

# EXPERIMENTAL OPTIMIZATION OF A CONTINUOUS-FLOW REACTIVE DISTILLATION REACTOR FOR BIODIESEL PRODUCTION

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**ABSTRACT.** A comprehensive study of biodiesel preparation from canola oil was performed on a continuous-flow reactive distillation (RD) reactor system. Optimization of six process variables was studied experimentally and analyzed statistically on the overall performance of the RD reactor system. These variables include the feed methanol to triglycerides molar ratio, reaction time, reboiler temperature, catalyst concentration, methanol circulation mode, and catalyst formulation. An experimental design was used in the experiments, and statistical multiple response regression models were employed for process optimization. Under the operating conditions explored, product yields ranged from 41.5% to 94.9%, productivity ranged from 16 to 55.8 kmol/m<sup>3</sup>·h (5.6 to 19.5 m<sup>3</sup>/m<sup>3</sup>·h), and soap formation varied from 4.44 to 29.1 mol/100 mol (0.19 to 1.27%wt.). For different optimization criteria, the following optimum variable ranges were found: feed molar ratio from 3.65:1 to 4.50:1, reaction time from 3.76 to 5.56 min, reboiler temperature from 100°C to 130°C, and catalyst concentration from 0.13 to 0.24 mol/mol. Although the process variables individually affected the system performance to a certain extent, the interactive effect of the process variable combinations affected the system efficiency more significantly. When maximized, the product yields and productivity were 98.8% and 55.6 kmol/m<sup>3</sup>·h (18.5 m<sup>3</sup>/m<sup>3</sup>·h), respectively. However, when soap formation was minimized, the yield and productivity were 72% and 9.3 kmol/m<sup>3</sup>·h (3.1 m<sup>3</sup>/m<sup>3</sup>·h), respectively. It is recommended that the optimization of the RD reactor system be based on the maximization of product yield and reactor productivity.

**Keywords.** Biodiesel, Canola oil, Continuous-flow reactor, Process optimization, Reactive distillation.

**B**iodiesel demand and production in the U.S. have been increasing dramatically in recent years. Different reactor technologies for biodiesel production have widely been developed and practiced, from traditional batch operations by small producers to single- or multi-stage semi-continuous and continuous operations by larger producers. Many of these reactor technologies are state-of-art and patented (e.g., Connemann et al., 1994; Wimmer, 1995; Peter et al., 2001; Barthorst et al., 2002; Haas et al., 2002). Generally, continuous transesterification is preferred over batch processes in large-capacity commercial biodiesel production since it provides consistent product quality and low capital and operating costs per unit product.

It has been known that transesterification of vegetable oils or animal fats to fatty acid esters or biodiesel consists of a number of consecutive and reversible reactions (Freedman et al., 1986; Nouredini and Zhu, 1997; Darnoko and Cheryan, 2000). Studies of the mechanism and kinetics have also shown that transesterification is a homogeneous liquid reaction that follows a second-order consecutive reaction and

a fourth-order shunt reaction (Freedman et al., 1986). Completion of the reaction depends on multiple parameters including the feed molar ratio, catalysts, temperature, reaction time, and properties of the feedstock. In early stage of the transesterification, the reaction is limited by the mass transfer of alcohol to vegetable oil phase (Van Gerpen, 2005). As the reaction progresses, the formation of esters improves the solubility of alcohol in the oil phase, and the reaction rate is then governed by kinetics. In the third stage, the reaction reaches its dynamic equilibrium of conversion, which is primarily dependent on the alcohol-to-triglycerides molar ratio. As an effective means of conversion enhancement, excess alcohol above the stoichiometric ratio (3:1 molar) is typically used.

Considering the characteristics of the transesterification reaction, a laboratory-scale continuous-flow reactor system using a reactive distillation (RD) technique was developed and investigated in our Biofuels Research Laboratory as an effort in exploring a technically and economically sound reactor technology for commercial biodiesel production from canola oil and methanol. It was demonstrated that application of the RD technique to biodiesel production was very effective and efficient. This novel reactor system bears the advantages of significant reduction in the use of excess methanol (a feed methanol to triglycerides ratio of 4:1), high unit productivity (up to 6.6 m<sup>3</sup> biodiesel per m<sup>3</sup> reactor volume per hour), and a considerably shortened reaction time (<10 min). To further evaluate the RD reactor system performance and efficiency, we have continued to investigate the process variables and their effects. Along with the molar ratio of methanol to triglycerides in the feed (abbreviated as feed molar ratio hereafter), we also studied the reaction time, operating temperature of the reboiler, catalyst formulation

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**Table 1. Average molecular weights of canola oil and its derivatives.**

Average MW (g/mol)	Tri-glycerides (canola oil)	Mono-glycerides	Di-glycerides	Potassium Soap	Canola Methyl Esters
	887.3	357.2	622.2	321.27	297.1

and concentration, and the mode of the condensed methanol being circulated back to the system. This article details the results of the experimental investigation on the effects of these process variables on product yield, reactor productivity, and soap formation. Process optimization was conducted statistically and experimentally on the process variables to determine the best performance of the RD reactor system.

## MATERIALS AND METHODS

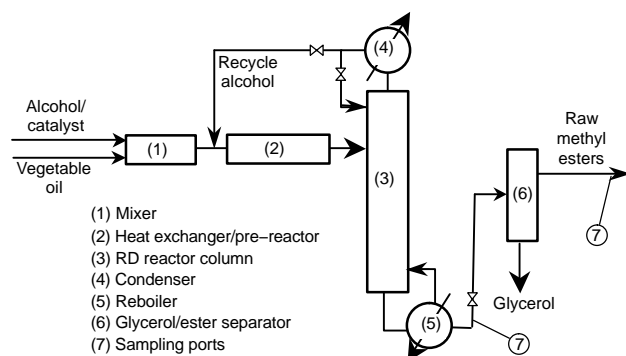
### CHEMICALS AND REAGENTS

Crude canola oil and methanol were used in this research as the feedstocks, and potassium hydroxide and potassium methoxide were used as different formulations of catalysts. The canola oil was screw-pressed at our pilot seed processing plant at the University of Idaho and filtered to remove any particulates. No further treatments were performed. The acid value of the canola oil was 1.97 mg KOH/g. The fatty acid profile of the oil was determined using GC (Hammond, 1991). Based on the fatty acid profile, the average molecular weights of the oil and its derivatives were calculated (table 1). These values were used in data processing and process evaluating parameter calculations.

Methanol (analytical grade) and potassium hydroxide (ACS certified, purity >87.9% wt) were from J.T. Baker (Phillipsburg, N.J.). Potassium methoxide (32% w/w solution in methanol) was obtained from Degussa Corporation (Germany). Other analytical reagents and standard chemicals of triolein, diolen, methyl oleate, and glycerol were all analytical grade and purchased from Sigma-Aldrich Co. (St. Louis, Mo.).

### EXPERIMENTAL SETUP

A laboratory-scale continuous-flow RD reactor system was used in this study (fig. 1). The reactor was a glass-distilling column with perforated Oldershaw plates (ChemGlass, Vineland, N.J.). This column had ten plates with an inner diameter of 28 mm, a weir height of 1.7 mm, and a distance between plates of 25 mm. The nominal liquid hold-up on each plate was 1 mL, totaling 10 mL for the column. The



**Figure 1. Schematic of the laboratory RD reactor system setup.**

column had a vacuum jacket around it as a means of thermal insulation to prevent heat loss from the column during operation.

In preparation of the alcohol/catalyst premix before each experiment, the stock alcoholic potassium hydroxide (KOH) or potassium methoxide (KOCH<sub>3</sub>) was prepared so that the corresponding amount of catalyst would give the desired methanol-to-glyceride molar ratio once mixed with the canola oil. The methanol/catalyst premix and the canola oil at room temperature were fed into a 5 mL in-line static mixer (Cole-Parmer, Vernon Hills, Ill.) by two separate calibrated Masterflex peristaltic pumps (Cole-Parmer, Vernon Hills, Ill.). The mixed reactants entered the second static mixer (10 mL capacity), which was heated by an electrical heating tape so that the outlet mixture temperature was maintained at 55 °C prior to entering the RD column at the top plate. This secondary static mixer also acted as a heat exchanger and pre-reactor. In the RD column, each plate of the RD column served as a mini-reactor to further react the glycerides with methanol in the liquid phase. A reboiler (250 mL flask with 50 to 100 mL working volume) was fitted to the bottom of the column to drive methanol off the product mixture before discharging to the separator. The unreacted methanol vapors that made their way to the top of the column were condensed by a water-cooled condenser and fed back into the system using two different recirculation modes: (1) recycling the methanol from condenser completely to the feed stream (“recycle”), and (2) refluxing back into the column directly from top (“reflux”). The product mixture was withdrawn from the reboiler to a glycerol/ester separator, a  $\phi 70 \times 300$  mm column with an adjustable entry point, where the glycerol and esters were separated by gravity. During the continuous operation, samples were taken at the reboiler. Temperatures of the pre-reactor, condenser, RD column, and reboiler were monitored and controlled using Fuji PXR3 and PXR4 PID controllers (TTI, Inc., Williston, Vt.).

### CHEMICAL ANALYSIS

The first sample was taken from the reboiler after 2 h of operation in continuous mode, when the operation reached steady state, and the subsequent samples were taken at 1 h intervals. Triplicates of 5 mL from each sample were treated with 3 mL of 0.1 N HCl to stop the reaction, and centrifuged at 3,000 rpm for 15 min to separate the glycerol phase that contained most of the methanol, soap, and residual catalyst. The ester layer was analyzed without further treatment for the contents of methyl esters and tri-, di-, and mono-glycerides using an HP 1090 HPLC with an ELSD detector (Altech Associates, Inc., Deerfield, Ill.). The column, an Alltama C18 5  $\mu$ m SGX (a silica gel adsorbent), was maintained at 40 °C while the detector was held at 60 °C. The flow rate of the nebulizer gas (nitrogen) was 1.5 L/min. Gradient elution was conducted with aqueous-organic and non-aqueous mobile phase steps: 70% acetonitrile/30% water at 0 min, 100% acetonitrile at 10 min, and 50% acetonitrile/50% 2-propanol-hexane (5:4 v/v) at 20 min with 7.5 min holdup time (Komers et al., 2001). Separate analyses were conducted on the same ester layer for the contents of soap and residual catalyst using the modified AOCS method (Van Gerpen et al., 2005). The results obtained from the above analyses were transformed into molar bases before further data processing and calculations.

## PROCESS VARIABLES

Six major process variables that affect the performance of the RD reactor system were identified from our preliminary studies. These variables include: (A) feed molar ratio, (B) reaction time, (C) reboiler temperature, (D) catalyst concentration, (E) methanol circulation mode (“recycle” or “reflux”), and (F) catalyst formulation (KOH or KOCH<sub>3</sub>). The reaction time used in this study was calculated as the liquid retention time in the pre-reactor and the RD column, which is inversely related to the feed flow rate for the fixed reactor volume. This set of experiments was carefully designed using the computer application SAS JMP (SAS Institute, Inc., Cary, N.C.) to obtain maximum information with the least numbers of runs. Table 2 lists the process variables and their levels.

## PROCESS EVALUATING PARAMETERS

The parameters that were chosen for evaluating the performance of the RD reactor system were: (1) product (fatty acid esters) yield, (2) RD reactor productivity, and (3) soap formation. The reactant (triglycerides) conversion is also defined below as it was used in the process performance analysis. All results obtained from chemical analyses and subsequent calculations were transformed into relative molar basis, e.g., mol of esters per unit mol of feed triglyceride (canola oil) in order to make it comparable to other systems (Komers et al., 2001). The definitions of the process evaluation parameters and other related terms are described below.

**Yield (YLD)** – the targeted product (fatty acid esters or biodiesel) formed from the maximum (theoretical) amount possible from the triglycerides in percentage:

$$YLD (\%) = \frac{ME}{ME_{\max}} \times 100 \quad (1)$$

where *ME* and *ME*<sub>max</sub> are the mol of methyl esters produced per unit feed (mol/mol) and the theoretical amount of methyl esters possibly formed per unit feed (3 mol/mol), respectively.

**Productivity (PROD)** – the production capacity of the RD reactor, defined as the amount of fatty acid esters (kmol) produced per unit reactor volume (m<sup>3</sup>) per unit time (h) and calculated as:

$$PROD (\text{kmol/m}^3 \cdot \text{h}) = \frac{F_{oil} \times ME}{V_{reactor}} \quad (2)$$

where *F*<sub>oil</sub> and *V*<sub>reactor</sub> are the total molar flow of canola oil (kmol/h) and the reactor volume (both the pre-reactor and the column liquid hold-up volumes, m<sup>3</sup>), respectively.

**Soap Formation (SOAP)** – the amount of soap formed due to the side reactions between fatty acids and the alkaline catalysts used. The soap and catalyst results, in units of grams per gram of esters, were transformed into relative mol per mol of triglycerides. The soap formed was then calculated as mol of soap formed per 100 mol of feed triglycerides:

$$SOAP (\text{kmol}/100\text{kmol}) = S \times 100 \quad (3)$$

where *S* is the mol of soap formed in the reaction mixture per mol of feed triglycerides.

**Reactant Conversion Rate (CONV)** – the completeness of the major reactant (triglycerides), defined as the total triglycerides reacted through the system per unit of triglycerides fed to the reactor:

$$CONV (\%) = (1 - TG) \times 100 \quad (4)$$

where *TG* is the mol of triglycerides in the product mixture per mol of triglycerides in the feed.

Once the process parameters were calculated from the analytical results, they were analyzed using the statistical package DOE PRO XL (Digital Computations, Inc., Colorado Springs, Colo.). DOE PRO XL is a Microsoft Excel plug-in that is capable of performing multiple response regression modeling, multiple response optimizations, and multiple-interaction plot generation. Effects of various process variables on the process parameters were determined using the results of the statistical analyses. The combination of optimum process variables was then determined by

**Table 2. Experimental design and levels of process variables.**

Experiment	Process Variables						
	A	B	C	D		E	F
	Feed Molar Ratio (mol/mol)	Reaction Time (min)	Reboiler Temp. (°C)	Catalyst (mol/mol)	Conc. (% wt)	Methanol Circulation Mode	Catalyst Formulation
1	4.0	4.44	140	0.10	0.73	Reflux	KOH
2	4.5	6.67	140	0.15	1.10	Recycle	KOCH <sub>3</sub>
3	4.5	2.67	100	0.20	1.46	Reflux	KOH
4	4.0	3.33	100	0.25	1.83	Recycle	KOCH <sub>3</sub>
5	3.0	3.33	160	0.15	1.10	Reflux	KOH
6	3.5	4.44	100	0.15	1.10	Reflux	KOCH <sub>3</sub>
7	3.5	3.33	140	0.20	1.46	Recycle	KOH
8	3.5	6.67	120	0.25	1.83	Reflux	KOH
9	4.0	6.67	160	0.20	1.46	Reflux	KOCH <sub>3</sub>
10	4.5	3.33	120	0.10	0.73	Reflux	KOCH <sub>3</sub>
11	3.0	6.67	100	0.10	0.73	Recycle	KOH
12	3.0	2.67	140	0.25	1.83	Reflux	KOCH <sub>3</sub>
13	3.5	2.67	160	0.10	0.73	Recycle	KOCH <sub>3</sub>
14	4.0	2.67	120	0.15	1.11	Recycle	KOH
15	3.0	4.44	120	0.20	1.46	Recycle	KOCH <sub>3</sub>
16	3.5	4.44	160	0.25	1.83	Recycle	KOH

maximizing the process yield, conversion, and/or productivity while minimizing soap formation.

## RESULTS AND DISCUSSIONS

Table 3 summarizes results of the runs based on the experimental design in table 2. The results were obtained by analyzing the samples taken at the reboiler of the RD reactor system at steady-state operation, according to the procedures described in the Materials and Methods section. The molar composition profiles of the samples were determined by HPLC and converted to the molar basis per unit molar feed triglycerides for easy data processing and comparison (Komers et al., 2001). The yields, productivity, and soap formation were then calculated. The small standard deviations of the process evaluation parameters showed that the RD reactor system, once operated at steady-state, generated very consistent results. Relatively larger deviations in composition were observed with methanol recycling back to the pre-reactor, which were likely caused by the less consistent flow of recycled methanol from the condenser. This could be corrected by employing a buffer reservoir between the condenser and the pre-reactor.

### EFFECTS OF PROCESS VARIABLES

Statistical analyses of the experimental data resulted in near-perfect-fit multiple response regression models between the process variables and the product yield (YLD), productivity (PROD), and soap formation (SOAP). The large F-values (557, 1511, and 120 for YLD, PROD, and SOAP, respectively) at a high degree of freedom (dof = 47),  $R^2$  close to unity, and small standard errors are all verifications of the regression models. Probability values of less than 0.05 for product yields indicate that two-thirds of the process parameters and two-way interactions analyzed were significant in contributing to the product yields in the regressions model. The remaining one-third, including the feed molar ratio (A) and two-way interactions of molar ratio to reboiler temperature ( $A \times C$ ), reaction time to reboiler temperatures

( $B \times C$ ), reaction time to catalyst concentration ( $B \times D$ ), and reaction time to catalyst formulation ( $B \times F$ ), were not statistically significant in contributing to the yield. The unimportance of the feed molar ratio, which was consistent with the conclusion drawn from the Pareto plot of the process variables (fig. 2), was caused by the high nominal methanol-to-triglycerides molar ratio on each plate through methanol recycling under the operating conditions of the RD system. Estimated indirectly through measurement of the methanol condensation rate, the overall methanol to triglycerides molar ratio at the feeding plate (the first mini-reactor) could be as high as 15:1 to 20:1 after considering the reaction completed in the pre-reactor. As a result, a high local feed molar ratio was noted. For productivity (PROD) and soap formation (SOAP), all process variables were significant in the multiple response regression models except reboiler temperature (C), which was not significant to soap formation. Statistical analysis also showed that all three regression models were multicollinear. In other words, all the process variables interacted with each other and collectively contributed to the regression models.

Pareto charts of the multiple response regression models allow visual identification of the relative importance of the individual process variables and some two-way interactions on the process evaluating parameters (fig. 2). The two-way interactions of the process variables had much higher coefficients than those of individual parameters in general. However, not all coefficients affected the process evaluation parameters in a favorable manner. The process variables of feed molar ratio (A), reaction time (B), and methanol circulation mode (E) positively contributed to yield and productivity, as did the interaction of A and B, which had a larger impact. The effects of these variables on soap formation were negative or in favor of reducing soap formation in general. The catalyst concentration (D) and the catalyst formulation (F) contributed negatively to yield, productivity, and soap formation. Likewise, interactions of variable A with variables C and D, and variable B with variables C and D also negatively contributed to yield,

Table 3. Results of process evaluation parameters.<sup>[a]</sup>

Experiment	CONV (%)	YLD (%)	PROD (kmol/m <sup>3</sup> ·h)	SOAP (mol/100 mol)
1	68.33 ±0.05	64.89 ±1.03	22.76 ±0.36	6.10 ±0.10
2	76.67 ±0.11	68.95 ±1.60	15.91 ±0.37	6.64 ±1.79
3	92.67 ±0.04	90.00 ±0.60	51.50 ±0.34	12.31 ±0.37
4	97.00 ±0.01	94.94 ±0.49	44.69 ±0.23	7.14 ±0.89
5	75.33 ±0.10	63.31 ±0.58	30.97 ±0.28	7.87 ±0.59
6	89.33 ±0.01	85.31 ±0.41	30.71 ±0.15	5.50 ±0.85
7	75.67 ±0.08	66.18 ±1.41	31.76 ±0.67	9.23 ±0.43
8	95.67 ±0.01	92.45 ±0.47	22.18 ±0.12	29.10 ±1.32
9	95.00 ±0.05	90.31 ±0.49	21.67 ±0.12	11.84 ±0.71
10	84.33 ±0.01	81.05 ±0.31	37.40 ±0.14	4.44 ±0.64
11	45.00 ±0.03	41.46 ±0.30	10.33 ±0.07	6.66 ±1.65
12	95.33 ±0.11	91.70 ±1.82	55.86 ±1.11	6.48 ±0.78
13	90.33 ±0.11	78.79 ±1.80	47.27 ±1.08	7.04 ±0.68
14	59.00 ±0.09	54.30 ±1.75	32.07 ±1.03	6.76 ±0.31
15	96.33 ±0.05	93.67 ±1.14	34.58 ±0.42	6.55 ±0.74
16	79.67 ±0.20	67.12 ±2.01	24.16 ±0.72	11.37 ±1.01

<sup>[a]</sup> CONV, YLD, PROD, and SOAP are the conversion rate, yield, productivity, and soap formation, respectively. The data are presented in the form of average ± standard error, i.e., 68.33 ±0.05 means an average value of 68.33 with a standard deviation of 0.05.

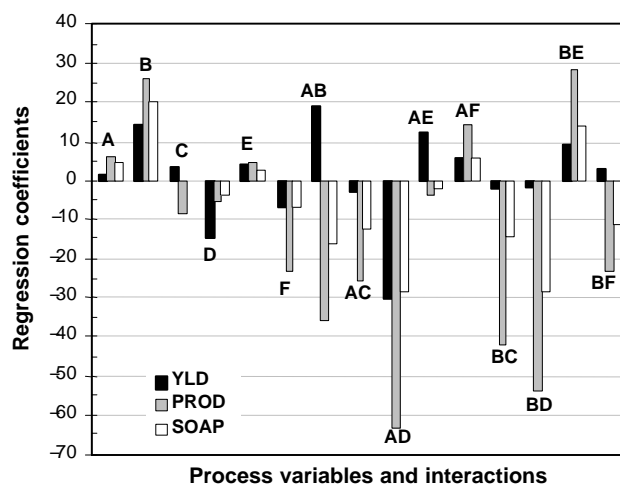


Figure 2. Relative effects of process variables on yield, productivity, and soap formation. Process variables: A = feed molar ratio (mol/mol), B = reaction time (min), C = reboiler temperature ( $^{\circ}$ C), D = catalyst concentration (mol/mol), E = methanol circulation mode, and F = catalyst formulation. Two-letter labels are the two-way interactions of the individual variables.

productivity, and soap formation. Other process variables, including the catalyst concentration (D) and interactions of  $A \times B$ ,  $A \times E$ , and  $B \times F$ , affected the process evaluation parameters in mixed ways, i.e., affecting one parameter positively and another negatively.

The process variables, considered individually, contributed to the process evaluation parameters in less significant ways. Figure 3 summarizes the effects of individual process variables on the product yield as extracted from the statistical analysis using the DOE PRO software. It is evident that the feed molar ratio (variable A), reaction time (variable B), and reboiler temperature (variable C) all had about the same level of contribution to the yield in the range tested. The catalyst concentration (variable D) affected the product yield more significantly at higher levels (e.g.,  $>0.2$  mol/mol) than at lower levels. Considering the methanol circulation mode (variable E), total reflux mode contributed more than recycled mode. A significant difference in yield was evident when the catalyst was introduced in different forms (variable F). Potassium methoxide concentrate was more effective than KOH pellets. This is due to the fact that the reaction between KOH and methanol produces some water, which can lead to hydrolysis of fatty acid esters and thus a higher level soap formation and lower yield.

Effects of the individual process variables on the productivity of the RD reactor system showed a similar pattern to that of yield (fig. 4). No significant differences were found among the levels of the feed molar ratio (variable A), reboiler temperature (variable C), catalyst concentration (variable D), and methanol recycling modes (variable E). All these variables contributed to the productivity at the 30 to 40  $\text{kmol/m}^3\text{-h}$  level. Once again, potassium methoxide concentrate was showed to be a superior catalyst over pelletized KOH, leading to a 10  $\text{kmol/m}^3\text{-h}$  difference. The sole exception was reaction time (variable B), which demonstrated a consistent decreasing trend. It is understandable that,

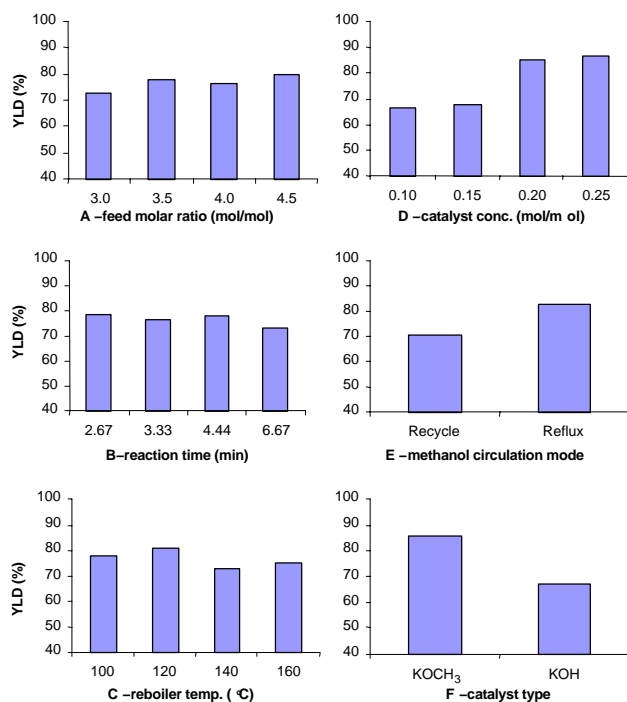


Figure 3. Effects of process variables on product yields.

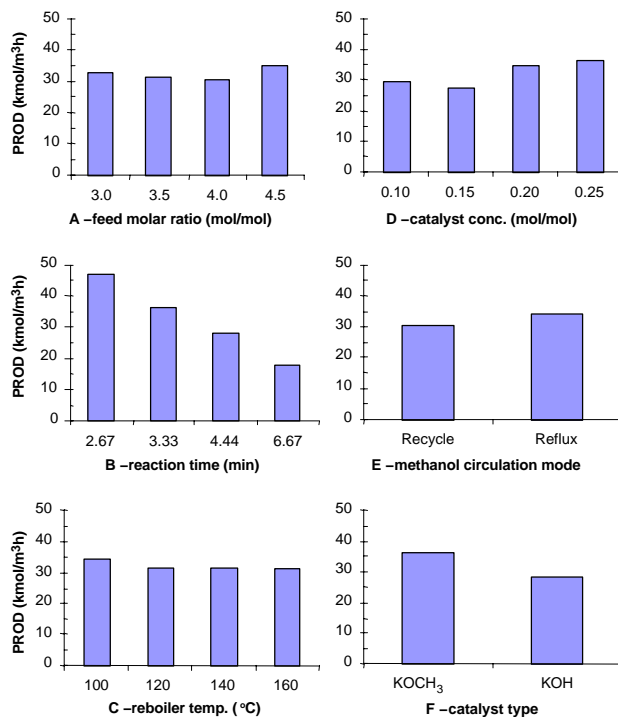


Figure 4. Effects of process variables on productivity.

if the maximum amount of esters were produced, the per-unit productivity would decrease as the reaction time increased.

The individual variables affected soap formation quite differently (fig. 5). A feed molar ratio (variable A) of 3.5 and reboiler temperature (variable C) of  $120^\circ\text{C}$  showed more significant effects on soap formation than any other feed molar ratios or reboiler temperatures tested. Since soap was

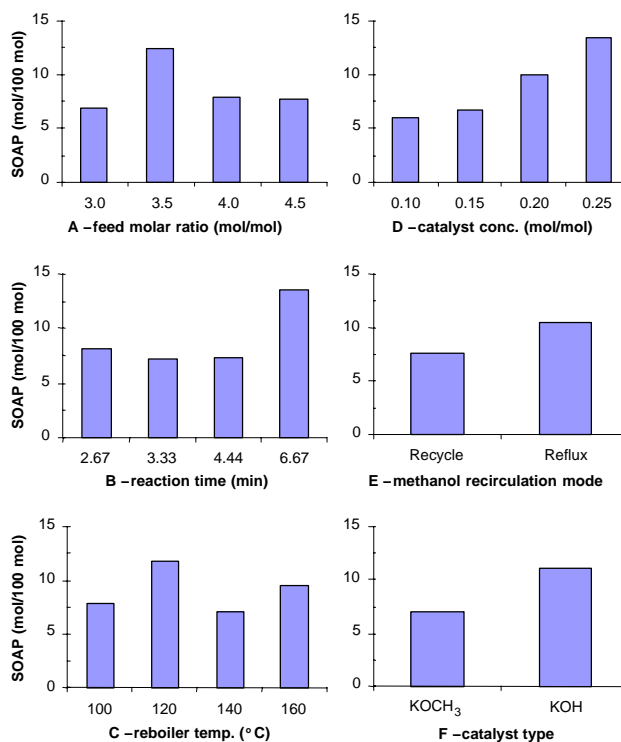


Figure 5. Effects of process variables on soap formation.

formed as the result of undesired side reactions between the catalyst and fatty acids, it was expected that the higher catalyst concentration would favor soap formation. Additionally, the use of potassium hydroxide as a catalyst led to higher level of soap formation since it introduced water into the system, which led to the hydrolysis of esters to free fatty acids.

Careful observation of figures 3 through 5 reveals that none of the individual process variables contributed to the yield, productivity, and/or soap formation to the levels of the experimental results (table 3). This is because the interactions of the process variables had much more significant effects than the individual variables. The high level of multicollinearity of the multiple response regression models suggests a strong correlation between the process variables. Statistically, it prevents variables from being evaluated independently. Therefore, the optimization of the operating process variables should be conducted by considering all possible interactions. Due to the limited sets of data, only two-way interactions of the process variables could be analyzed and evaluated, as discussed below.

#### OPTIMUM OPERATING CONDITIONS

Process variables have varying effects on the process evaluating parameters. A wide range of data on process evaluating parameters was obtained with the 16 experiments. The product yield achieved using the RD reactor ranged from 41.46% to 94.94% with an average of 76.32%. Similarly, the productivity varied from 16 to 55.8 kmol/m<sup>3</sup>·h with an average of 32 kmol/m<sup>3</sup>·h, which is equivalent to 5.6 to 19.5 m<sup>3</sup>/m<sup>3</sup>·h with an average of 13.1 m<sup>3</sup>/m<sup>3</sup>·h. The overall reactor efficiency was determined as a combined optimization of the different process evaluating parameters. Using the multiple response optimization tools of the DOE PRO

software, the optimum sets of process variables were determined for each response as well as for the combination of responses (table 4). For the optimum RD process operation, the process variables were obtained by maximizing product yield and reactor productivity, and/or minimizing soap formation.

To verify the predictability of the multiple response regressions models, a separate set of experiments was conducted according to the information obtained from the system optimization. The results of the experiments shown in table 5 were from the analyses of the raw product mixture without any post-treatments such as washing and methanol stripping. The average make-up of the raw product was: 94.56% wt esters, 1.3% wt methanol, 0.1% wt glycerol, and about 0.5% wt soap. The overall oil (or feed triglycerides) conversion rate was 98.25%. The experiments produced a product yield of 96.6% and a productivity of 34.0 kmol/m<sup>3</sup>·h (or 11.4 m<sup>3</sup>/m<sup>3</sup>·h). The soap in the raw product mixture was 0.48%, or 11 mol/100 mol of feed triglycerides. The small standard error of methyl ester composition indicates that the RD reactor yielded a raw biodiesel product consistently. Compared to the optimum condition being verified (set 7 in table 4), the results were very much in agreement.

The importance of each process variable may differ according to one's perspective and applications. However, the experimental and statistical optimizations of the RD reactor system provided the necessary information on the effects of all process variables on product yield, reactor productivity, and undesirable soap formation. Under the operating conditions and feedstocks used, soap formation was not a serious obstacle to system efficiency in the RD reactor, as shown in this study. The maximization of product yield and productivity are desired for practical biodiesel production.

Table 4. System optimization of the operating variables and their interactions through statistical analyses.

Set	Optimized Parameter	Optimum Criteria	Process Variables <sup>[a]</sup>						Optimum Values
			A	B	C	D	E	F	
1	Yield only	Maximize	4.50	4.92	129	0.13	Reflux	KOCH <sub>3</sub>	98.8% 55.6 kmol/m <sup>3</sup> ·h 24.5 mol/100 mol
2	Productivity only	Maximize	3.78	5.56	127	0.24	Either	Either	87.5% 21.8 kmol/m <sup>3</sup> ·h 16.2 mol/100 mol
3	Soap formation only	Minimize	3.88	3.76	112	0.17	Either	KOCH <sub>3</sub>	72.2% 9.39 kmol/m <sup>3</sup> ·h 0.4 mol/100 mol
4	Yield and soap formation	Maximize and minimize	4.02	4.03	103	0.19	Reflux	Either	98.7% 33.5 kmol/m <sup>3</sup> ·h 7.6 mol/100 mol
5	Productivity and soap formation	Maximize and minimize	3.65	4.31	127	0.17	Recycle	Either	73.5% 24.3 kmol/m <sup>3</sup> ·h 5.2 mol/100 mol
6	Yield, productivity, and soap formation	Maximize, maximize, and minimize	4.08	3.91	106	0.15	Reflux	Either	95.0% 35.2 kmol/m <sup>3</sup> ·h 8.8 mol/100 mol
7	Yield only <sup>[b]</sup>	Maximize	3.78	4.43	100	0.20	Reflux	KOCH <sub>3</sub>	96.8% 39.8 kmol/m <sup>3</sup> ·h 9.6 mol/100 mol

<sup>[a]</sup> A = feed molar ratio (mol/mol), B = reaction time (min), C = reboiler temperature (°C), D = catalyst concentration (mol/mol), E = methanol circulation mode (recycle or reflux), and F = catalyst formulation (KOH or KOCH<sub>3</sub>).

<sup>[b]</sup> Optimization by considering the independent variables only (see table 5).

**Table 5. Experimental results by applying the modified optimum operating conditions.<sup>[a]</sup>**

Run	Product Composition (% wt)							Yield (%)	Conversion (%)	Productivity		
	ME	MG	DG	TG	GL	Catalyst	Soap			MeOH	kmol/m <sup>3</sup> ·h	m <sup>3</sup> /m <sup>3</sup> ·h <sup>[b]</sup>
1	94.40	2.84	0.00	1.25	0.09	0.00	0.29	1.13	96.31	98.72	33.6	11.3
2	94.29	0.00	2.06	1.41	0.10	0.01	0.33	1.82	96.54	98.55	34.1	11.4
3	95.00	0.58	0.00	2.46	0.10	0.02	0.84	1.01	96.99	97.48	34.1	11.4
Average	94.56	1.14	0.69	1.71	0.10	0.01	0.48	1.32	96.61	98.25	34.0	11.4
Std. Dev.	0.38	1.50	1.19	0.66	0.00	0.01	0.31	0.43	0.34	0.67	0.27	0.09

<sup>[a]</sup> The operating conditions were the same as in set 7 in table 4 with the feed molar ratio (variable A) and reaction time (variable B) modified to 3.85 mol/mol and 2.67 min, respectively.

<sup>[b]</sup> The average density and molecular weight of canola methyl esters were 886 kg/m<sup>3</sup> and 297 kg/kmol, respectively.

## CONCLUSIONS

The optimization of the transesterification of canola oil for biodiesel preparation was realized using a continuous-flow reactive distillation (RD) system. Six different process variables were studied experimentally and through statistical modeling for their effect on the performance of the RD reactor system. Process variables A through D (i.e., feed molar ratio, reaction time, reboiler temperature, and catalyst concentration) were more important than variables E and F (i.e., methanol circulation mode and catalyst formulation). For different optimization goals, the feed molar ratio ranged from 3.65:1 to 4.50:1 and the reaction time varied from 3.76 to 5.56 min. Although higher reboiler temperatures were tested in this study, the optimum reboiler temperatures were in the lower to medium range of 100°C to 130°C. The catalyst concentration for optimizations ranged from 0.13 to 0.24 mol/mol depending on the optimization goals.

It was found that, although the individual process variables affected the system performance separately to a certain extent, the interaction between the process variables seemed to have a synergistic effect and affected the system efficiency more significantly. The total reflux mode for methanol circulation and the use of potassium methoxide (KOCH<sub>3</sub>) as the catalyst formulation were preferred for process optimization in some cases. However, these variables did not differ significantly in other cases. The optimum product yields ranged from 96.8% to 98.6%, while the optimum productivity ranged from 21.8 kmol/m<sup>3</sup>·h (7.2 m<sup>3</sup>/m<sup>3</sup>·h) to 55.6 kmol/m<sup>3</sup>·h (18.5 m<sup>3</sup>/m<sup>3</sup>·h). When soap formation was minimized, the yield and productivity were at the levels of 72% and 9.3 kmol/m<sup>3</sup>·h (3.1 m<sup>3</sup>/m<sup>3</sup>·h), respectively. In general, soap formation was not a serious detriment to system efficiency under the operating conditions and feedstocks used. It was concluded that the importance of each process variable may differ according to optimization criteria; however, the maximization of product yield and reactor productivity is recommended for practical biodiesel production using the RD reactor system investigated in this study.

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## REFERENCES

- Barthorst, J. A., M. D. Staley, and D. A. Oester. 2002. Transesterification process. U.S. Patent No. 6,489,496.
- Connemann, J., A. Krallmann, and E. Fischer. 1994. Process for the continuous production of alkyl esters of higher fatty acids. U.S. Patent No. 5,354,878.
- Darnoko, D., and M. Cheryan. 2000. Kinetics of palm oil transesterification in a batch reactor. *J. American Oil Chem. Soc.* 77(12): 1263-1267.
- Freedman, B., R. Butterfield, and E. Pryde. 1986. Transesterification kinetics of soybean oil. *J. American Oil Chem. Soc.* 63(10): 1375-1380.
- Haas, M., S. Bloomer, and K. Scott. 2002. Process for the production of fatty acid alkyl esters. U.S. Patent No. 6,399,800.
- Hammond, E. G. 1991. Organization of rapid analysis of lipids in many individual plants: Vol. 12. Essential oils and waxes. In *Modern Methods of Plant Analysis*, 321-330. H. F. Linskens and J. F. Jackson, eds. Berlin, Germany: Springer-Verlag.
- Komers, K., R. Stioukal, J. Machek, and F. Skopal. 2001. Biodiesel from rapeseed oil, methanol, and KOH: 3. Analysis of composition of actual reaction mixture. *European J. Lipid Sci. Tech.* 103(6): 363-371.
- Noureddini, H., and D. Zhu. 1997. Kinetics of transesterification of soybean oil. *J. American Oil Chem. Soc.* 74(11): 1457-1463.
- Peter, S., R. Ganswindt, and E. Weidner. 2001. Methods for producing fatty acid esters. U.S. Patent No. 6,211,390.
- Van Gerpen, J. 2005. Biodiesel processing and production. *Fuel Processing Tech.* 86(10): 1097-1107.
- Van Gerpen, J., R. Pruszko, D. Clements, B. Shanks, and G. Knothe, eds. 2005. *Building a Successful Biodiesel Business*. Ames, Iowa: Self-published.
- Wimmer, T. 1995. Process for preparing fatty acids esters of short-chain monohydric alcohols. U.S. Patent No. 5,434,297.