

BIODIESEL PRODUCTION USING STATIC MIXERS

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ABSTRACT. *Static mixers, devices used for mixing immiscible liquids in a compact configuration, were found to be effective in carrying out initial transesterification reactions of canola oil and methanol. The objective of this study was to explore the possibilities of using static mixers as a continuous-flow reactor for biodiesel production. Biodiesel (canola methyl ester) was produced under varying conditions using a closed-loop static mixer system. Sodium methoxide was used as the catalyst. Process parameters of flow rate or mixing intensity, catalyst concentration, reaction temperature, and reaction time were studied. A full-factorial experimental design was employed, and samples were analyzed for unreacted glycerides as an indicator for biodiesel quality control. It was found that static mixers can be used for biodiesel production. In fact, given enough residence time, appropriate temperature, and high mixing rate, a reactor could consist solely of static mixers and pumps in a continuous-flow design. Temperature and catalyst concentration had the most influence on the transesterification reaction. The data clearly indicates separate inverse linear relationships between temperature and catalyst concentration versus total glycerin. The ASTM D6584 specification for total glycerin (0.24% wt, max.) was met at three of the four temperatures tested, utilizing two of the four catalyst concentrations. The most favorable conditions for completeness of reaction were at 60°C and 1.5% catalyst for 30 min.*

Keywords. *Biodiesel, Continuous flow, Reactor, Sodium methoxide, Static mixer.*

Global oil reserves are in decline, markets are becoming more competitive, many of the oil-producing countries are becoming unstable, and global warming issues are looming large on the horizon. As these problems escalate and diesel prices exceed three dollars a gallon in the U.S., biodiesel is getting unprecedented attention. Much of this attention is focused on production technology as efficiency and energy conservation are becoming more important than ever. Continuous-flow biodiesel production has become the industry standard, and the technologies are continuously evolving. Continuous transesterification of vegetable oils to mono-alkyl esters was proposed as early as in the 1940s (Trent, 1945; Allen et al., 1945) and studied widely until recent years (Bam et al., 1995; Nouredini et al., 1998; Darnoko and Cheryan, 2000; Antolin et al., 2002; Peterson et al., 2002; Van Gerpen and Knothe, 2005). A novel continuous-flow reactor using a reactive distillation (RD) technique has been successfully developed at the University of Idaho and has proven much more effective than existing biodiesel production technologies (He et al., 2005, 2006). In developing the process, we observed that in-line static mixers performed effectively as a pre-reactor, in addition to its function as a reactant mixer and a heat exchanger (He et al., 2007). Further investigations have shown

that a high percentage, up to 80%, of the reaction was accomplished in a short retention time (less than 5 min) in the static mixers placed prior to the RD column. A question was raised from this observation: is it feasible to use static mixers effectively as a reactor for biodiesel production?

In-line static mixers consist of specially designed stationary geometric mixing elements fixed within a pipe, which use the energy of the flow stream to create mixing. They are very effective in mixing liquids that are not readily miscible under normal conditions. Static mixers have no moving parts and thus bear the advantages of low maintenance and operating costs, as well as low space requirements. They are widely used in the chemical, pharmaceutical, petroleum, waste treatment, and food processing industries (Paul et al., 2003). As a mixing device, static mixers have been used in continuous-flow systems for biodiesel production (Nouredini et al., 2004; Peterson et al., 2002). However, to our knowledge, stand-alone static mixers as biodiesel reactors have not been reported. The objective of this study, therefore, is to explore the possibilities of using static mixers as a continuous-flow reactor for biodiesel production.

MATERIALS AND METHODS

CHEMICALS AND REACTANTS

Food-grade canola oil purchased from a local market and 99.9% reagent-grade methanol (J.T. Baker, Phillipsburg, N.J.) were used as the reactants throughout this study. The initial acid value (ASTM, 2004) of the oil was 0.10 mg KOH/g sample. Sodium methoxide (25% wt solution in methanol) was obtained from Degussa Corporation, Germany, and used as the catalyst.

EXPERIMENTAL SETUP AND OPERATION

A full-factorial experimental design was constructed with the aid of DOE Pro XL (Digital Computations, Colorado

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Table 1. Variable conditions.

	Variable A	Variable B	Variable C	Variable D
Stage	Mixing Intensity ^[a]	Catalyst Conc. (% wt)	Temp. (°C)	Time (min)
I	Low	0.5	30	15
	High	1.5	60	30
II	Low	0.5	30	30
	Low	0.75	40	30
	Low	1.5	60	30

^[a] In this study, mixing intensity is indirectly expressed by the flow rate of the reactant circulating in the static mixer. “Low” mixing reflects the low flow rate (474 mL/min), which has a nominal linear flow rate of 0.42 m/s. “High” mixing reflects the high flow rate (1740 mL/min), which has a nominal linear flow rate of 1.54 m/s. Considering the mechanism of static mixers, the change in Reynolds numbers is considerable between the two flow rates.

Springs, Colo.), a Microsoft Excel plug-in capable of performing multiple-response regression modeling, optimizations, and plot generation. Stage I was set up to look at extreme conditions over four process variables. There were 16 conditions run randomly in triplicate. From those results, a second set of trials was conducted to target the high-responding variables (temperature and catalyst concentration). Mixing intensity and reaction time were fixed and not used as variables (table 1). All of the trials were run with a 6:1 molar ratio of alcohol to oil.

The hardware for this experiment consisted of two stainless steel static mixers (4.9 mm ID × 300 mm long, Stratos Tube Mixer 250, Koflo Corp., Cary, Ill.). The Koflo Stratos Tube Mixer consists of 34 fixed right- and left-hand helical mixing elements designed for mixing light-viscosity to high-viscosity fluids. Both the elements and housing are constructed of 316L SS, and the mixing elements are fixed by 316L stainless steel TIG welds. The static mixers were coupled together with an assortment of 6.3 mm compression and pipe fittings and three 6.3 mm SS ball valves (inlet, outlet, and vent). The mixer loop was connected to an adjustable, piston-head metering pump (0 to 2200 mL/min, FMI, model QDX3, A.O. Smith, Milwaukee, Wisc.) via 6.3 mm rigid Teflon tubing. A glass funnel was fitted to the end of one of the tubes for ease of introducing the reactants, and a thermocouple was mounted to the end of the other mixer tube for temperature monitoring and control (fig. 1). Two sections of silicone rubber heat tape (12.7 × 600 mm, Omegalux, Stanford, Conn.) were wrapped around the mixer tubes to provide heat controlled via a Fuji PXR4 PID temperature controller (TTI, Inc., Williston, Vt.). The heat tape was wrapped with glass wool, and a length of foam pipe insulation was installed over the mixer loop.

The total capacity of the reactor system was 30 mL. The catalyst concentrations (0.5% to 1.5% by wt of oil) were made up to correspond to 24 mL of oil and 6 mL of catalyst/methanol solution. At the start of each trial, 24 mL of oil was introduced into the system and heated with the pump running. When the target temperature was achieved, 6 mL of the appropriate catalyst solution was added and the reactants were pumped around the loop for the appropriate period of time. At the end of each run, a 6 to 7 mL sample was drawn into a centrifuge tube containing 3 mL of 0.1 N HCl solution. The tube was inverted several times to stop the reaction and eventually spun to clarify the sample. Prior to

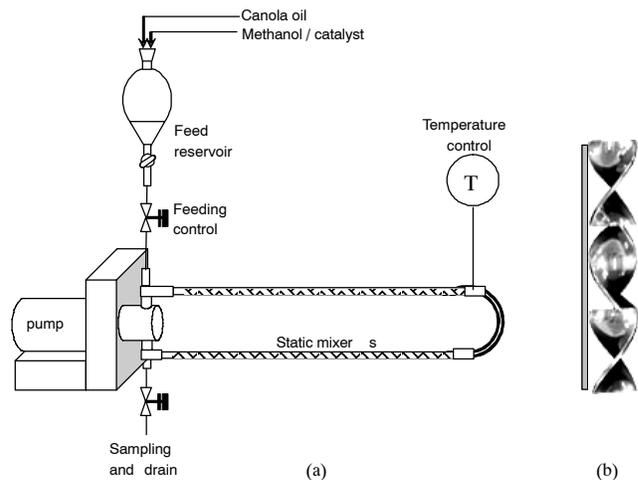


Figure 1. Experimental setup: (a) static mixer closed-loop system, and (b) internal structure of static mixers.

taking this sample, a small amount of the reacted mixture was wasted to flush out the sampling port. After taking the sample, the remainder of the mixture was taken, weighed, and titrated for soap and catalyst content (stage II only).

Unreacted glycerides were measured on a sample from each trial (72 total from 24 sets of conditions) per ASTM D6584 (ASTM, 2000). This method utilizes two internal standards and yields mono-, di-, and triglycerides data. Bound glycerin (unreacted glycerides) was calculated as a weighted percentage of the combination of mono-, di-, and triglycerides. The unreacted glycerides in the product mixture was termed the total glycerides and was used as the process evaluation parameter. Free glycerin was very low (within the ASTM D6751 specification) in every case; it was not of interest to the results of this study, and so was disregarded in the discussions.

ANALYTICAL PROCEDURES

Catalyst and soap measurements were made using AOCs Cc 17-79 (AOCs, 1996), and unreacted glycerides determinations were made by GC following ASTM D6584 (ASTM, 2000). The test procedures for catalyst and soap were modified slightly to identify all of the sodium that went into the process, whether in the form of sodium methoxide, the intact catalyst, or sodium soaps. The samples were titrated with 0.1 N HCl, first to identify the amount of base neutralized using phenolphthalein as the indicator, and then to identify the point at which all of the soaps have been split with the use of bromophenol blue as the indicator. This is a very useful tool in determining the effectiveness of the washing process. It was used in this study to determine loss of yield due to saponification.

SAFETY NOTE

These experiments were carried out in a fume hood to minimize the operator’s exposure to methanol vapors. Additionally, because of the corrosive nature of sodium methoxide, the operator was required to wear nitrile gloves and face protection in the event of a spill or explosion. Since methanol is highly flammable and may be explosive if mixed with air, it was necessary to have the FMI pump fitted with an explosion-proof motor and switch. The temperature controller was breaker protected and placed outside of the hood in a safe elevated position.

RESULTS AND DISCUSSIONS

EFFECTS OF PROCESS VARIABLES

The total glycerides contained in the product stream was used as the indicator for biodiesel quality and thus process effectiveness: the lower the total glycerides content in the product, the better quality of the product and the better effectiveness of the process. To evaluate the effectiveness of the static mixer as affected by process parameters, a full-factorial experimental design was employed. The experiments were randomly conducted regardless of the experiment number, and experiment results were obtained from triplicate samples. The averages and standard deviations of the total glycerides data from stage I are summarized in table 2. At higher catalyst concentration (1.5%) and higher reaction temperature (60°C), such as experiments 7, 8, 12, and 15, the total glycerides content was low and met the ASTM standard (0.24% wt). Experiment 4 was close to the ASTM standard but with a relative high standard deviation. It appears obvious from the data that the higher temperature and catalyst concentration had a greater effect in reducing total glycerides. Mixing intensity and reaction time did not play as important a role as did the catalyst concentration and reaction temperature. The statistical analysis further confirmed this observation.

ANOVA analysis and regression modeling (data not shown) were performed on all four process variables and their possible two-way and three-way interactions using DOE Pro XL (Digital Computations, Colorado Springs, Colo.). Statistical analysis of the experimental data resulted in very good fit response regression model between the process variables and the process evaluation variable (total glycerides content). The large F-values are the verifications of the viable regression on catalyst concentration and reaction temperature (table 3). Low probability values (0.017 for catalyst concentration, and 0.009 for reaction temperature) indicate that catalyst concentration and reaction temperature were significant in contributing to the total glycerides in the regressions model. The other two variables (mixing and reaction time) were not statistically significant in the

Table 2. Levels of variables and experiment results in stage I.

Exp. No.	Variables				Results	
	A	B	C	D	Total Glycerides (% wt)	
	Mixing	Conc. (% wt)	Temp. (°C)	Time (min)	Avg.	SD ^[a]
1	Low	0.5	30	15	5.64	0.50
2	Low	0.5	30	30	4.19	2.07
3	Low	0.5	60	15	1.09	0.10
4	Low	0.5	60	30	0.40	0.05
5	Low	1.5	30	15	1.18	0.98
6	Low	1.5	30	30	0.71	0.17
7	Low	1.5	60	15	0.18	0.01
8	Low	1.5	60	30	0.17	0.03
9	High	0.5	30	15	4.93	0.85
10	High	0.5	30	30	4.09	0.94
11	High	0.5	60	15	1.03	0.16
12	High	0.5	60	30	0.29	0.05
13	High	1.5	30	15	1.04	0.24
14	High	1.5	30	30	0.87	0.46
15	High	1.5	60	15	0.17	0.02
16	High	1.5	60	30	0.18	0.00

^[a] SD = standard deviation.

Table 3. ANOVA analysis of the four process variables.

Source	SS	df	MS	F	P	% Contrib.
Flow rate (A)	0.1697	1	0.1697	0.376	0.544	0.10
Cat. conc. (B)	55.10	1	55.10	122.1	0.000	31.20
Temp. (C)	68.70	1	68.70	152.2	0.000	38.89
Time (D)	3.584	1	3.584	7.934	0.008	2.03
A×B	0.1905	1	0.1905	0.422	0.521	0.11
A×C	0.0692	1	0.0692	0.153	0.698	0.04
A×D	0.1415	1	0.1415	0.313	0.579	0.08
B×C	31.30	1	31.30	69.37	0.000	17.73
B×D	1.7908	1	1.7908	3.964	0.055	1.01
C×D	0.4130	1	0.4130	0.914	0.346	0.23
A×B×C	0.0794	1	0.0794	0.176	0.678	0.04
A×B×D	0.0123	1	0.0123	0.027	0.870	0.01
A×C×D	0.1564	1	0.1564	0.346	0.560	0.09
B×C×D	0.011	1	0.0106	0.023	0.879	0.01
Error	14.91	33	0.4520			8.43
Total	176.74	47				

explored ranges. All two-way and three-way interactions showed insignificance except the catalyst concentration interactions with reaction temperature (B×C) and time (B×D), which showed slight significance. A Pareto chart allows visual identification of the relative importance of the individual process variables and two-way interactions on the total glycerides (fig. 2). Observations and analysis all showed that temperature and catalyst concentration (variables B and C) had a significant effect on reducing unreacted glycerides.

In order to confirm the relationships between total glycerides content and the significant variables (temperature and catalyst concentration), a second stage of trials were set up to determine the intermediate settings (table 4). Since there were no significant effects for flow rate and time from stage I, they remained constant (low and 30 min, respectively) in stage II. The same protocol was followed as in stage I, with the added measurements of catalyst and soap (AOCS Cc 17-79). Table 4 shows that the biodiesel produced met the total glycerol specification at three of the conditions (experiments 4, 7, and 8).

The soap formation and concentration of residual catalyst in biodiesel (table 4) are affected by the catalyst concentration. The more catalyst used, the higher catalyst and soap measurements are, which is a drawback for the use of the higher catalyst concentrations. It is interesting to note that

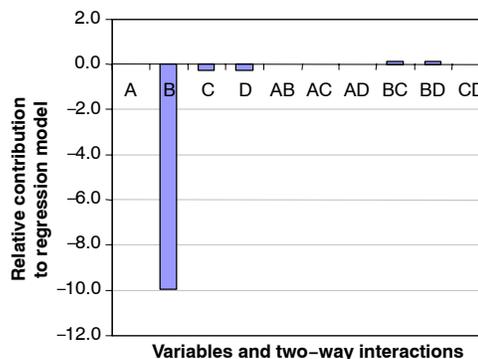


Figure 2. Relative effects of process variables on total glycerides content. Process variables: A = mixing intensity (low or high), B = catalyst concentration (% wt), C = reaction temperature (°C), D = reaction time (min). Two-letter labels are the two-way interactions of individual variables.

Table 4. Stage II experimental design and results.

Exp. No.	Variables ^[a]		Experiment Results ^[b]					
	B	C	Total Glycerides (% wt)		Residual Catalyst (ppm)		Soap Formation (ppm)	
	Cat. Conc. (% wt)	Temp. (°C)	Avg.	SD	Avg.	SD	Avg.	SD
1	0.75	30	4.11	0.12	4,560	306	1,591	259
2	1.0	30	1.66	0.59	5,849	181	1,854	825
3	0.75	60	0.29	0.08	4,085	601	2,433	699
4	1.0	60	0.20	0.02	5,361	210	2,788	430
5	0.5	40	3.05	0.69	2,610	475	2,826	1,057
6	0.5	50	1.93	0.25	2,321	418	3,818	1,053
7	1.5	40	0.23	0.04	7,453	461	2,599	413
8	1.5	50	0.19	0.03	8,258	472	2,158	648

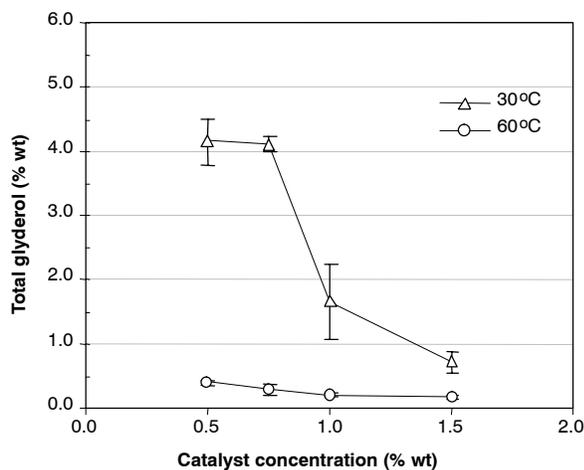
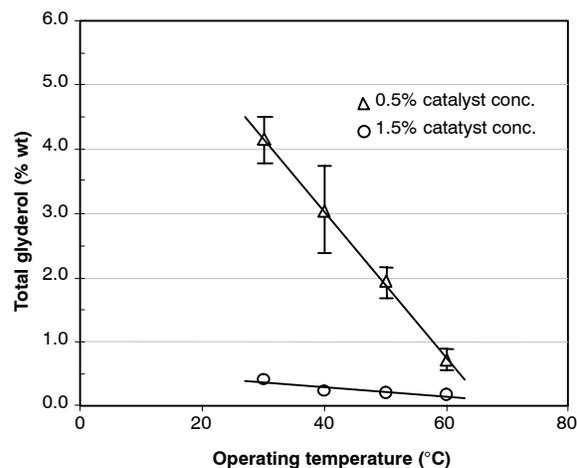
[a] The other two process variables (mixing intensity and reaction time) were kept constant at low and 30°C, respectively.

[b] SD = standard deviation.

with 0.5% wt catalyst, more of the sodium was found as soap than as catalyst, whereas with the other three concentrations, more of the sodium was measured as sodium methoxide than as soap. By combining results from stages I and II, trend lines were established for catalyst concentration and temperature while holding flow rate and time constant, as indicated in table 4.

Figure 3 shows that an inverse relationship exists between catalyst concentration and total unreacted glycerides. At 30°C, the reaction does not progress enough in 30 min to produce fuel that meets the ASTM total glycerin specification. It was met, however, at 60°C using 1% wt and 1.5% wt catalyst concentrations.

Figure 4 shows a similar inverse relationship between reaction temperature and unreacted total glycerides for two catalyst concentrations. At 0.5% wt sodium methoxide, none of the trials made fuel that met the total glycerin specification. However, at 1.5% wt, the specification was met at three of the four temperatures (40°C, 50°C, and 60°C). Combining the results discussed above, it was concluded that quality biodiesel can be produced in a reactor that consists solely of static mixers and pumps in a continuous-flow mode. The operating conditions to achieve quality biodiesel that met ASTM standard were higher reaction temperatures of 40 to 60°C with a catalyst concentration of 1.5% wt. Meanwhile, the reaction time and mixing were kept at moderate

**Figure 3. Total glycerides at varying catalyst concentrations.****Figure 4. Total glycerides at varying temperatures.**

conditions, e.g., 15 to 30 min, and medium mixing intensity, respectively. Another condition that produced satisfactory quality biodiesel was 60°C reaction temperature and 1% wt catalyst concentration.

CONCLUSIONS

Static mixers, which are normally used in conjunction with more elaborate biodiesel production schemes, can be used as a stand-alone reactor system. Different combinations of four process variables (temperature, flow rate, reaction time, and catalyst concentration) were tested in a full-factorial experimental design, and fuel samples were analyzed for total glycerides. Experiment results indicated inverse relationships between temperature and catalyst concentration verses total glycerides. Four of the process variable combinations produced fuel that met ASTM 6584 for total glycerin. Those conditions were temperatures of 40°C to 60°C with a catalyst concentration of 1.5% wt of oil, and 60°C with 1% wt catalyst concentration. The condition with the lowest total glycerides was 60°C and 1.5% wt catalyst.

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