Process Optimization of Biodiesel Production Using Alkaline Catalysts

A. Singh, B. He, J. Thompson, J. Van Gerpen

ABSTRACT. *The most commonly used method for biodiesel preparation is via transesterification of vegetable oil using alkaline catalysts. Biodiesel yield and oil conversion are affected by operating conditions including the catalyst formulation and concentration. Application of alkaline catalysts can also lead to undesired soap formation. This study evaluated the alkaline catalyst effects on biodiesel yield and soap formation in transesterifying methanol and canola oil at different catalyst concentrations, reaction temperatures, and methanol-to-oil molar ratios. Four different alkaline catalysts, i.e., potassium hydroxide, sodium hydroxide, potassium methoxide, and sodium methoxide, were studied and compared on molar basis through a 4-factor 3-level experimental design. It was observed that methoxide catalysts led to better biodiesel yields than hydroxide catalysts. The methoxide catalysts not only accelerated the reaction but also elevated the conversion equilibrium. Based on statistical optimization, the operating conditions for maximizing biodiesel yield and minimizing soap formation were potassium methoxide as catalyst at 0.2 mol/mol (1.59%wt), reaction temperature of 50°C, and methanol-to-oil molar ratio of 4.5:1. Experimental verification gave 95.8% biodiesel yield and 0.75%wt soap.*

Keywords. *Biodiesel, Alkaline catalyst, Transesterification, Canola oil.*

Several ways have been researched and demonstrated for preparing biodiesel from virgin and waste vegetable oils, but base-catalyzed transesterification is still the most widely used method in biodiesel production. Among the most commonly used alkaline catalysts in the biodiesel industry are potassium hydroxide (KOH) and sodium hydroxide (NaOH) flakes which are inexpensive, easy to handle in transportation and storage, and are preferred by small producers. Alkyl oxide solutions of sodium methoxide ($NaOCH_3$) or potassium methoxide ($KOCH_3$) in methanol, which are now commercially available, are the preferred catalysts for large continuous-flow production processes. In transesterification, the effective species of catalysis is the methoxide radicals (CH_3O-). The activity of a catalyst depends upon the amount of methoxide radicals available for the reaction (Komers et al., 2001a, b). For sodium or potassium hydroxide, methoxide ion is prepared *in situ* by reacting hydroxide and methanol:

$$OH^- + CH_3OH \rightarrow CH_3O^- + H_2O \tag{1}$$

This reaction also yields water that remains in the system. Hydrolysis of triglycerides and alkyl esters may occur due to the presence of water, which further leads to the formation of free fatty acids and thus to undesired soap. Saponification will also occur if a strong base, e.g., NaOH or KOH, is present in the system by reacting with esters and triglycerides directly. On the other hand, the water problem can be avoided if sodium and potassium methoxide solutions, which can be prepared water-free, are applied. Additionally, although the use of methoxides cannot avoid soap formation if the feedstock contains free fatty acids, which is also true for use of KOH or NaOH, but very little saponification of esters or triglycerides occurs because methoxides behave as weak Lewis bases.

The extent of transesterification and side reactions depends upon the types of feedstock, catalyst formulation, catalyst concentration, reaction temperature, and methanol-to-oil ratio. Free fatty acid and moisture content in the reactant mixture also play important roles in biodiesel production (Ma and Hanna, 1999). In the transesterification of vegetables oils and animal fats, each mole of triglycerides reacts stoichiometrically with 3 moles of a primary alcohol and yields 3 moles of alkyl esters (biodiesel) and 1 mole of glycerol (by-product). The actual mechanism of the transesterification reaction consists of sets of equilibrium reactions in series and all of the reactions are reversible (Freedman et al., 1986; Noureddini and Zhu, 1997; Darnoko and Cheryan, 2000).

Freedman et al. (1986) showed that $NaOCH_3$ is a more effective catalyst formulation than NaOH and almost equal oil conversion was observed at 6:1 alcohol-to-oil molar ratio for 1%wt NaOH and 0.5%wt $NaOCH_3$; whereas Ma et al. (1998) observed NaOH was a better catalyst than $NaOCH_3$ in transesterification of beef tallow. Vicente et al. (2004) reported higher yields with methoxide catalysts, but the rate of reaction was highest for NaOH and lowest for $KOCH_3$ at 65°C, a methanol-to-oil ratio of 6:1, and a catalyst concentration of 1%wt.

Because of the difference in the chemical molecular weights, the amount of methoxides available for each mole of triglyceride will differ at the same weight concentration. Therefore, the proper comparison of the effectiveness of

Catalyst Formulation	Formula	Molecular Weight	mol/mol at 1 %wt[a]
Sodium hydroxide	NaOH	40.0	0.220
Potassium hydroxide	KOH	56.1	0.157
Sodium methoxide	NaOCH$_3$	54.0	0.163
Potassium methoxide	KOCH$_3$	70.1	0.126

[a] Based upon the molecular weight of canola oil = 882.1g/mol which was averaged according to the fatty acid profiles of canola oil used in this study.

catalysts should be conducted based on the molar concentration of the catalyst formulation, not the weight concentration. Table 1 summarizes the molecular weights and molar percentages of the catalyst formulations when 1%wt of each catalyst was used against canola oil. Sodium hydroxide shows the highest molar concentration due to its low molecular weight.

This article reports the study on process optimization in transesterifying methanol and canola oil using four alkaline catalyst formulations by examining their effects on biodiesel yield and soap formation at different catalyst molar concentrations, reaction temperatures, and methanol-to-oil molar ratios. Optimum operating conditions for maximizing biodiesel yield and minimizing soap formation were determined by statistically analyzing the experimental data using a multiple response optimization statistical software and further verified through experimentation.

MATERIALS AND METHODS

CHEMICALS AND REAGENTS

Crude canola oil and methanol were used in this research as the feedstocks. The canola oil was obtained from the oil seed processing plant at the Department of Biological and Agricultural Engineering of the University of Idaho (Moscow, Idaho). The oil was screw-pressed and left to settle for several weeks, effectively allowing for some natural degumming to occur. The acid value of the oil was 1.97-mg KOH/g sample. Methanol (analytical grade) was purchased from J.T. Baker (Phillipsburg, N.J.). The four alkaline catalyst formulations used in this study were potassium hydroxide (KOH), sodium hydroxide (NaOH), potassium methoxide (KOCH$_3$), and sodium methoxide (NaOCK$_3$). Sodium hydroxide (ACS certified, purity 99.99%) and potassium hydroxide (ACS certified, purity > 87.9%wt) were from J.T. Baker (Phillipsburg, N.J.). Potassium methoxide (32% wt solution in methanol) and sodium methoxide (25% wt solution in methanol) was obtained from Degussa Corporation (Dusseldorf, Germany).

EXPERIMENTS

The set of experiments was constructed using a Taguchi experimental design and randomly conducted to evaluate the four factors at three levels each (table 2). The four factors were: A) catalyst formulation, B) catalyst concentration, C) reaction temperature, and D) methanol-to-oil molar ratio. The catalyst concentration was compared on a molar basis while corresponding weight percent was also mentioned. The reactions were carried out in a 250-mL baffled-conical flask placed in a water bath shaker with temperature control. The

speed of the shaker was fixed at 240 r/min for all experiments. Canola oil (100 g) and the desired methanol and catalyst amount were transferred into the flasks and placed in the water bath operated at the desired temperature. All 12 experiments were run in triplicate. After 10-min agitation the reacted mixtures were transferred to separatory funnels and the glycerol was separated after settling. The methanol was then removed from both methyl ester and glycerol layer by heating at 90°C for 30 min.

The experiments were compared based on two process parameters: yield and total soap formed per mol of oil. The statistical analysis on process parameters was performed using the statistical package DOE PRO XL (Digital Computations, Colo.). DOE PRO XL is an experimental design Microsoft Excel (Redmond, Wash.) plug-in and capable of performing multiple response regression modeling, multiple response optimizations, and multiple interaction plot generation. The effects of various process variables on yield and total soap were determined based on the results of the statistical analyses. The optimum process variable combination was then determined by maximizing the process yield and conversion while minimizing soap formation.

CHEMICAL ANALYSIS

The ester phase was washed after being neutralized with 0.5-mL 0.1N HCl/mL sample, and centrifuged at 3000 r/min for 15 min. The product was analyzed for the compositions of methyl esters, tri-, di-, and mono-glycerides using an HP 1090 HPLC with ELSD detector according to the method described by Komers et al. (2001a). Both the ester and glycerol phase were analyzed for soap and catalyst content using modified AOCS method Cc-17-79 (Van Gerpen et al., 2005).

RESULTS AND DISCUSSION

The results of product yield and soap formation of all experimental runs are summarized in table 2. The standard deviations for the yield were lower compared to those for the soap formation. The values for yields varied from 53.24% to 94.27% while the soap values varied from 1.69- to 37.09-mmol/mol oil. The amount of soap produced included the soap formed from the neutralization of the free fatty acids and triglyceride saponification. Acid value tests showed that all of the free fatty acids were converted to soap during the reaction.

EFFECTS OF PROCESS VARIABLES

Preliminary ANOVA analysis performed on all four process variables and their possible two-way interactions showed that only the catalyst formulation to its concentration (A×B) and catalyst formulation to reaction temperature (A×C) had significant contributions among the two-way interactions. The rest were insignificant and negligible. Additional ANOVA analysis was performed on all individual process variables and only the two-way interactions of A×B and A×C. The effects of process variables on product yield and soap formation were evaluated by statistically averaging the response values of particular factor levels (fig. 1). Results showed that there were significant differences in product yields among the four catalyst formulations. Potassium-based catalysts gave better yields than the sodium-based

Table 2. Process evaluation parameters and experimental results.

Run No.	Catalyst Formulation (A)	Catalyst Concentration (B)		Temperature (C) (°C)	MeOH-to-Oil Molar Ratio (D) (mol/mol)	Yield (%)	Total Soap	
		(mol/mol)	(% wt)				(mmol/mol oil)	(wt%)
1	KOH	0.1	0.63	40	3.0	67.90 ±0.67	11.79 ±2.02	1.17 ±0.20
2	KOH	0.2	1.27	50	4.5	91.27 ±0.28	18.41 ±0.49	1.82 ±0.05
3	KOH	0.3	1.90	60	6.0	89.27 ±0.24	37.09 ±1.96	3.87 ±0.19
4	NaOCH$_3$	0.1	0.61	50	6.0	85.41 ±0.39	8.96 ±0.46	0.89 ±0.05
5	NaOCH$_3$	0.2	1.22	60	3.0	89.13 ±0.16	13.72 ±1.77	1.36 ±0.17
6	NaOCH$_3$	0.3	1.84	40	4.5	90.44 ±0.42	1.69 ±0.96	0.17 ±0.10
7	KOCH$_3$	0.1	0.79	60	4.5	92.23 ±0.36	7.29 ±3.40	0.72 ±0.34
8	KOCH$_3$	0.2	1.59	40	6.0	91.79 ±0.53	7.72 ±1.59	0.76 ±0.16
9	KOCH$_3$	0.3	2.38	50	3.0	94.27 ±0.27	15.35 ±1.88	1.52 ±0.19
10	NaOH	0.1	0.45	50	4.5	82.50 ±0.50	8.88 ±0.30	0.88 ±0.03
11	NaOH	0.2	0.90	40	3.0	53.24 ±0.30	5.93 ±1.15	0.59 ±0.11
12	NaOH	0.3	1.35	60	6.0	90.19 ±0.17	15.38 ±1.10	1.52 ±0.11

catalysts and methoxide catalysts gave higher yields than corresponding hydroxide catalysts:

$$KOCH_3 > NaOCH_3 > KOH > NaOH$$

Effects of catalyst formulation on soap did not follow a clear trend. Generally, potassium-based catalysts resulted in higher soap formation than the corresponding sodium-based catalysts. Only KOH was found to have a significantly higher level of soap formation than the other three and was the worst catalyst in terms of soap formation:

$$NaOCH_3 > NaOH > KOCH_3 >> KOH$$
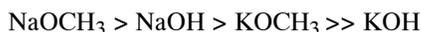
It is true that the rate of reaction is hindered with the decrease in catalyst activity. In alkaline-catalyzed transesterification, the catalyst activity decreases due to its consumption by side reactions. This would explain the lack of a linear increase in yield with the increase in catalyst concentration (fig. 1b). On the other hand, soap formation increased exponentially with catalyst concentration (fig. 1f). An increase in reaction temperature had a positive effect on both transesterification and saponification reactions. Temperature also influenced the reaction rate and equilibrium for both reactions (fig. 1c, 1g). Increasing the feed molar ratio had a positive effect on reaction yields because it increased the

reactant concentration that helps drive the reaction equilibrium forward. The molar ratio, however, had an unpredicted effect on the saponification. Theoretically, methanol as a catalyst carrier should not have any effect on soap formation. At the same level of catalyst application, the catalyst concentration in the methanol phase was relatively high with lower methanol-to-oil ratios, which resulted in a higher diffusion rate of catalyst in the oil phase, thus a higher reaction rate with free fatty acids or triglycerides. While at higher methanol-to-oil ratio, the catalyst concentration was relatively low but the oil solubility in methanol increased, which should have a decrease of soap formation. The results showed a decrease in soap formation once the molar ratio increased from 3:1 to 4.5:1, but an increase when the molar ration increased from 4:5:1 to 6:1 (fig. 1h). The explanation of this is unclear to the authors.

The experimental data (table 2) were analyzed with multiple regression model procedure of the statistic software DOE Pro to fit the following second order polynomial equation:

$$Y = a_0 + a_1 A + a_2 B + a_3 C + a_4 D$$
$$+ a_5 AB + a_6 AC + a_7 A^2 + a_8 B^2 + a_9 C^2 + a_{10} D^2 \quad (2)$$
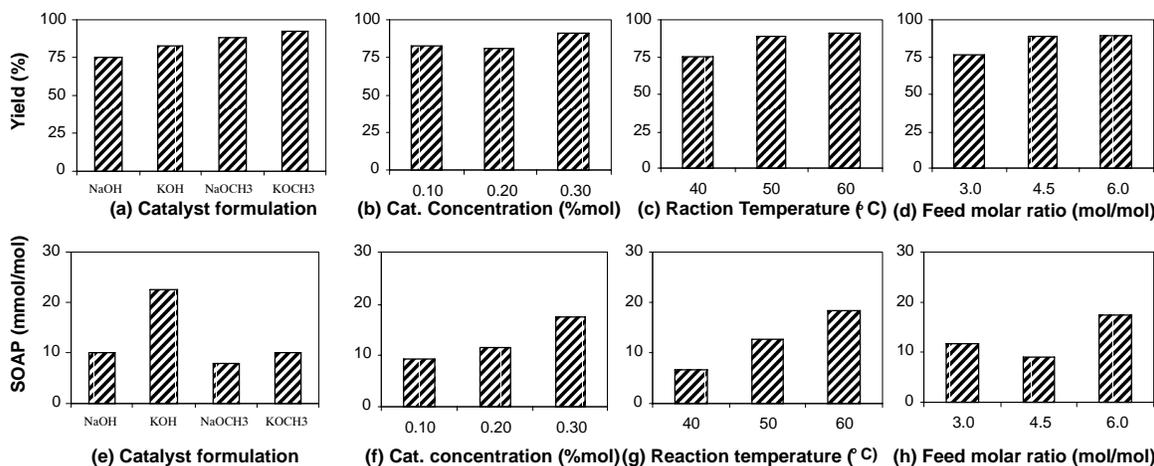
Figure 1. Effects of process variables on product yield and soap formation.

where Y is the response, either product yield or total soap formation; a's are the regression coefficients; A, B, C, and D are coded independent variables: A = 1 (KOH), 2 ($NaOCH_3$), 3 ($KOCH_3$), or 4 ($NaOH$), B = 0.1 – 0.3 (mol/mol), C = 40 – 60 (°C), and D = 3 – 6 (molar ratio). The regression models for both responses were governed by the following equations, respectively:

$$Yield\ (\%) = 100.44 - 2.71A + 6.15B + 4.82C$$
$$+ 3.93D - 15.64AB + 19.85AC$$
$$- 12.92A^2 - 10.76B^2 - 8.73C^2$$
$$+ 6.81D^2$$

(3)

$$(R^2 = 0.8547)$$

$$Total\ Soap\ (mmol/mol) = 4.22 - 5.26A + 2.79B$$
$$+ 4.59C + 0.593D - 5.49AB + 0.822AC$$
$$+ 0.802A^2 + 0.134B^2 - 2.85C^2 + 8.74D^2$$

(4)

$$(R^2 = 0.9198)$$

Process variables have varying effects on the process evaluating parameters. A wide range of data on process evaluating parameters has been obtained with the 12 experiments (table 2). The yield ranged from 53.24% to 94.27%. Similarly, the total soap varied from 5.93 to 37.09 mmol/mol (0.59% to 3.87%). The optimum set of process variables was determined by applying the multiple response optimization tool of the statistical software to the experimental data. To maximize yield and minimize soap formation, the conditions were $KOCH_3$ as the catalyst with 0.2 mol/mol, reaction temperature 50°C and 4.5:1 feed molar ratio. The calculated optimum results were 99% product yield and 8.6 mmol/mol (0.85%) total soap formation.

To verify the predictability of the multiple response regressions models, a separate set of experiments were conducted according to the information obtained from the process optimization. The results of the experiments shown in table 3 were from the analyses of the crude ester and glycerol layers. The experiments resulted in an average product yield of 95.8% with a standard deviation of 0.94% and a total soap formation of 7.56 mmol/mol, or 0.75%, with standard a deviation of 0.95 mmol/mol (0.09%). The small standard errors of methyl esters compositions indicate that the reaction under the optimum conditions yielded a raw biodiesel product consistently. Compared to that obtained from the statistical analysis, the results were agreeable: the yield was 3.1% lower than the predicted but the soap formation was 1 mmo/mol (relatively 12%) less.

The optimum conditions may differ according to the feedstocks used and process applications. However, the

above experimental and statistical optimizations provided the necessary information of the effects of the four process variable combination on product yield and undesirable soap formation. An important piece of information obtained was that a high product yield can be achieved with a methanol to canola oil ratio of 4.5 under the conditions used in this study.

CONCLUSIONS

From the comparison at different concentrations, reaction temperatures, and feed molar ratios, potassium-based catalyst formulations gave better yields than the sodium-based catalysts; methoxide catalysts gave higher yields than corresponding hydroxide catalyst formulations. However, potassium-based catalyst formulations resulted in higher soap formation than the corresponding sodium-based catalyst formulations. The optimum set of process variables was determined by maximizing product yield and minimizing soap formation. The optimized set of conditions were: $KOCH_3$ as the catalyst at a concentration of 0.2 mol/mol, reaction temperature of 50°C, and a 4.5:1 feed molar ratio. Process optimization predicted an optimum yield of 99% with a total soap formation of 0.85%. The verification experiments under the optimum process conditions resulted in 95.8% yield and 7.56 mmol/mol (0.75%) total soap formation.

REFERENCES

Darnoko, D., and M. Cheryan. 2000. Kinetics of palm oil transesterification in a batch reactor. *J. Am. Oil Chem. Soc.* 77(12): 1263-1267.

Freedman, B., R. Butterfield, and E. Pryde. 1986. Transesterification kinetics of soybean oil. *J. Am. Oil Chem. Soc.* 63(10): 1375-1380.

Komers, K., R. Stioukal, J. Machek, and F. Skopal. 2001a. Biodiesel from rapeseed oil, methanol and KOH. 3. Analysis of composition of actual reaction mixture. *Eur. J. Lipid Sci. Techol.* 103(6): 363-371.

Komers, K., R. Stioukal, J. Machek, and F. Skopal. 2001b. Biodiesel from rapeseed oil, methanol and KOH. 2. Composition of solution of KOH in methanol as reaction partner of oil. *Eur. J. Lipid Sci. Techol.* 103(6): 359-362.

Ma, F., L. D. Clements, and M. A. Hanna. 1998. Effects of catalyst, free fatty acids and water on transesterification of beef tallow. *Transactions of the ASAE* 41(5): 1261-1264.

Ma, F., and M. Hanna. 1999. Biodiesel production: A review. *Bioresource Technol.* 70(1): 1-15.

Noureddini, H., and D. Zhu. 1997. Kinetics of transesterification of soybean oil. *Applied Engineering in Agriculture* 74(11): 1457-1463.

Van Gerpen, J. 2005. Biodiesel processing and production. *Fuel Processing Technology* 86(10): 1097-1107.

Vicente, G., M. Martinez, and J. Aracil. 2004. Integrated biodiesel production: a comparison of different homogeneous catalysts system. *Bioresource Technol.* 92(3): 297-305.

Table 3. Experimental results under the optimum operating conditions.

Run No.	Composition (%wt)				Yield (%)	Soap	
	ME	MG	DG	TG		(mmol/mol)	(%wt)
1	97.28	0.89	0.55	1.28	96.86	7.58	0.75
2	95.88	0.91	1.23	1.98	95.46	6.60	0.65
3	95.50	1.29	1.73	1.48	95.08	8.50	0.84
Average	96.22	1.03	1.17	1.58	95.80	7.56	0.75
Std	0.94	0.23	0.59	0.36	0.94	0.95	0.09