

FUNCTION AND PERFORMANCE OF A PRE-REACTOR TO A REACTIVE DISTILLATION COLUMN FOR BIODIESEL PRODUCTION

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ABSTRACT. *This article describes an in-depth follow-up to previous studies showing that an oil-methanol mixer prior to an RD reactor played an important role in enhancing the overall performance of the RD reactor system. An in-line static mixer was used for the purpose of providing initial mixing of the reactants, heating the mixture up to the desired operating temperature, and carrying out a substantial part of the transesterification reaction in the early stage. It performed three functions: a reactant mixer, a heat exchanger, and a pre-reactor. This article reports the systematic investigations of the pre-reactor performance by examining the effects of process variables on the process evaluating parameters, and the operating conditions for optimum operation. A wide range of results was observed under different operating conditions. The product yield was as high as 84.60% and as low as 1.63%. The soap formation was in the range of 2.80% to 10.37%. The feed molar ratio, reaction time, and catalyst concentration all contributed positively to the product yield and soap formation. Although an optimum condition produced a product yield of 80.46% and soap formation of 5.18% with a 1.33 min reaction time, the optimization should be based on the integration of the whole RD reactor system rather than a collection of individually optimized components. This study of the pre-reactor serves as an analysis tool for part of the RD reactor system.*

Keywords. *Biodiesel, Canola oil, Continuous-flow reactor, Reactive distillation, Static mixer.*

A laboratory-scale continuous-flow reactor system using a reactive distillation (RD) technique has been developed and studied for preparing biodiesel from canola oil and methanol at the Biofuels Research Laboratory, University of Idaho (He et al., 2006). The major process variables, including methanol-to-oil molar ratio, reaction time, reboiler temperature, catalyst concentration, methanol circulation mode, and catalyst type, were systematically studied and optimized based on the overall performance of the RD reactor system (He et al., 2005). It was demonstrated that application of the RD technique to biodiesel production was very effective and efficient. This novel RD reactor system is superior to traditional systems, with the advantages of significantly reduced use of excess methanol, high unit productivity, and a considerably shortened reaction time. Under optimized conditions, the product yields and productivity were up to 98.8% and 18.5 m³/m³-h, respectively, with a soap formation of 0.48% wt in the crude biodiesel product.

Transesterification of vegetable oils to fatty acid esters is a homogeneous liquid reaction. Studies have shown that transesterification follows second-order kinetics and consists of a number of consecutive, reversible reactions (Freedman et al., 1986; Noureddini and Zhu, 1997; Darnoko and

Cheryan, 2000). The reaction rate in the early stage of transesterification is controlled by the mass transfer of alcohol to vegetable oil phase due to the limited solubility of methanol in vegetable oils (Van Gerpen, 2004). The reaction proceeds stoichiometrically with a fairly rapid rate before equilibrium is reached. The degree of triglycerides conversion is dependent on the excess alcohol used beyond its stoichiometry. Upon analysis of the transesterification mechanism and characteristics, an in-line static mixer was used prior to the RD reactor to carry out the early-stage reaction (He et al., 2005, 2006).

Previous studies have also shown that the oil-methanol mixer played an important role in enhancing the overall performance of the RD reactor system. The unit provided the initial mixing of the reactants, heated the mixture up to the desired temperature, and carried out a substantial part of the transesterification reaction in the early stage. Therefore, it performed three functions: a reactant mixer, a heat exchanger, and a pre-reactor. To examine its function and performance, systematic investigations were conducted on the pre-reactor. This article reports the experimental results of the performance of the pre-reactor by examining the effects of process variables on the process evaluating parameters, and the operating conditions for optimum operation of the pre-reactor.

MATERIALS AND METHODS

CHEMICALS AND REAGENTS

The crude canola oil and methanol used in this research as feedstocks were the same as in the previous study (He et al., 2005). The oil was screw-pressed 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 the derived fatty acids were calculated and used

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in data processing and calculations. Methanol (analytical grade) was purchased from Baker (Phillipsburg, N.J.) and used directly.

Potassium hydroxide and potassium methoxide were used as catalysts. Potassium hydroxide (KOH, ACS certified, purity >87.9% wt) was obtained from Baker (Phillipsburg, N.J.). Potassium methoxide (KOCH₃, 32% w/w solution in methanol) was obtained from Degussa Corporation, Germany. The alcohol/catalyst premix was prepared in such a way that when the KOH/methanol or KOCH₃/methanol was mixed with canola oil quantitatively, it would give the desired methanol-to-oil molar ratio. Analytical reagents and standard chemicals of triolein, diolein, methyl oleate, and glycerol used in analytical calibrations were all analytical grades and purchased from Sigma-Aldrich (St. Louis, Mo.).

EQUIPMENT AND EXPERIMENTAL SETUP

A laboratory-scale continuous-flow RD reactor system setup similar to that reported previously (He et al., 2005) was used in this study, except that the sampling port was located immediately after the pre-reactor but prior to the RD reactor column (fig. 1). The pre-reactor consisted of two sections. The first was a 150 mm (5 mL capacity) in-line static mixer (Cole-Parmer, Vernon Hills, Ill.) to blend the oil with the methanol/catalyst solution at room temperature. The second was an in-line static mixer of 10 mL capacity (Cole-Parmer, Vernon Hills, Ill.), which was heated by an electrical heating tape so that the outlet mixture temperature was maintained at 55°C. The temperature control of the pre-reactor was achieved by Fuji PXR4 PID controllers (TTI, Inc., Ft. Worth, Texas). The operating modes with and without methanol recycling were evaluated.

CHEMICAL ANALYSIS

The first sample was taken after 2 h, when the operation was in steady state, and subsequent samples were taken at 1 h intervals. The 5 mL samples were each treated with 3 mL of 0.1N HCl to stop the reaction and centrifuged at 3,000 rpm for 15 min to separate the glycerol phase that contained methanol, soap, and residual catalyst. The upper ester layer was analyzed without further treatment for the content of methyl esters and tri-, di-, and monoglycerides using an HP 1090 HPLC with an Altech 2000 ELSD (Altech Associates, Inc., Deerfield, Ill.). The analytical data were transformed into molar bases relative to the oil triglycerides in the feed before further processing. Separate samples were prepared and analyzed for the contents of soap and residual catalyst using the modified AOCS method (AOCS Cc 17-95; Van Gerpen et al., 2005). The composition profiles of the samples were converted to molar quantities per unit molar feed triglycerides for easy data processing and analysis (Komers et al., 2001).

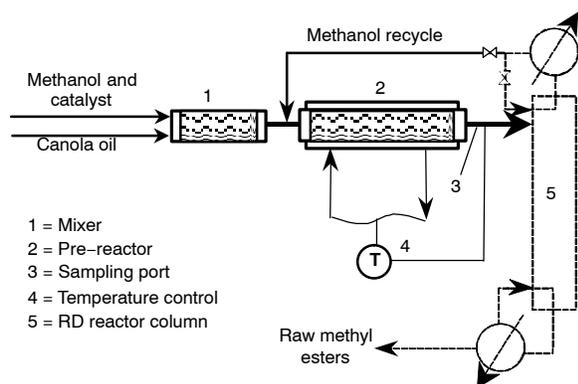


Figure 1. Diagram of the pre-reactor setup in the RD reactor system.

PROCESS VARIABLES

To determine the effects on the overall performance of the pre-reactor, five major process variables identified previously were chosen for this study: (A) feed methanol-to-triglycerides molar ratio or feed molar ratio, (B) reaction time (liquid retention time in the pre-reactor), (C) catalyst concentration in the feed, (D) catalyst type (KOH or KOCH₃), and (E) methanol recycle mode (with or without methanol recycle to the entrance of pre-reactor). Experiments were carefully arranged according to the experimental design (table 1) to obtain the maximum information.

PROCESS EVALUATING PARAMETERS AND DEFINITIONS

The parameters to evaluate the performance of the pre-reactor system included the fatty acid ester yield (YLD) and the by-product soap formation (SOAP). The reactant or triglycerides conversion rate (CONV) was also used in the process performance analysis. These parameters were defined the same as previously (He et al., 2005). All results obtained from chemical analyses and subsequent data processing were transformed into relative molar basis, e.g., mol of esters per unit mol of feed triglycerides (canola oil), to make the results comparable to those from other systems (Komers et al., 2001).

Once obtained from the analytical results, the process parameters were analyzed using the statistical package DOE Pro XL (Digital Computations, Colorado Springs, Colo.). DOE Pro XL is an experimental design 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 from the results of the statistical analyses.

RESULTS AND DISCUSSION

The effectiveness of the in-line static mixer as a biodiesel reactor was first tested separately. The effects of methanol-to-oil molar ratio, operating temperature, reaction time, and catalyst concentration were evaluated on the basis of oil conversion rate and product yield. Used as a pre-reactor to prepare the reactant mixture for the RD reactor system, the

Table 1. Experimental design and levels of process variables.

Exp. No.	Process Variables					Methanol Recycle
	A Feed Ratio (mol/mol)	B Reaction Time (min)	C Catalyst Concentration (mol/mol) (% wt)		D Catalyst Type	
1	4.0	2.22	0.10	0.73	KOH	No
2	4.5	3.33	0.15	1.10	KOCH ₃	Yes
3	4.5	1.33	0.20	1.46	KOH	No
4	4.0	1.67	0.25	1.83	KOCH ₃	Yes
5	3.0	1.67	0.15	1.10	KOH	No
6	3.5	2.22	0.15	1.10	KOCH ₃	No
7	3.5	1.67	0.20	1.46	KOH	Yes
8	3.5	3.33	0.25	1.83	KOH	No
9	4.0	3.33	0.20	1.46	KOCH ₃	No
10	4.5	1.67	0.10	0.73	KOCH ₃	No
11	3.0	3.33	0.10	0.73	KOH	Yes
12	3.0	1.33	0.25	1.83	KOCH ₃	No
13	3.5	1.33	0.10	0.73	KOCH ₃	Yes
14	4.0	1.33	0.15	1.11	KOH	Yes
15	3.0	2.22	0.20	1.46	KOCH ₃	Yes
16	3.5	2.22	0.25	1.83	KOH	Yes

in-line static mixer has a very short retention time or reaction time, typically 1.5 to 3.5 min (table 2). Under such a short reaction time and low catalyst application (0.10 mol/mol KOCH₃), the oil conversion rate and product yield were both low, regardless of the variations of the feed molar ratios, operating temperatures, and the reaction time. A higher oil-to-methanol ratio in the feed did not show a clear effect on the product yield due to the very early stage of the reaction. The reaction time change from 1.7 min to 2.5 min did not show an expected trend either. Temperature played a relative influential role; the product yield increased by about 60% as the temperature increased from 35 °C to 55 °C. Dramatic increases in oil conversion rate and product yield were observed when higher amounts of catalyst were used. With 2 min reaction time at 50 °C and 4:1 feed molar ratio, the conversion rate increased to 90% if the catalyst concentration was 0.25 mol/mol (1.83% wt), although the catalyst application should also be adjusted in practice according to other factors such as soap formation and economics.

To systematically investigate the performances of the pre-reactor scientifically, experiments were conducted based on the experimental design (table 1), and the results are summarized in table 3. The results were obtained by analyzing the samples, which were taken in triplicate at steady-state operation according to the procedures described in the Materials and Methods section. The small standard deviations show that the system generated consistent results when operated at steady state.

EFFECTS OF PROCESS VARIABLES

To understand the effects of the individual process variables and their interactions, the experimental data were analyzed using the DOE Pro statistical software. Multiple-response regression was performed on all the individual process variables (variables A through E in table 1) and the two-way interactions of the feed molar ratio (variable A) and reaction time (variable B) with the rest of the variables on the effects of CONV, YLD, and SOAP (table 3).

Statistical analyses of the experimental data of conversion rates and yields resulted in near perfect-fit multiple-response regression models, indicated by the large F-values at the specified degrees of freedom and small standard errors. Probability values far less than 0.05 in table 3 indicate that all

process parameters and the two-way interactions analyzed are significant in contributing to CONV and YLD. For soap formation, all process variables were insignificant (with probability values greater than 0.05) in the regression model except variables B (reaction time) and C (catalyst concentration), which have the probability values less than 0.01. This meant that soap would form at a constant rate regardless of the operating conditions, unless the reaction time and the concentration of the catalyst were increased. These two variables positively contributed to soap formation.

Tolerance in table 4 is the proportion of orthogonality for each variable. A tolerance of unity indicates an orthogonal (or non-linear) relationship, and a tolerance less than one is a sign of multi-collinearity with other variables in the regression model. Table 4 shows that all tolerance values are much less than unity, i.e., all process variables interacted with each other and contributed to the models. The relative importance and contribution of the process variables and some two-way interactions can be visualized from the Pareto charts of the multiple response regression models (fig. 2). Variables A, B, and C positively contributed to YLD and CONV, especially variable C, and its two-way interaction with B showed the strongest effects. On the other hand, variables D and E and their interactions with B and C contributed negatively to YLD and CONV. In other words, altering the catalyst from KOCH₃ to KOH or having no methanol recycle decreased the product yield. Careful observation revealed that feed molar ratio (variable A) and most of its two-way interactions affected soap formation negatively, i.e., increasing feed molar ratio would lead to less soap formation.

Figure 3 summarizes the statistical analyses of the effects of individual process variables on YLD, CONV, and SOAP. It is evident that CONV was affected by the process variables with similar trends as YLD. When variable A increased from 3:1 to 4:1, YLD fluctuated in the range of 30% to 40%. The lower product yield at feed molar ratio 3.5:1 was reflected by the higher soap formation. Further increasing the feed molar ratio to 4.5:1 led to a decrease in YLD and CONV. The cause of this unexpected observation is unclear. Longer reaction time (>2 min) gave higher product yields but also resulted in higher soap formation. There was a clearly increasing trend

Table 2. Preliminary experiments on static mixer as a pre-reactor.^[a]

Experimental Variable	Value	Product Composition (% wt)					YLD (%)	CONV (%)
		ME	MG	DG	TG	Me		
Feed molar ratio ^[b]	3:1	3.94	0.09	0.90	92.64	2.62	3.72	7.94
	4:1	3.19	0.12	0.94	95.98	9.77	3.08	15.04
	6:1	2.17	0.08	0.55	90.87	6.33	2.08	10.62
Temperature (°C) ^[c]	35	8.22	0.16	3.50	86.51	1.61	7.94	12.07
	45	3.99	0.15	1.15	93.25	1.56	3.86	7.80
	55	13.06	0.15	4.47	80.79	1.53	12.62	16.75
Reaction time (min) ^[d]	1.7	6.97	0.06	1.66	87.47	3.84	6.73	12.94
	2.0	5.42	0.06	1.63	92.89	0.00	5.23	7.74
	2.5	3.75	0.10	1.29	90.14	4.71	3.62	10.63
Catalyst concentration (% wt) ^[e]	1.5	18.23	0.09	4.29	77.39	--	13.39	23.04
	2.0	48.99	1.25	9.63	40.14	--	40.08	42.76
	2.5	90.40	0.43	2.50	6.67	--	71.48	90.45
	3.0	98.63	0.10	0.33	0.94	--	77.92	98.60

^[a]ME, MG, DG, TG, and Me are the compositions of the methyl esters, mono-glycerides, di-glycerides, triglycerides, and methanol, respectively, in the product mixture; YLD is the product ester yield; and CONV is the oil conversion rate.

^[b]Other operating conditions: 1% KOCH₃, 50 °C, 1.67 min.

^[c]Other operating conditions: 1% KOCH₃, molar ratio 4:1, 2.5 min.

^[d]Other operating conditions: 1% KOCH₃, 50 °C, molar ratio 4:1.

^[e]Other operating conditions: 50 °C, molar ratio 4:1, 2 min.

Table 3. Product compositions and calculated process evaluation parameters.^[a]

Exp. No.	Product Composition (mol/mol of triglycerides)								CONV (%)	YLD (%)	SOAP (mol/100 mol)
	ME	MG	DG	TG	Me	GL	CT	SP			
1	0.069 ±0.009	0.013 ±0.001	0.006 ±0.006	0.969 ±0.006	3.931 ±0.009	0.013 ±0.002	0.032 ±0.003	0.028 ±0.002	3.12 ±0.61	2.32 ±0.30	2.80 ±0.15
2	0.499 ±0.065	0.039 ±0.006	0.112 ±0.015	0.746 ±0.030	4.001 ±0.065	0.103 ±0.020	0.002 ±0.004	0.049 ±0.024	25.41 ±2.98	16.62 ±2.18	4.94 ±2.42
3	0.508 ±0.007	0.039 ±0.012	0.105 ±0.007	0.748 ±0.002	3.992 ±0.007	0.109 ±0.004	0.184 ±0.014	0.042 ±0.002	25.22 ±0.19	16.95 ±0.23	4.20 ±0.22
4	2.567 ±0.232	0.018 ±0.001	0.077 ±0.054	0.087 ±0.041	1.433 ±0.232	0.817 ±0.096	0.103 ±0.012	0.046 ±0.011	91.33 ±4.14	85.55 ±7.75	4.56 ±1.13
5	0.203 ±0.004	0.018 ±0.002	0.022 ±0.005	0.912 ±0.003	2.797 ±0.004	0.049 ±0.004	0.025 ±0.002	0.040 ±0.003	8.78 ±0.35	6.76 ±0.14	4.04 ±0.28
6	1.196 ±0.008	0.048 ±0.005	0.153 ±0.009	0.483 ±0.005	2.304 ±0.008	0.316 ±0.005	0.046 ±0.010	0.034 ±0.004	51.67 ±0.47	39.87 ±0.27	3.45 ±0.44
7	0.129 ±0.001	0.013 ±0.011	0.019 ±0.007	0.940 ±0.001	3.371 ±0.001	0.028 ±0.005	0.035 ±0.004	0.051 ±0.010	5.98 ±0.14	4.31 ±0.04	5.10 ±0.98
8	1.842 ±0.053	0.016 ±0.003	0.151 ±0.004	0.280 ±0.015	1.658 ±0.053	0.553 ±0.020	0.209 ±0.015	0.104 ±0.003	71.99 ±1.53	61.40 ±1.78	10.37 ±0.34
9	2.258 ±0.036	0.020 ±0.003	0.142 ±0.004	0.146 ±0.011	1.742 ±0.036	0.692 ±0.014	0.169 ±0.061	0.047 ±0.006	85.42 ±1.07	75.25 ±1.22	4.73 ±0.64
10	0.077 ±0.023	0.012 ±0.001	0.022 ±0.000	0.955 ±0.008	4.423 ±0.023	0.011 ±0.007	0.045 ±0.013	0.024 ±0.003	4.46 ±0.77	2.58 ±0.76	2.35 ±0.27
11	0.087 ±0.017	0.014 ±0.002	0.014 ±0.004	0.957 ±0.008	2.913 ±0.017	0.015 ±0.005	0.011 ±0.004	0.032 ±0.001	4.29 ±0.80	2.89 ±0.57	3.15 ±0.12
12	2.538 ±0.060	0.017 ±0.001	0.100 ±0.003	0.082 ±0.018	0.462 ±0.060	0.802 ±0.020	0.186 ±0.013	0.048 ±0.010	91.80 ±1.84	84.60 ±2.00	4.82 ±0.99
13	0.315 ±0.041	0.023 ±0.006	0.165 ±0.009	0.777 ±0.013	3.185 ±0.041	0.034 ±0.017	0.024 ±0.001	0.040 ±0.005	22.27 ±1.32	10.49 ±1.36	4.04 ±0.50
14	0.049 ±0.007	0.014 ±0.001	0.003 ±0.004	0.977 ±0.004	3.951 ±0.007	0.006 ±0.002	0.027 ±0.003	0.041 ±0.003	2.26 ±0.41	1.63 ±0.22	4.11 ±0.32
15	2.264 ±0.018	0.179 ±0.010	0.093 ±0.006	0.124 ±0.002	0.736 ±0.018	0.604 ±0.014	0.032 ±0.010	0.058 ±0.005	87.64 ±0.18	75.46 ±0.61	5.82 ±0.50
16	1.250 ±0.131	0.030 ±0.002	0.094 ±0.032	0.511 ±0.047	2.250 ±0.131	0.365 ±0.045	0.043 ±0.059	0.070 ±0.005	48.93 ±4.69	41.68 ±4.36	7.00 ±0.51

^[a] ME, MG, DG, TG, Me, GL, CT, and SP are the compositions of the methyl esters, mono-glycerides, di-glycerides, triglycerides, methanol, glycerol, catalyst, and soap, respectively, in the product mixture; CONV, YLD, and SOAP are the conversion rate, ester yield, and soap formation, respectively. The data are presented in the form of average ±standard error.

Table 4. Regression table of the process variables on the evaluation parameters.

Process Variables	Tolerance	Yield (YLD)		Conversion Rate (CONV)		Soap Formation (SOAP)	
		Coeff.	P (2 tails)	Coeff.	P (2 tails)	Coeff.	P (2 tails)
A (molar ratio)	0.114	3.22	0.038	3.34	0.007	-0.71	0.168
B (reaction time)	0.505	10.71	0.000	13.42	0.000	0.90	0.000
C (catalyst conc.)	0.096	44.35	0.000	46.90	0.000	1.41	0.011
D (catalyst type)	0.287	-13.90	0.000	-16.01	0.000	0.34	0.140
E (MeOH recycle)	0.157	-3.63	0.000	-4.01	0.000	-0.22	0.477
A×B	0.090	5.67	0.008	7.11	0.000	-0.70	0.315
A×C	0.107	16.91	0.000	21.61	0.000	-1.14	0.132
A×D	0.221	10.91	0.000	15.19	0.000	0.03	0.925
A×E	0.267	2.73	0.009	2.42	0.003	-0.41	0.224
B×C	0.023	40.42	0.000	43.89	0.000	0.22	0.872
B×D	0.150	10.11	0.000	10.74	0.000	-0.06	0.887
B×E	0.044	-15.58	0.000	-17.68	0.000	0.37	0.613
C×D	0.090	-23.69	0.000	-21.51	0.000	0.74	0.175
C×E	0.423	-5.52	0.000	-6.02	0.000	0.40	0.115
D×E	0.142	-6.12	0.000	-6.26	0.000	0.51	0.116
Constant		37.41	0.000	45.10	0.000	4.78	0.000
R ²		0.9961		0.9979		0.8792	
Std Error		2.447		1.917		0.8284	
F		542		1,038		15.5	

(continued)

Table 4 (continued). Regression table of the process variables on the evaluation parameters.

Process Variables	Tolerance	Yield (YLD)			Conversion Rate (CONV)			Soap Formation (SOAP)		
		Coeff.	P (2 tails)	MS	Coeff.	P (2 tails)	MS	Coeff.	P (2 tails)	MS
Source		SS	df	MS	SS	df	MS	SS	df	MS
Regression		48,730	15	3,249	57,251	15	3,817	160	15	10.7
Error		191.6	32	6.0	117.6	32	3.7	22.0	32	0.7
Total		48,921	47		57,369	47		182	47	

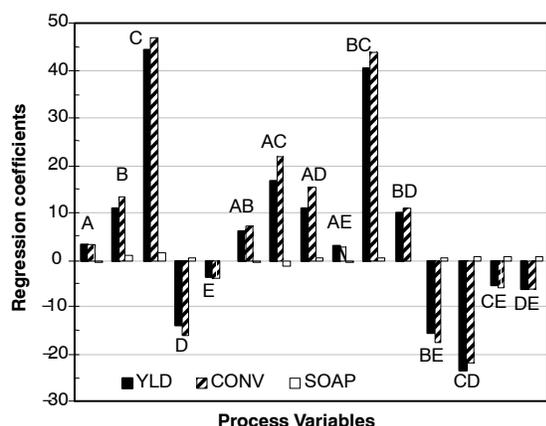
Table 5. System optimization of the operating variables and their interactions through statistical analyses.

Optimized Parameter	Optimum Criteria	Process Variables					Optimum Values (YLD and SOAP)
		A (mol/mol)	B (min)	C (mol/mol)	D (--)	E (--)	
Yield only	Maximize	4.28	2.47	0.19	KOCH ₃	Yes	64.10% 3.05 mol/100 mol
Soap formation only	Minimize	3.26	4.15	0.12	KOCH ₃	No	12.54% 4.39 mol/100 mol
Yield and soap formation	Maximize and Minimize	4.09	2.79	0.14	KOH	Yes	11.40% 4.12 mol/100 mol

Table 6. Experimental results by applying the modified optimum operating conditions.^[a]

Experiment	Product Composition (% wt)									YLD (%)	CONV (%)	SOAP (mol/100 mol)
	ME	MG	DG	TG	GL	Cat.	Soap	MeOH				
1	72.75	2.89	5.97	10.25	0.23	0.92	1.86	5.13	79.81	88.71	4.85	
2	72.70	0.95	5.82	12.24	0.23	0.89	2.03	5.14	79.59	86.54	5.31	
3	74.72	2.59	5.68	8.81	0.23	1.00	2.07	4.89	81.98	90.30	5.40	
Average	73.39	2.15	5.83	10.43	0.23	0.94	1.99	5.05	80.46	88.52	5.18	
Std Dev	1.15	1.04	0.14	1.72	0.00	0.06	0.11	0.14	1.32	1.88	0.29	

[a] The operating conditions for variables A through E were 4:1, 1.33 min, 0.20 mol/mol KOCH₃ and with methanol recycle, respectively.

**Figure 2. Relative effects of process variables on yield, productivity, and soap formation.**

for YLD and CONV as the catalyst concentration (variable C) increased. This is consistent with the observations discussed above (fig. 2). It was also shown that using KOCH₃ led to a significant increase in product yield and a lowered rate of soap formation than using KOH. Although a higher product yield was observed, the effect of methanol recycling on YLD and CONV was not as significant as expected. Meanwhile, no observable difference existed between methanol recycle modes in the pre-reactor.

OPTIMUM OPERATING CONDITIONS

Wide ranges of data on YLD, CONV, and SOAP were observed during the 16 experiments under different operating conditions. The product yield was as high as 84.60% and as low as 1.63%. To determine the overall efficiency of the pre-reactor under optimum conditions, the multiple-response optimization tools of the DOE Pro statistical software were

used, and the optimum sets of process variables as well as the combination of responses were determined (table 5).

To verify the predictability of the multiple-response regression model, a separate set of experiments was conducted according to the information obtained from the system optimization. The results of these experiments, shown in table 6, were from the analyses of the raw product mixture without any post-treatments such as washing and methanol stripping. The average esters content was 73.39% with a standard error of 1.15%. Besides unreacted glycerides, the methanol content was 5.05%, glycerol was 0.14%, and soap was 0.5%. The overall oil (or feed triglycerides) conversion rate was 88.5%. The experiments produced a yield of 80.46% with about 2% soap, which was equivalent to a relative high soap content of 5 mol soap per 100 mol of feed triglycerides. Comparing the results of the whole system reveals that the soap formation may occur more in the early stage (in the pre-reactor) than in the late stage (in the RD column) (He et al., 2005).

CONCLUSIONS

Experiments have confirmed that the in-line static mixer performed effectively as a reactant mixer, a heat exchanger, and a pre-reactor. The pre-reactor reached a product yield of 80% in a short reaction time. However, soap was produced under all operating conditions. As the feed molar ratio, reaction time, and catalyst concentration increased, yield and soap formation increased as well. The use of KOCH₃ as catalyst with methanol recycle showed a decrease in yield and soap formation. The pre-reactor is part of the reactive distillation reactor system for biodiesel production. The optimization should be based on the integration of the whole system (i.e., the reactants and catalyst preparation, the pre-reactor, the RD column, and the post-processing system) rather than

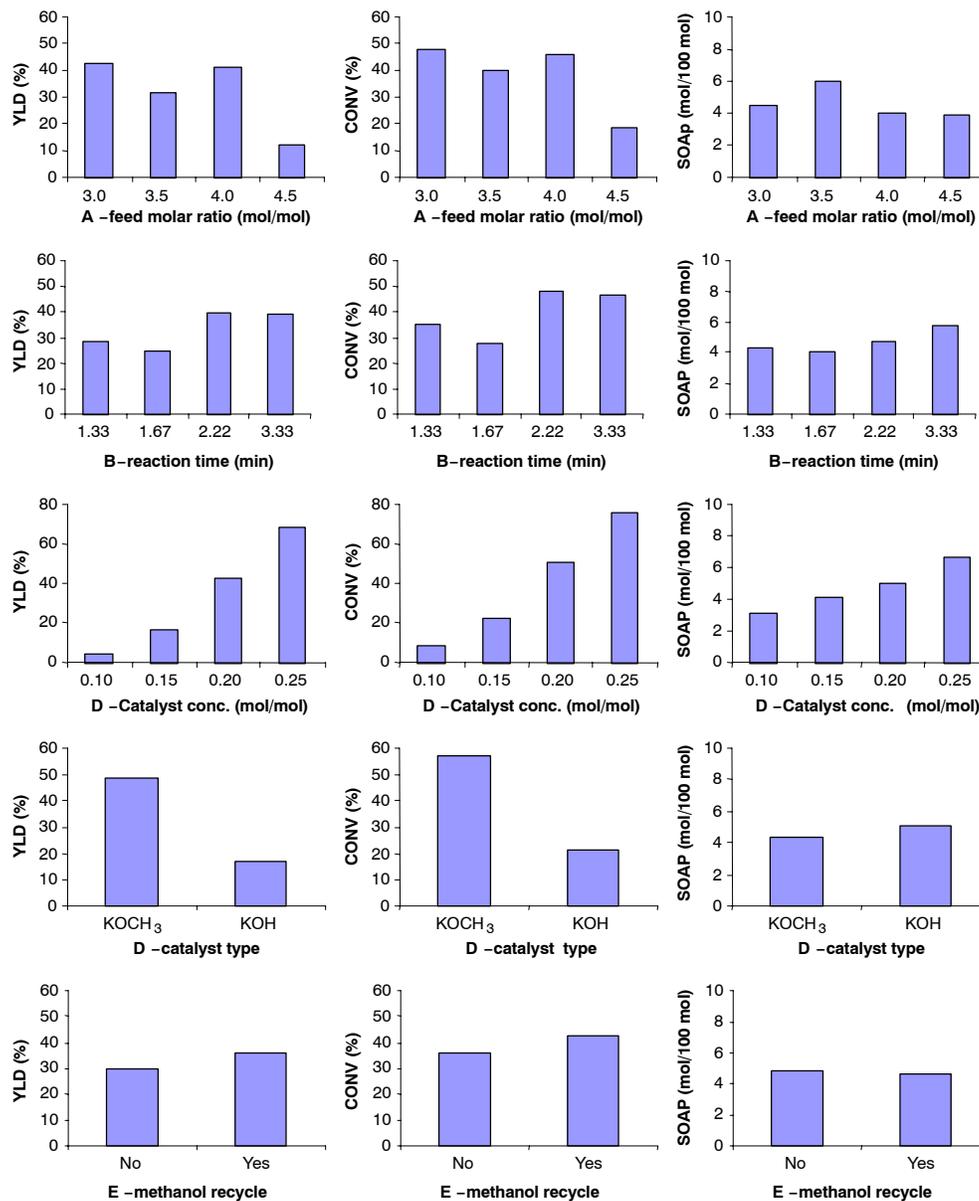


Figure 3. Effects of process variables on product yield, oil conversion rate, and soap formation.

a collection of optimized individual components. Therefore, the study of the pre-reactor serves as an analysis tool for part of the RD reactor system, and determination of its operating conditions should be eventually decided by the overall efficiency of the RD system.

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