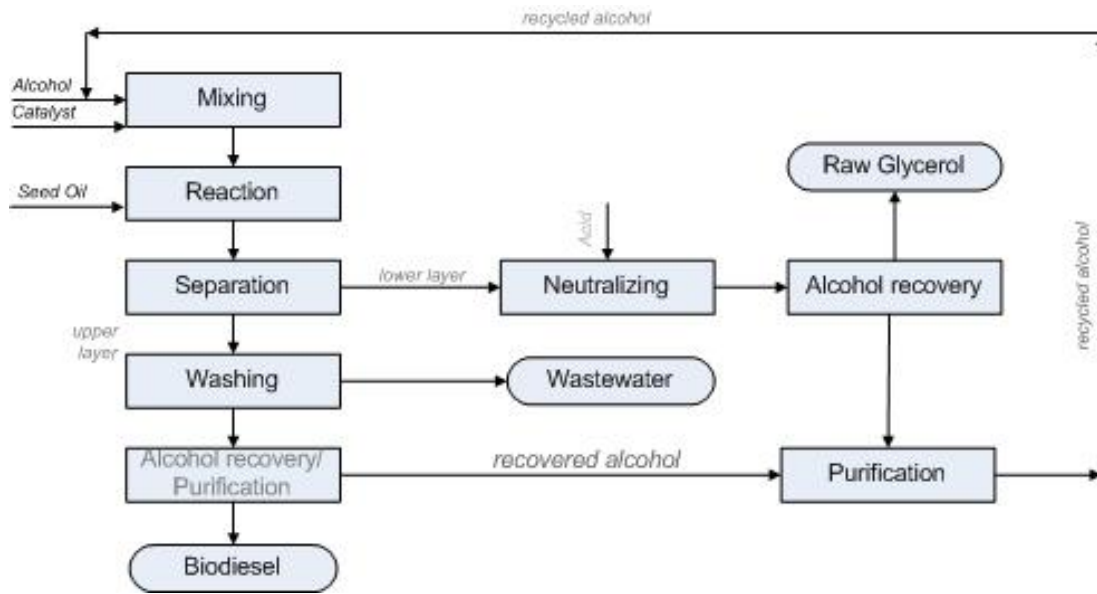
Figure 1. Illustration of biodiesel production from seed oils.

The excess alcohol in conventional systems remains unreacted and is contained in the crude biodiesel and the glycerol by-product streams. It has to be recovered and purified for reuse through rectification and distillation, which are energy-consuming processes. In the RD process, chemical reaction and product separation occur simultaneously in one unit (Fig. 2 and 3). The RD reactor consists of perforated plates. Each plate holds certain amount of reacting liquid, 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 uniform mixing. The thru-vapor is condensed at the top of the RD column and refluxes partially back to the top of the column and the rest combines with the feeding stream. It is this portion of the recycled alcohol that creates a local excess alcohol to ensure the reactions in the mini-reactors to a completion. Therefore, the excess alcohol needed at the input stream is considerably reduced. Combining with elevated operating temperature, the RD technique significantly shortens the reaction from that of conventional process and greatly increases the productivity.
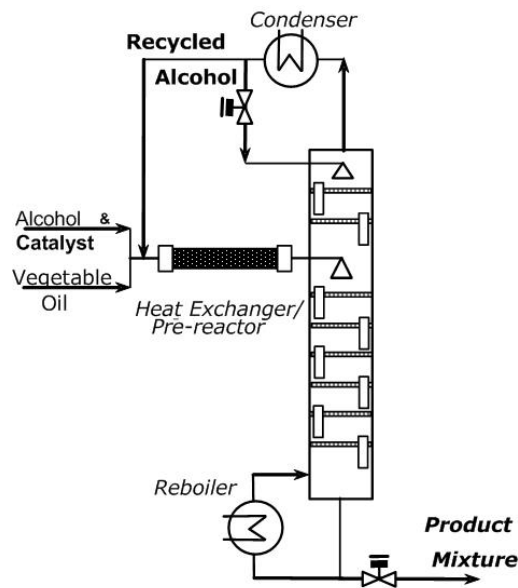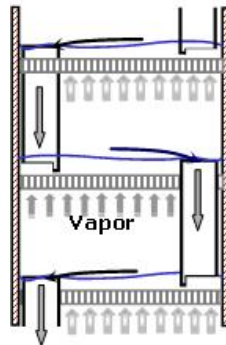
Figure 2. Diagram of the RD process.

Figure 3. Close-up of the perforated plates

In summary, the RD reactor system bears three major advantages over the traditional process:

1. RD reactor system has short reacting time and high unit productivity, which is highly desirable in commercial production units.

2. RD reactor system requires much less excess alcohol, which greatly reduces the effort of downstream alcohol recovery and reduces the operating cost considerably.

3. RD reactor system is compact and the downstream alcohol recovery system is down-sized by three times which significantly reduces the initial capital cost.

MATERIALS AND METHODOLOGY

Chemicals and Reagents

Crude canola oil and methanol were used in this research as the feedstock. Potassium hydroxide and potassium methoxide were used as catalysts. The canola oil was obtained from the oil seed processing plant at the Department of Biological and Agricultural Engineering of the University of Idaho (Peterson, et al., 1983). The oil was screw-pressed and filtered to remove any particulates. No further treatments were performed on the oil. The acid value of the oil was 1.97 mg KOH/g sample. The fatty acid profile of the canola oil was analyzed using the GC method (Hammond, 1991) (see Table 1). Methanol (analytical grade) and potassium hydroxide (A.C.S certified, purity greater than 87.9 percent weight) were from J. T. Baker (Phillipsburg, NJ). Potassium methoxide (32 percent w/w solution in methanol) was obtained from Degussa Corporation, Germany. Other analytical reagents and standard chemicals of GPO-trinder Reagent, triolien, diolien, methyl oleate, and glycerol were all analytical grade and purchased from Sigma-Aldrich Co. (St. Louis, MO).

Table 1. Fatty Acid Profile of Canola Oil

Fatty Acids	Test 1	Test 2	Average wt percent
Palmitic (16:0)	4.48	4.58	4.53
Stearic (18:0)	1.83	1.83	1.83
Oleic (18:1)	61.95	61.61	61.78
Linoleic (18:2)	19.43	19.45	19.44
Linolenic (18:3)	9.66	9.67	9.67
Eicosic (20:1)	1.83	1.83	1.83
Erucic (22:1)	0.81	1.02	0.92

Based upon the above fatty acid profile, average molecular weight of the canola oil and its derivatives were calculated (Table 2). These average molecular weight values were used to calculate the amount of reactants used for each experimental run.

Table 2. Average Molecular weights of Canola oil and its derivatives

	Triglycerides	Di-glycerides	Mono-glycerides	Potassium Soap	Canola Methyl Esters
Average Mol. Weight (g/mol)	887.30	622.22	357.16	321.17	297.07

Experimental Setup

A bench-scale continuous-flow RD system (Fig. 4) was developed and tested with optimum process parameters obtained from laboratory scale studies. The central system component is a stainless steel, perforated plate distilling column.

Figure 4. Bench-scale continuous-flow RD reactor unit for biodiesel production.

Table 3. Bench-scale RD Column Details

Column	Sieve tray	Tray details	
Actual Number of Trays	20	Hole dia. (mm)	1.20
Tray spacing (mm)	53	Plate thickness (mm)	1.22
weir height (mm)	6.5	Triangular pitch (mm)	4.00
weir pipe dia. (mm)	8.9	# of holes	98
Column dia. (mm)	50	Hole area (cm^2)	1.11
Total plate area (cm^2)	19.6	Liquid covered area (cm^2)	17.3
Downcomer area (cm^2)	0.6	Liquid volume/ tray volume	0.88
Net area (cm^2)	19.0	Liquid hold-up volume (mL)/ tray	11.2
Active area (cm^2)	18.4		

Other major components of the bench-scale biodiesel production facility include:

- Thermo-siphon reboiler, 750 W Heating Capacity
- Overhead condenser, with reflux valve
- Pre-reactor, in-line static mixer, heat wrapped
- Feed pumps (calibration: Appendix I)
- Flow-meters (calibration: Appendix I)
- Temperature display and control unit
- Gravity based continuous glycerol-biodiesel separator

Experimental Procedures

Feed preparation

a) Oil. The feedstock was first checked for free fatty acid content according to ASTM 975 and moisture using Karl Fischer method. Feedstock having FFA greater than3 percent or moisture greater than1 percent should not be used directly for transesterification in the reactive distillation column. The oil needed for experimental run was transferred to a covered container and placed near the process area.

b) Methanol-Catalyst Premix. The methanol (greater than 99.9 percent) and the desired base catalyst were transferred, in desired amounts, to a three-gal container and stirred to completely dissolve the catalyst in methanol. The amount of methanol and catalyst was determined based upon the required methanol-to-oil ratio and catalyst concentration.

Example calculation:

- Methanol-to-oil molar ratio: 4:1
- Catalyst: $KOCH_3$ (32 percent wt in methanol)
- Catalyst conc.: 0.15 percent mol
- Oil flow rate: 70 mL/min, or $70 \times 0.91 = 63.7$ g/min (oil density $\rho = 0.91$ g/mL)
- Therefore, total methanol required: $4 \times (63.7/882.1) \times 32 = 9.24$ (g/min)
- Catalyst requirement: $(63.7/882.1) \times 0.15 \times 70 = 0.75$ g/min
- $KOCH_3$ (32 percent) requirement: $0.75/0.32 = 2.36$ g/min, or $2.36/1.2 = 1.97$ mL/min (density of $KOCH_3$ solution 32 percentwt $\rho = 0.91$ g/mL)
- Methanol associated with catalyst solution: $2.36 \times (1-0.32) = 1.60$ g/min
- Fresh methanol required $= 9.24 - 1.60 = 7.64$ g/min, or $7.64/0.79 = 9.67$ mL/min
- Methanol-catalyst mix ratio: $2.36/7.64 \times 100 = 30.9$ g catalyst/ 100g of methanol, or $1.97/9.67 \times 100 = 20.4$ mL of catalyst/ 100 ml of methanol
- Methanol-catalyst flow rate: $2.36 + 7.64 = 10$ g/min, or $1.97 + 9.67 = 11.64$ mL/min

Startup Procedures:

- At the start of each test the reactor and reboiler section were drained of all liquids before anything was fed to the reactor. Approx. 300 ml solution, containing 200 ml of previously prepared biodiesel and 100 ml of methanol were injected into the column. The reboiler heater was set to 100°C and allowed to heat for approx. 30-45 minutes till the temperature of the top tray reached 60°C.

- The oil and methanol-catalyst were pumped at 50 percent rate into the top tray of the column via pre-reactor. The calibration of pumps and flow meters (appendix 1) was used to adjust the required flow. The pre-reactor heater was set to 55°C. After 30 minutes the flow rates were increased to actual calculated flow rates.

Steady-operation and sampling

At actual feed flow rates, the liquid level in the reboiler section was maintained to the flow circulation level using the product output needle valve as a control medium. Fluctuation in the level at the sight tube was difficult to avoid but could be maintained at an acceptable level. The product from the reboiler was transferred to the vertical gravity settler to separate glycerol phase from the biodiesel.

At two hour intervals, samples were collected from different sampling ports: after pre-reactor; after reboiler, settled biodiesel and all tray-sampling ports. Approximately 6 ml of each sample was collected in plastic centrifuge tubes containing 3 ml of 0.1N HCL to stop the reaction and wash out the glycerol, methanol and catalyst from the ester phase. The sample tubes were gently shaken then centrifuged.

Note: A logbook was maintained to register all major difficulties; actions and important things happened during the operation.

Analytical Procedures

The neutralized samples collected from the reactor were centrifuged for 10 minutes at 2500 rpm. For each sample, 1 ml of the upper phase was diluted with 9 mls of 2-propanol- hexane (5:4 v/v) and one ml of the diluted solution was then filter into HPLC vials.

Compositions of the reaction mixtures were analyzed by using HP 1090 HPLC with ELSD (Altech2000). Load 'CANOLA.m' method, which was calibrated for canola oil and its methyl esters. The method used gradient elution with aqueous-organic and non-aqueous mobile phase steps: 70 percent acetonitrile + 30 percent water in 0 min, 100 percent acetonitrile in 10 min, 50 percent acetonitrile + 50 percent 2-propanol- hexane (5:4 v/v) in 20 min and 7.5 min final hold up. The column used was a C18, 7um SGX. The column temperature was maintained at 40°C while the temperature of ELSD was kept at 60°C and the flow rate of the nebulizer gas was 1.5 l/min. The LC report was configured to provide the composition as percent TG, DG, MG and methyl esters.

RESULTS AND DISCUSSIONS

The feed stream flow rates for the test run were chosen carefully in order to avoid any column flooding or weeping problems. The feed stream details and calculated liquid residence times are tabulated in Table 4. The column was operated as per procedures discussed in section above.

Table 4. Feed Input Details

Feed Stream:

Feed Composition (%mol)	
Canola Oil, % mol	20
Methanol, % mol	80
Methanol-to-Oil Ratio	4
Catalyst (KOCH$_3$) Concentration, %mol	0.15
Total Feeding rate (g/min)	72.9
Oil Feed flow (ml/min)	70
Methanol feed flow (ml/min)	11.7
Feed temperature, degrees C	55
Feed density, g/ml	0.8948

**Reactor retention time**

Oil residence time per tray (min)	0.16
Total residence time (min)	1.60

A set of three readings was obtained for each sampling location with sampling time interval of 2 hours. The average results as weight percentage with respect to cumulative residence time at each sampling location is listed in Table 5.

Table 5. Average Results as Weight Percentage

Stage	MG	ME	DG	TG	Cumulative residence time (min)
Initial	0.00	0.00	0.00	100.00	0.00
Feed point	0.41	1.34	1.54	96.70	0.10
Tray 2	1.32	7.00	5.87	85.80	0.38
Tray 4	2.02	29.24	7.02	61.74	0.66
Tray 6	2.72	64.71	4.52	28.04	0.94
Tray 8	1.81	75.45	3.64	18.43	1.22
Tray 10	0.99	84.66	4.10	10.24	1.50
After Reboiler	1.20	90.71	1.76	6.32	4.63

It was found that most of the reaction takes place in the column with a reaction time of less than 2 min. Some portion of the reaction also takes place in the reboiler section, which has additional 3 minutes residence time. Despite of the sufficient residence in the reboiler not enough reaction conversion was achieved, this is possibly due to 1) high reboiler temperatures keep the methanol away from liquid phase, and 2) at high temperature the catalyst decomposes. All three sets of data and their averages are plotted (Fig. 5 and 6) with respect to cumulative residence time. The concentration profiles obtained on a RD column follows the same pattern as in a batch reactor obtained by various researchers (Noureddini, et al., 1997; Darnoko, et al., 2000; Freedman, et al., 1986).
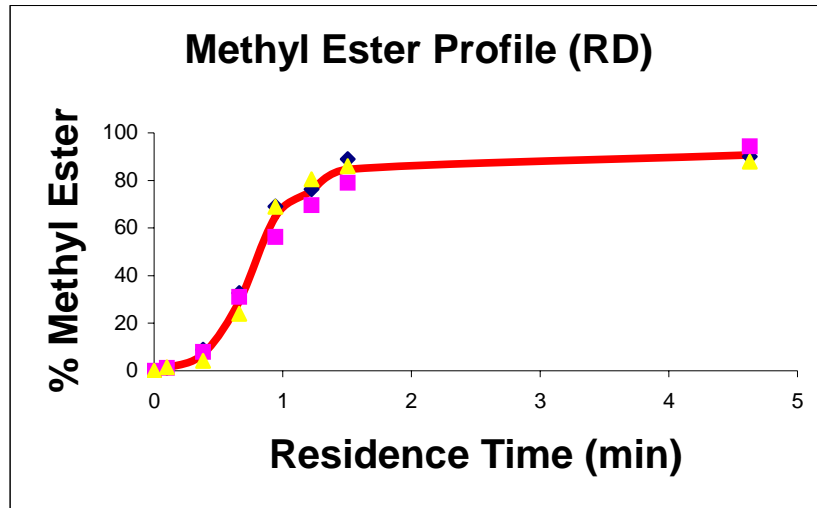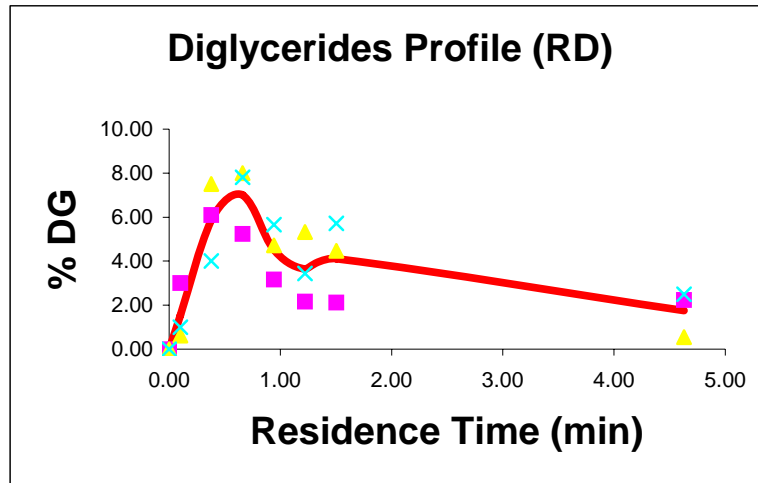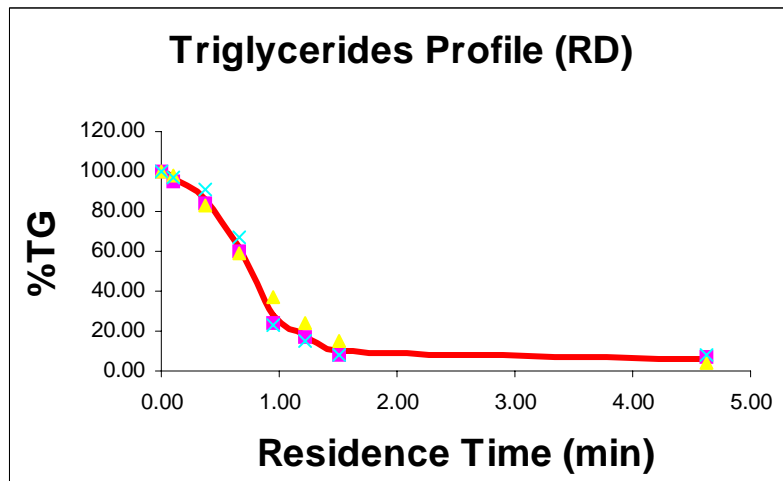
(a)
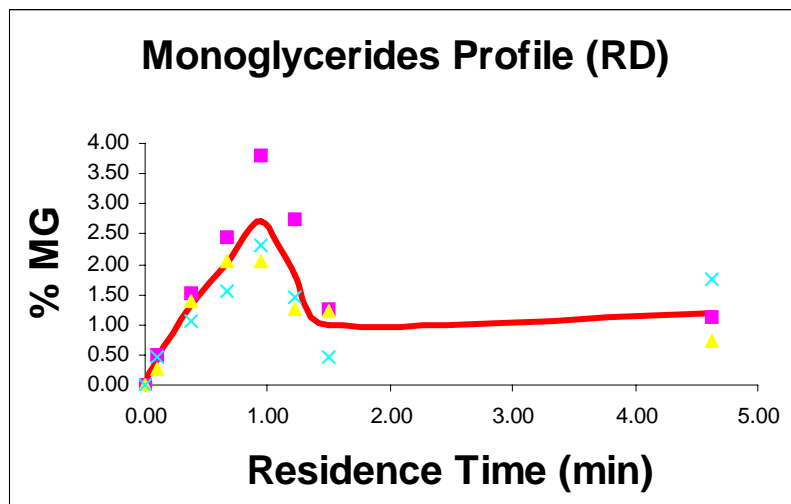
(b)

Figure 5. Concentration profiles for (a) methyl ester ,and (b) monoglycerides obtained at different sampling locations in a bench-scale RD reactor unit.

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Diglycerides Profile (RD)

(c)

Triglycerides Profile (RD)

(d)

Figure 6. Concentration profiles for (c) diglycerides and (d) triglycerides obtained at different sampling locations in a bench-scale RD reactor unit.

All three sets of data follows similar pattern but the repeatability for monoglycerides and diglycerides concentration profile was poor. Overall very good concentration profiles were obtained from the test run on the RD reactor unit. The performance of the RD reactor was compared with that of batch reactor operated with similar operating conditions (Fig. 7).
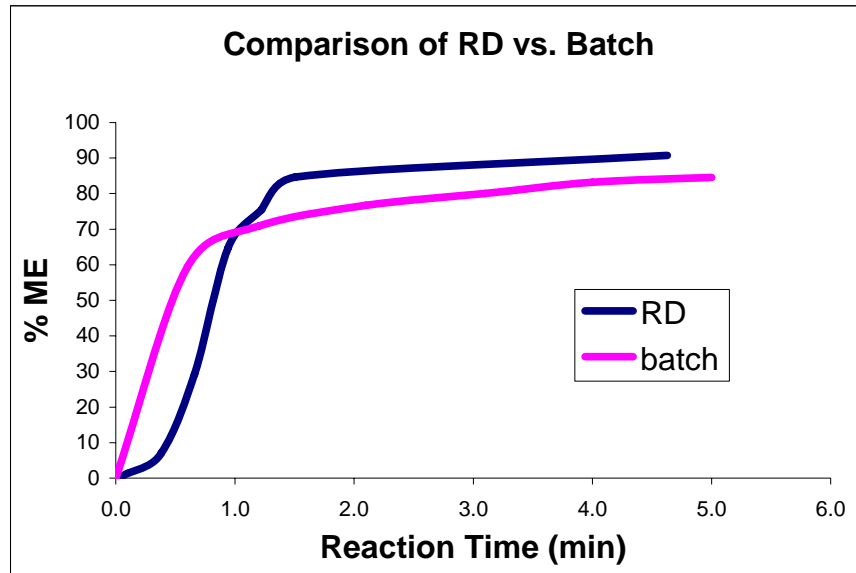
Comparison of RD vs. Batch

Figure 7. The comparison of reactive distillation reactor technique with batch reactor for biodiesel production via transesterification.

The comparison shows that the batch reactor had higher initial reaction rate than the RD. This was due to the shear mixing provided in the batch reactor. This shows that the initial rate of reaction is governed by the mass transfer limitation due to insolubility of methanol and oil phase. This problem is overcome with the formation of methyl esters, which act as a co-solvent for both reactants. However in RD reactor, the actual kinetics of reaction is faster than in the batch reactor. This is due to the high temperature and higher methanol-to-oil ratio achieved inside the column. At the end of the last reactive tray in the RD column, the ester content has reached up to 85 percent as compared to about 70 percent with batch reactor with same reaction time provided. This shows that reactive distillation can achieve higher process yield with shorter reaction times as compared to the conventional batch reactor technology for biodiesel production via transesterification.

Injector Coking

A machine vision system for scoring the results of the injector coking was used to compare the coking effect of canola methyl esters (CME) compared to that of diesel. Figure 4 shows three pictures from the system used for evaluation. On the left is a profile of a clean injector, next to it is the profile of an injector after 50 hours run on diesel and the third is the same type of injector

run on CME for 50 hours. The number of pixels that make up the tip and shoulders is measured and the area calculated. Coked injectors are measured in the same way and compared to the clean one. The difference in area is the amount of coke built up on the injector. A coking index with diesel set at one was developed for the comparison (Jones et al, 2001). At 50 hours the set of three injectors was indexed, evaluated and averaged. The coking on the injectors was approximately 1.5 times that of diesel.
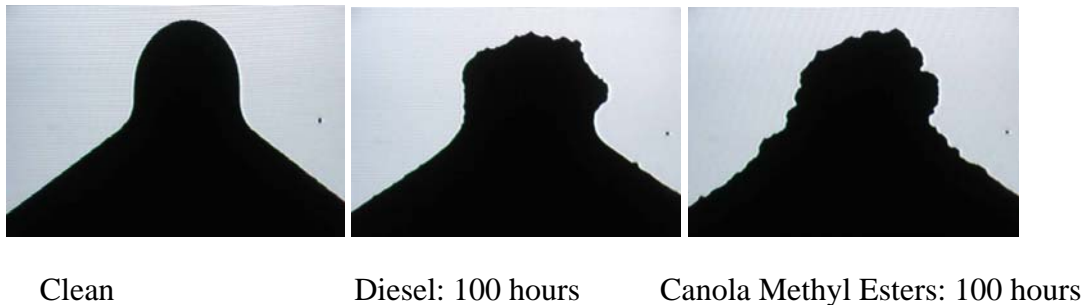

| Clean | Diesel: 100 hours | Canola Methyl Esters: 100 hours |

Figure 4. Injector coking profiles.

Summary

A bench-scale RD rector for biodiesel preparation has been designed, fabricated, and tested. Experiments have shown that the bench-scale RD process can produce biodiesel at a production rate of about 75mL/min continuously with an alcohol-oil ratio of 4:1, which is reduced by two-thirds comparing to that typically used in current technology. The retention time (reaction time) of the feedstocks in the column is about 5 min compared to 60 to 180 min in existing processes used in industry. The conversion profile of the feedstock, which was monitored at multiple locations, clearly illustrated the progression of the reaction along the column. The RD reactor was easy to start up, operate, and control. There were no difficulties experienced in long-term operation.

The preliminary results from this and previous stage of research have shown that RD reactor is a very promising technology for biodiesel production. A proposal based on the results was sent to USDA National Research Initiative competitive grant program for a pilot-scale RD reactor testing and ranked high priority (top 13 out of 198 proposals). Unfortunately, it was not funded last year due to the limited available funds. The PI is continuing to explore the possibilities for external funding to further develop the RD reactor for commercial uses.

The research group has also found a couple of new technical issues at the engineering level, i.e., possible ester decomposition and trace water accumulation during long-term operations of the RD reactor. Experiments are under way to further study these issues.
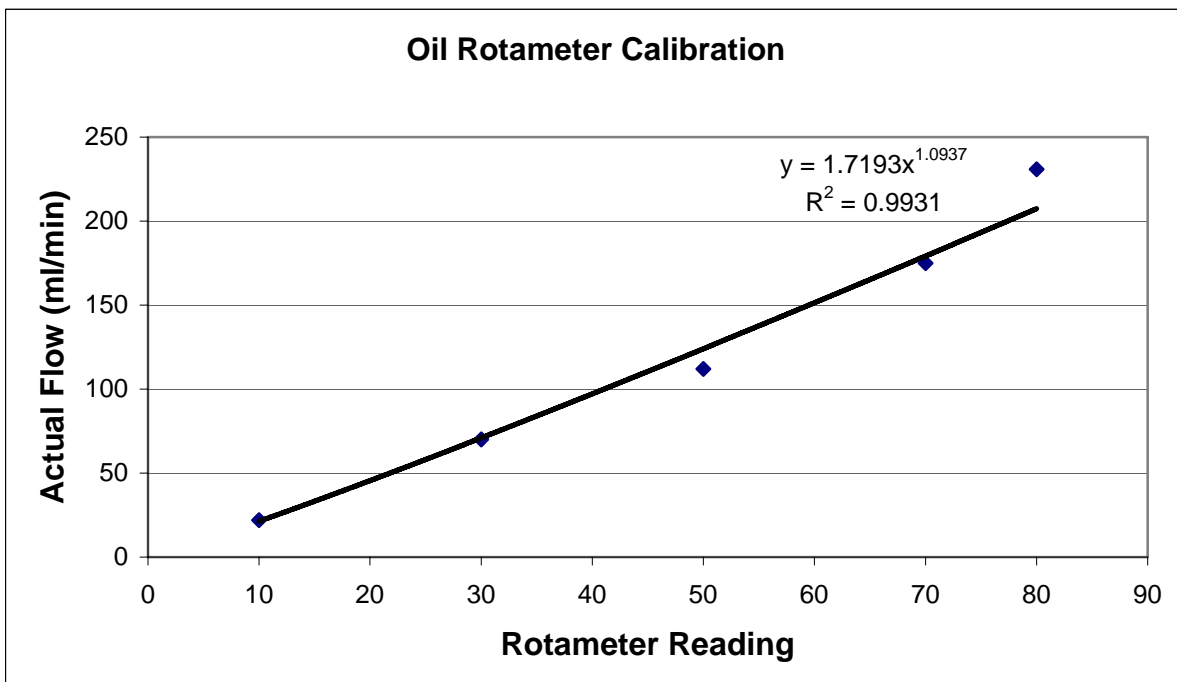
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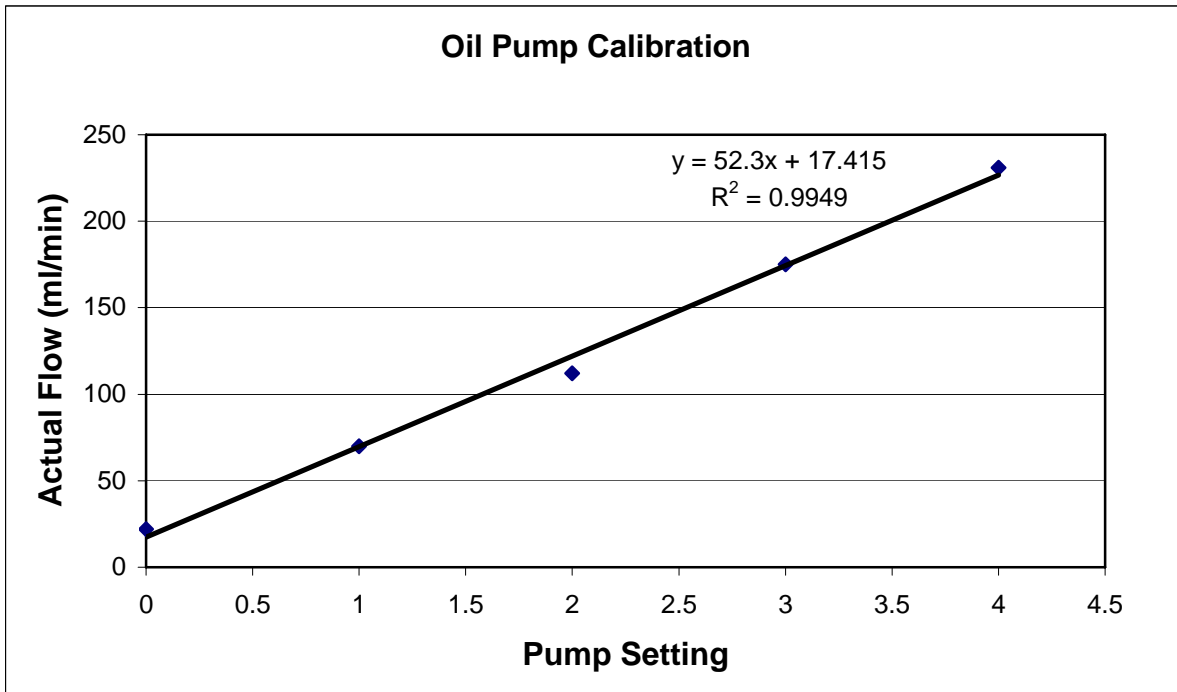
APPENDIX

Flow Control Device Calibration Tables

I. Oil Pump and Rotameter Calibration

Rotameter Reading	Pump Setting	Actual Flow ml/min
10	0	22
30	1	70
50	2	112
70	3	175
80	4	231

Oil Rotameter Calibration

$y = 1.7193x^{1.0937}$
$R^2 = 0.9931$

Actual Flow (ml/min) vs Rotameter Reading

Oil Pump Calibration

$y = 52.3x + 17.415$
$R^2 = 0.9949$

(Chart: x-axis "Pump Setting" from 0 to 4.5; y-axis "Actual Flow (ml/min)" from 0 to 250)

II. Methanol Pump Calibration

Pump Setting	Actual Flow
0	1
1	15
2	24
3	32
4	36
5	36.4

Methanol Pump Calibration

$y = -1.5714x^2 + 14.943x + 1.1143$

$R^2 = 0.9991$

Actual Flow (ml/min) vs. Pump Setting