BIOdiesel Tech NOTES

Issue TN #5 (Summer 2006)

Biodiesel Education Program, University of Idaho
Sponsored by USDA under the Farm Bill

COMPARISON OF ALKALINE CATALYSTS FOR BIODIESEL PRODUCTION

Base-catalyzed transesterification is the most widely used method for biodiesel production. The most commonly used base catalysts are potassium hydroxide (KOH) and sodium hydroxide (NaOH), and solutions of sodium methoxide ($NaOCH_3$) or potassium methoxide ($KOCH_3$) in methanol. In transesterification, the active catalyst species is the methoxide radical (CH3O-). The activity of a particular catalyst depends upon the amount of methoxide radicals that are available for the reaction.

Hydrolysis of triglycerides and alkyl esters may occur if water is present, which leads to the formation of free fatty acids and thus to undesired soap. Saponification will also occur if a strong base reacts with esters and triglycerides directly. Use of methoxides does not avoid soap formation, especially if the feedstock contains free fatty acids, but methoxides cause less saponification of esters or triglycerides than KOH and NaOH.

The extent of transesterification and side reactions depends upon the type 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. In the transesterification of vegetables oils and animal fats, each mole of triglyceride reacts 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 a set of equilibrium reactions in series and all of the reactions are reversible. Because of the difference in the chemical molecular weights, the amount of methoxide available for each mole of triglyceride will differ at the same weight concentration of catalyst. Therefore, the proper comparison of the effectiveness of catalysts should be conducted based on the molar concentration of the catalyst formulation, not the weight concentration.

Our study compares the results of four alkaline catalysts including yield and soap at different catalyst molar concentrations, reaction temperatures, and methanol-to-oil molar ratios.

RESULTS AND DISCUSSION

The results for product yield and soap formation of all the experimental runs are summarized in Table 1. Yield is defined as the weight of methyl esters in the product divided by the theoretical amount from the oil. 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

Table 1. Yield and Soap Formation for Different Catalysts

Run No.	Process Variables					Experimental Results		
	Catalyst Formulation	Catalyst Concentration		Temperature (°C)	MeOH-to-Oil Molar Ratio	Yield	Total Soap	
		(mol /mol)	(% wt)		(mol/ mol)	(%)	(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

and from triglyceride saponification in both the biodiesel and glycerin. Acid value tests showed that all of the free fatty acids were converted to soap during the reaction.

Table 2. Analysis of methyl ester and glycerin.

Composition (% wt)					Yield	Soap	
Run No.	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 dev.	0.94	0.23	0.59	0.36	0.94	0.95	0.09

EFFECTS OF PROCESS VARIABLES

Preliminary analysis of variance performed on the four process variables and their possible two-way interactions showed that only the catalyst formulation-concentration and catalyst formulation-reaction temperature had significant contributions among the two-way interactions. The effects of the process variables on product yield and soap formation were evaluated by statistically averaging the response values of the particular factor levels. 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 catalysts and methoxide catalysts gave higher yields than the corresponding hydroxide catalysts. Generally, potassium-based catalysts resulted in higher soap formation than the corresponding sodium-based catalysts.

KOH was found to have a significantly higher level of soap formation than the other three and was the worst catalyst in terms of resistance to soap formation. The rate of reaction was hindered by the decrease in catalyst activity. In base-catalyzed transesterification, the catalyst activity decreases due to its consumption by side reactions. On the other hand, soap formation increased exponentially with the catalyst concentration. An increase in reaction temperature increased the rate of both the transesterification and saponification reactions. Increasing the alcohol-to-oil molar ratio had a positive effect on reaction yields because it increased the reactant concentration that helped drive the reaction equilibrium forward.

Process variables have varying effects on the yield and soap levels. The optimum set of process variables was estimated by applying the multiple response optimization tool of the statistical software to the experimental data. To maximize yield and minimize soap formation, the optimum conditions were: $KOCH_3$ as the catalyst at 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 prediction of the multiple response regression models, a separate set of experiments were conducted at the conditions obtained from the process optimization.

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 a standard deviation of 0.95 mmol/ mol (0.09%). The small standard errors indicate that the reaction under the optimum conditions provided consistent data. The results were close to the estimate although the yield was 3.1% lower than the statistical prediction but the soap formation was 1 mmo/mol (12%) less. The optimum conditions may differ according to the feed stocks used and process applications. However, the above experimental and statistical optimizations provided the necessary information regarding the effects of the four process variable combinations 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 only 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 higher yields than the sodium-based catalysts. Methoxide catalysts gave higher yields than the corresponding hydroxide catalyst formulations. However, potassium-based catalyst formulations resulted in higher soap formation than the corresponding sodium-based catalyst formulations. Optimum sets of process variables were estimated by maximizing the product yield and minimizing soap formation. The optimized set of conditions were: KOCH3 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%. Verification experiments under the optimum process conditions resulted in 95.8% yield and 7.56 mmol/mol (0.75%) total soap formation.

For more information, see; Singh, A. B.He, J. Thompson, and J. Van Gerpen, (2006) "Process Optimization of Biodiesel Production using Different Alkaline Catalysts," Applied Engineering in Agriculture, 22(4) pp. 597-600.