Phase Distributions of Alcohol, Glycerol, and Catalyst in the Transesterification of Soybean Oil

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ABSTRACT: Two-phase base-catalyzed transesterification of vegetable oils is the most common method for making biodiesel. The reaction starts as separate oil and alcohol phases. At the end of the reaction, the mixture, if allowed to settle, consists of an upper ester-rich layer and a lower glycerol-rich layer. The compositions of these layers from the methanolysis and ethanolysis of soybean oil were measured. Synthetic mixtures and actual reaction mixtures were used either to represent or generate steady-state reaction mixtures resulting from the initial condition of 6:1 alcohol/oil molar ratio and catalyst concentration (1.0 wt% sodium methoxide or 1.26 wt% sodium ethoxide). At 23°C, for methanolysis, 42.0% of the alcohol, 2.3% of the glycerol, and 5.9% of the catalyst were in the ester-rich phase at steady state. In ethanolysis, 75.4% of the ethanol, 19.3% of the glycerol, and 7.5% of the catalyst were in the ester-rich phase. The volume of the glycerol-rich phase decreased from methanolysis to ethanolysis to propanolysis; butanolysis remained monophasic throughout. The results explain some of the general kinetic behavior observed in transesterifications and provide useful information for alcohol recovery and product purification.

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KEY WORDS: Base-catalyzed transesterification, biodiesel, ethanol, methanol, phase behavior.

Two-phase base-catalyzed transesterification of vegetable oils is the most common method for making biodiesel. The reaction, as normally practiced, commences as two phases. These are an upper methanol phase, in which the catalyst is dissolved, and a lower vegetable oil phase. Stirring initiates the reaction, which transforms to another two-phase system comprising an ester-rich phase and a glycerol-rich phase. When stirring is stopped, the glycerol-rich phase settles to the bottom. Since the production of biodiesel standard fuel requires extremely high conversion and efficient isolation of the ester from the glycerol by-product, it is particularly important to characterize the steady-state compositions of the final phases.

Many studies (1–3) have shown that the transmethylation reaction decelerates prematurely. It was previously concluded that this was due to the destruction of catalyst through soap formation. Feuge and Gros (4) reported that for the ethanolysis of peanut oil, more than 50% of the catalyst was destroyed in the first 15–20 min at 50°C. Boocock *et al*. (5) measured the catalyst (NaOH) concentration for base-catalyzed methanolysis of soybean oil (SBO) at 23°C and found that 67–83% of the catalyst was "depleted" in about the same time. This was at first attributed to soap formation by the irreversible attack of hydroxide ion on ester groups. When the reaction mixture is acidified, this soap is converted into FA. However, if all of the catalyst is consumed (1.0 wt% sodium hydroxide based on the weight of oil) by this reaction, then after acidification the FFA content in the transesterified product will be 7.0%, which is equivalent to an acid number of 14 based on oleic acid. Such high values are not usually observed.

In a later study, Zhou and Boocock studied the phase behavior of two-phase base-catalyzed transesterification of TG (6). The results showed that the depletion of catalyst was largely due to its removal by the glycerol-rich phase, which separated. Recently, Chiu, Goff and Suppes (7) measured the phase distributions of methanol and catalyst in a simulated methanolyis mixture of vegetable oil, methyl ester and glycerol. They used potassium hydroxide (KOH) as the catalyst, whereas the biodiesel industry currently uses sodium methoxide. The authors did not cite the glyceride contents or the acid number (a measure of FA content) of the methyl ester that was used in their simulations. The presence of MG and DG could possibly affect the distribution of alcohol, glycerol, and catalyst between the ester-rich and glycerol-rich phases. In addition, FA neutralize and remove base to form soap.

In this study, we first used a base-free mixture of methanol, glycerol, and methyl ester to simulate the ester-rich and glycerol-rich phases at the end of the methanolysis reaction. The base was not included because it was not possible to measure the liquid components in its presence. The concentrations of methanol, glycerol, and methyl ester in the ester-rich and glycerol-rich phases were measured. The catalyst concentrations in the two phases were also determined for both a base-containing synthetic mixture and an actual reaction mixture. For the reaction mixture, we used a 6:1 methanol/oil molar ratio and 1.0 wt% concentration (based on the oil) of sodium methoxide, which is equivalent to 0.74 wt% of sodium hydroxide or 0.98 wt% potassium hydroxide on a molar basis. The base concentration was approximately 50% higher than that used commercially. However, it is in line with that used in many literature studies. In addition, we wished to complete the reactions as much as possible and thus avoid complications that could arise

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from the surfactant influences of residual MG and DG. It should be noted that for a 6:1 methanol/oil molar ratio, half the alcohol is consumed at steady state. In addition, one mole of oil produces three moles of ester. Therefore, the simulation mixture should have a methanol/ester molar ratio of 1.0. We also investigated how the chain length of the linear primary alcohol affects the distribution of components in the ester-rich and glycerol-rich phases by studying ethanolysis and, to a lesser extent, propanolysis and butanolysis. We also used a base-free simulation mixture to study the steady-state phase composition after ethanolysis. A sufficiently pure ethyl ester was not available, so methyl ester was used to make the base-free simulating mixture for ethanolysis. Ethyl ester has only one more carbon atom than methyl ester in a relatively large molecule, so ethyl ester has a polarity essentially the same as methyl ester. The substitution was also possible because, in the absence of base, no transesterification occurred. Ethanolyis reactions were also performed as for methanolyis to measure the final distribution of the base.

The overall objective was to determine the distributions of the reaction components, including catalyst, between the two phases at the end of methanolysis and ethanolysis reactions. This information is relevant to the kinetics and steady-state positions of each reaction and is also useful for alcohol recovery, product purification, and waste disposal in biodiesel production. Propanolysis of SBO was carried out under the same molar conditions to measure the relative volumes of the final two phases, but their compositions were not measured. Butanolysis was also conducted and found to be monophasic throughout.

EXPERIMENTAL PROCEDURES

Materials. The SBO used for this study was a food-grade product (water content: 107 ppm, Presidents' Choice) purchased from Sunfresh Limited (Toronto, Ontario, Canada). The following chemicals were supplied by Sigma-Aldrich Chemical Company (Milwaukee, WI): methanol (anhydrous, 99.9+%, water content: 30 ppm), ethanol (anhydrous, water content: 352 ppm), 1-butanol (anhydrous, 99.9+%, water content: 283 ppm), glycerol (99.5%, spectrophotometric grade), sodium methoxide (25 wt% in methanol), THF (anhydrous, 99+%), sodium hydrogen sulfate monohydrate (+99%), *N*-methyl-*N*-trimethylsilytrifluoroacetamide (MSTFA), *N,N*-dimethylformamide (DMF) (anhydrous, 99.8%), and sulfuric acid volumetric standard (0.0995 N solution in water).

Preparation of ASTM methyl ester from SBO. Crude biodiesel was obtained by a one-phase base-catalyzed methanolysis of SBO. SBO (20.0 g), methanol (22.4 mL), and THF (22.0 mL) were placed in a 150-mL flat-bottomed flask equipped with a magnetic stirrer (methanol/oil molar ratio 24:1), and the mixture was stirred to form a homogeneous phase. The THF was used to form one phase throughout and thus allow the reaction to reach equilibrium. Sodium methoxide (0.20 g, 1.0 wt% based on the weight of oil) was then weighed and dissolved in 2.8 mL methanol (methanol/oil molar ratio 3:1) in a 20-mL vial. The resulting solution was added to the mixture and the stirring was continued for an additional 20 s. After 10 min of reaction time, the reaction was stopped by adding 0.78 g of sodium hydrogen sulfate monohydrate. The pH of the solution was 6–7 moist (wide-range indicator paper), and the resulting sulfate was removed by filtration. The excess methanol and THF were removed at reduced pressure (36 mm Hg) at 60°C by using a Büchi Rotavapour and a water aspirator. The resulting mixture was cooled to room temperature, and the glycerol layer was allowed to settle for 4 h. The crude biodiesel was then distilled, and the fractions boiling in the temperature range of 180–200°C at a pressure of 10 mm Hg were collected. The total glyceride content of the distilled product was determined by the ASTM D 6584 GC method (8). Only MG was present at a concentration of 0.27 wt%. The acid number as determined by the modified AOCS Official Method Cd 3a-63 (9) was 0.74, which is equivalent to 0.37 wt% of oleic acid. The water content was less than 0.02 wt% as determined by using an EM Science (Gibbstown, NJ) Aqua Star V-200 Titrator.

Base-free simulated alcoholysis mixtures. SBO methyl ester (10.50 g) and glycerol (1.05 g) were weighed and placed in a 20-mL vial, followed by the addition of methanol (1.40 mL) with a calibrated pipette. This provided an alcohol/methyl ester molar ratio of 1:1. The vial was capped, shaken, and placed in a water bath at 40°C for 1 h with occasional stirring. It was then removed from the water bath and cooled to room temperature. The mixture was centrifuged to ensure complete separation of the glycerol phase. The ester layer was removed using a Pasteur pipette and weighed. In the case of the base-free simulated ethanolysis mixture, SBO methyl ester (10.50 g), glycerol (1.05 g), and ethanol (2.00 mL) were placed in a 20-mL vial. All other conditions and procedures were the same as described above.

Base-containing simulated methanolyis mixture. The distribution of catalyst was determined by using both a synthetic mixture and an actual transesterification reaction mixture. SBO methyl ester (10.50 g), glycerol (1.05 g), methanol (1.00 mL), and 25 wt% sodium methoxide in methanol solution (0.46 mL) were placed in a 20-mL vial. The amount of sodium methoxide was adjusted so that any FFA in the biodiesel was neutralized to form soap and still provide 1.0 wt% catalyst concentration. A similar mixture could not be prepared to simulate methanolysis because no suitable ethyl ester was available, and the use of methyl ester would have resulted in transesterification.

Methanolysis and ethanolysis. For methanolysis, SBO (10.00 g), methanol (1.1 mL), and 25 wt% sodium methoxide solution (0.43 mL) were placed in a 20-mL vial. The vial was capped and vigorously shaken every 5 min over a period of 1 h. The reaction mixture was then centrifuged at 14,000 g to ensure complete separation of the glycerol-rich layer. The ester layer was removed with a Pasteur pipette. For ethanolysis, SBO (10.00 g), ethanol (1.50 mL), and 21 wt% sodium ethoxide solution (0.55 mL) were placed in a 20-mL vial. All other conditions and procedures were then the same as described for methanolysis.

Analyses. The concentrations of glycerol and methanol in the ester-rich and glycerol-rich phases of the base-free mixtures were determined by a GC method (10), in which ethanol and 1,4-butanediol were used as internal standards for quantitative measurement. The calibration curves for alcohol and glycerol were obtained using standard solutions containing different concentrations of methanol, ethanol, glycerol, and 1,4-butanediol in DMF.

To determine the catalyst concentration in the ester phase, a sample (5.0 g) was weighed in a 125-mL Erlenmeyer flask. Distilled water (5 mL) and 6 drops of 1 wt% of phenolphthalein indicator in isopropanol were added to the flask. The samples were then titrated with 0.01 M sulfuric acid to determine the base concentration. A similar titration was performed on samples (0.3 g) of the glycerol-rich phase.

RESULTS AND DISCUSSION

First, it should be noted that this study did not include the measurement of soap (salts of FA). In those cases where the methoxide catalyst was used, hydroxide ions were inevitably present in small amounts because the components contained trace amounts of water. These hydroxide ions could form soap. However, only a small amount was formed. For example, it can be shown that if the water concentration of the methanolyis mixture had been 200 ppm, then even the maximum soap formation possible could have produced only 0.25 wt% soap (based on the ester). This is even less than the soap formed (0.37 wt%) by interaction of the FA content of the methyl ester substrate with the sodium methoxide. The actual amount of soap formed would have been less than the total of these two percentages and was insufficient to influence phase distribution. This is reinforced by the study of Chiu, Goff, and Suppes (7), which used potassium hydroxide and yet obtained similar phase distributions in methyl ester systems to those reported here. In addition, throughout the reactions, the surfactant properties of the MG and DG would have overwhelmed those of any soap.

Figures 1 and 2 are the gas chromatograms of the ester-rich and glycerol-rich phases for a base-free simulated methanolysis. The signals for methyl palmitate, oleate, linoleate, and linolenate, which are seen in Figure 1, are not seen relative to the glycerol signal (peak 5) in Figure 2, which shows that there was little methyl ester in the glycerol-rich phase. This is because in the absence of surfactants (MG and DG), methyl ester is not soluble in the glycerol. Similar observations were made for the base-free simulated ethanolysis mixture.

Table 1 shows that the ester-rich phase in simulated methanolysis contained 0.21 wt% of glycerol and 4.3 wt% of methanol. These values exceeded the allowable free glycerol (0.02 wt%) and methanol content (0.3 wt%, calculated from the Flash Point) under the ASTM standard for biodiesel (B100) (8). Glycerol and methanol are highly soluble in water, whereas biodiesel is not. Therefore, in commercial processes, following separation of the glycerol phase and evaporation of methanol, residual methanol and glycerol may be removed from the biodiesel phase by a water wash.

From Table 1 one can see that in methanolysis, the methanol concentration in the glycerol-rich phase was 33.1 ± 1.0 wt%.

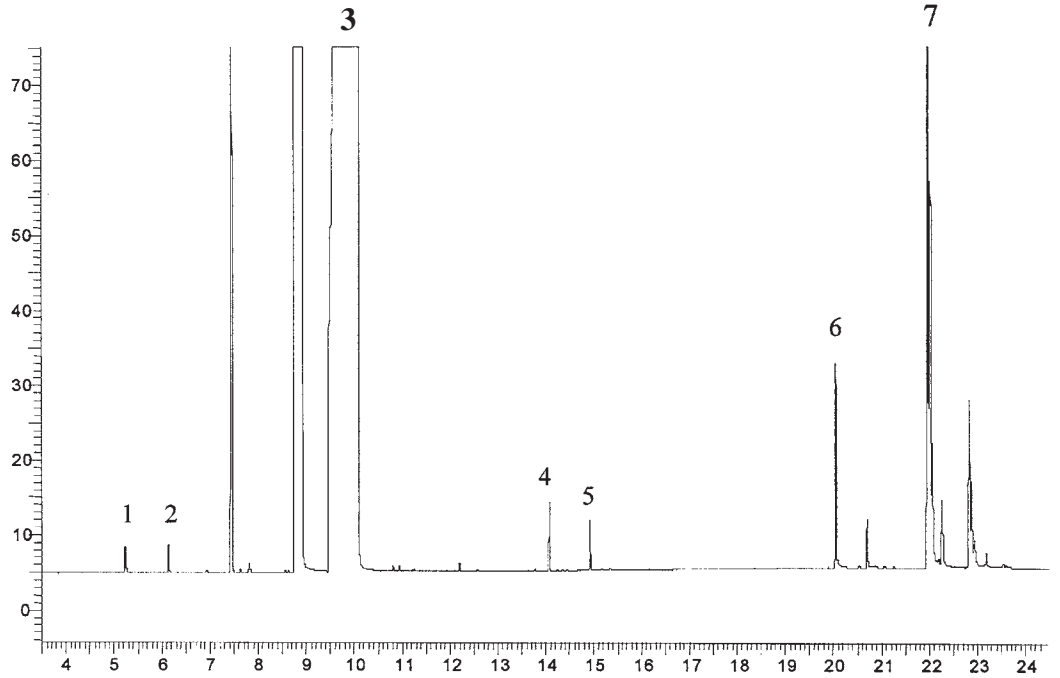

FIG. 1. Gas chromatogram of ester-rich phase in base-free simulated methanolysis. 1 = Trimethylmethoxysilane; 2 = Trimethylethoxysilane; 3 = N,N-dimethylformamide; 4 = Internal standard, 1,4 Bis-(trimethysilyloxy)-butane; 5 = Glycerol as 1,2,3-Tris-(trimethylsilyloxy)-propane; 6 = Methyl palmitate; 7 = Methyl oleate, linoleate and linolenate.

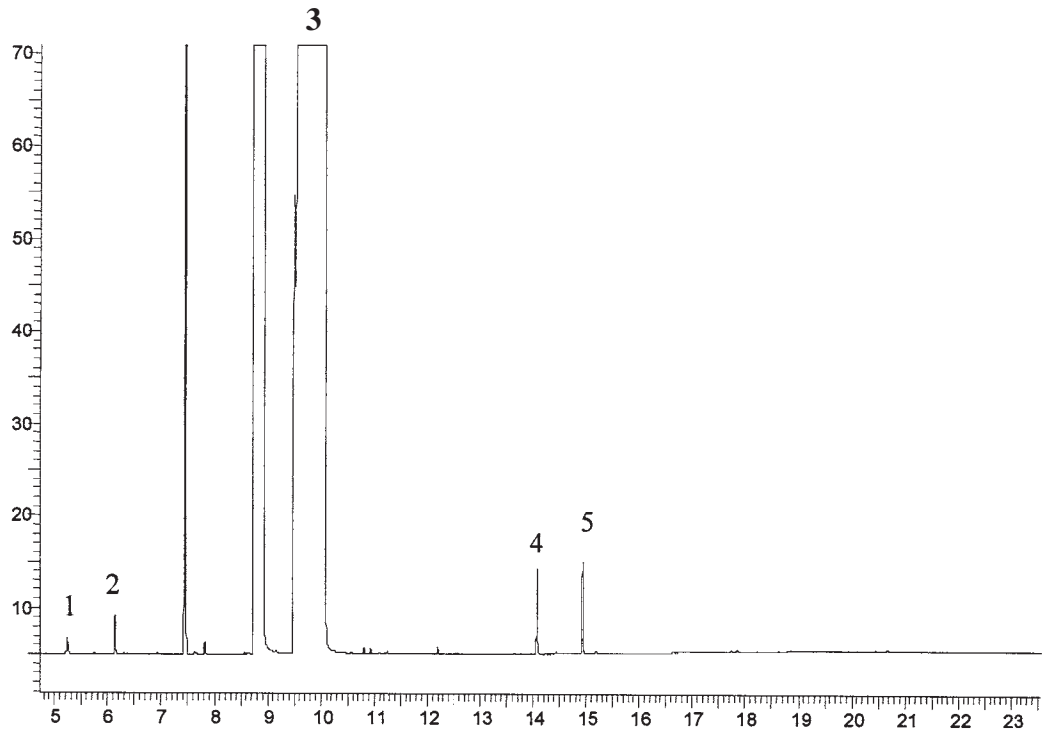

FIG. 2. Gas chromatogram of glycerol-rich phase in base-free simulated methanolysis. 1= Trimethylmethoxysilane; 2 = Trimethylethoxysilane; 3 = N,N-dimethylformamide; 4 = Internal standard, 1,4-Bis-(trimethysilyloxy)-butane; 5 = Glycerol as 1,2,3 Tris-(trimethylsilyloxy)-propane.

This value was obtained by taking the methanol concentration determined in the base-free simulation and correcting it for the catalyst concentration (5.57 ± 0.01 wt%), which was obtained from the actual methanolysis experiment. If the catalyst concentration was not included, then the value for the methanol concentration in the glycerol-rich phase was 35.1 ± 1.0 wt%. Chiu, Goff, and Suppes (7) reported a similar catalyst-excluded value (37.3 wt%, no error value given) measured at 25°C (see below for discussion of catalyst concentrations).

Table 1 also shows that for a base-containing simulation of methanolysis, the concentrations of sodium methoxide in the glycerol-rich and ester-rich phases were 5.57 and 0.05 wt%, respectively. In comparison, Table 2 shows that for an actual methanolysis mixture, the concentrations of sodium methoxide in the glycerol and biodiesel phases were not significantly different (5.76 and 0.06 wt%, respectively) from the simulation. Chiu, Goff and Suppes (7), who used simulation mixtures with potassium hydroxide as the catalyst, reported that the glycerol-rich phase contained 5.79 wt% of KOH, and the biodiesel-rich phase contained 0.06 wt% of KOH. Unfortunately, the molecular weights of sodium methoxide and potassium hydroxide are similar (54 and 56, respectively), so it is impossible to determine whether the steady-state concentrations of the catalysts were controlled by mass or molar concentrations, although the latter was more likely. If it is assumed that the volumes of the final glycerol-rich phases were the same in both studies, then we can divide the weight percentages of catalyst in both studies (5.57 and 5.79, respectively) by the molar masses of each catalyst to compare (but not compute) molar concentrations. In both cases the computed value was 0.103. However, this result could be entirely fortuitous and requires further investigation. In addition, Chiu *et al,* (7) used an ACS pure grade potassium

TABLE 1
Phase Compositions (wt%) of Simulated Alcoholysis Mixtures

	Methanolysis mixture[a]		Ethanolysis mixture[b]	
	Ester-rich phase	Glycerol-rich phase	Ester-rich phase	Glycerol-rich phase
Glycerol	0.21 ± 0.01%	60.3 ± 1.0%	1.60 ± 0.01%	70.5 ± 1.0%
Alcohol	4.3 ± 0.1%	33.1 ± 1.0%	12.7 ± 0.1%	27.5 ± 1.0%
Ester	95.5 ± 1.0%	<1.0%	84.3 ± 1.0%	<1.0%
NaOR	0.05 ± 0.01%	5.57 ± 0.01%	N/A	N/A

[a]R = CH_3
[b]R = C_2H_5. NA, not available.

TABLE 2
Catalyst Concentrations (wt%) and Distributions (%) for Transesterification Mixtures

	Methanolysis ($NaOCH_3$)		Ethanolysis ($NaOC_2H_5$)	
Catalyst	Ester-rich phase	Glycerol-rich phase	Ester-rich phase	Glycerol-rich phase
Concentration	0.06 ± 0.01%	5.76 ± 0.01%	0.08 ± 0.01%	7.98 ± 0.01%
Distribution	5.8%	94.2%	10.1%	89.9%

TABLE 3
Distribution of Ester, Alcohol, Glycerol, and Catalyst Between Glycerol-rich and Ester-rich Phases.

	Methanolysis mixture[a]		Ethanolysis mixture[b]	
	Ester-rich phase	Glycerol-rich phase	Ester-rich phase	Glycerol-rich phase
Glycerol	2.3%	97.7%	19.3%	80.7%
Alcohol	42.0%	58.0%	75.4%	24.6%
Ester	99.0%	1.0%	99.0%	1.0%
NaOR	5.8%	94.2%	10.1%	89.9%

[a]R = CH_3.
[b]R = C_2H_5.

hydroxide in their study. The specification for this is only ≥85% of the theoretical alkalinity. It is not known if the authors assayed their potassium hydroxide and made any appropriate corrections.

Table 2 shows that for an actual ethanolysis mixture, the concentrations of sodium ethoxide in the glycerol-rich and ester-rich phases were 7.98 and 0.08 wt%, respectively. The value for the catalyst distribution in the synthetic ethanolysis mixture containing methyl ester was not available, because in the presence of a base, transalkylation would have occurred, resulting in a mixture of glycerol, methanol, ethanol, methyl ester, and ethyl ester. The concentration of catalyst in the glycerol-rich phase compared with that in methanolysis is consistent with more alcohol having moved to the upper phase (see below). This makes the glycerol-rich phase more polar and thus more likely to dissolve catalyst.

Table 3 shows that 42.0% of the alcohol was in the ester-rich phase at the end of methanolysis, but this increased to 75.4% in ethanolysis . Similarly, 2.3% of the glycerol was found in the upper phase in methanolysis, but this increased to 19.3% in ethanolysis. The ester is nonpolar and therefore the less-polar ethanol was more soluble in it than was methanol in its ester. Consequently, the upper phase actually became more polar in the case of ethanolysis, and as a result, more glycerol moved into it. For butanolysis, the butanol was even less polar than ethanol, and the reaction mixture remained monophasic throughout with no glycerol separation. In industrial processes using methanolysis and possibly ethanolysis, it is necessary that the residual alcohol be removed and recovered by distillation before the water wash step. From the foregoing it is clear that this removal of alcohol would result in even more glycerol separation. Table 2 also shows that for both the methanol and ethanol systems, approximately 90% of catalyst went into the glycerol-rich phase at the end of the reaction. This suggests that the slowing of the reactions is due to the removal of the catalysts from the glycerides by glycerol separation and not to catalyst depletion by soap formation. This is reinforced by the fact that reactions that use sodium methoxide slow just as much as those that use sodium hydroxide.

This study showed that, as the chain length increased from methanol to ethanol, more alcohol and glycerol were found in the final ester phase of a transesterification reaction. For butanolysis, the reaction mixture remained one-phase throughout with no glycerol separation. However, this system was marginal because in one experiment of many, a very small glycerol phase was observed. This allowed us to predict that propanolysis under the same conditions would result in two phases, and that more alcohol and glycerol would be found in the upper phase than in ethanolysis. We conducted a propanolysis experiment under the same molar conditions whereupon a glycerol-rich phase separated, although we did not measure the composition of either phase. However, the volume of the glycerol-rich phase was 66% of that in methanolysis. For comparison, the volume of this phase in ethanolysis was 72% of that in methanolysis. In butanolysis the reaction remained monophasic throughout, i.e., no glycerol phase appeared.

This study ignored the slightly higher concentrations of MG and DG that existed at steady state in ethanolysis as compared with methanolysis (6). Although this may have contributed to some of the differences observed in the phase compositions and component distributions for methanolysis and ethanolysis, other effects appeared to have been more dominant.

The results reported here should be considered alongside the qualitative and quantitative phase behavior recently reported for these systems (6). For example, the separation of a glycerol-rich phase was generally considered to be advantageous in removing one of the products, thereby shifting the reaction in the desired direction. Unfortunately, as confirmed here, the glycerol-rich phase dissolves most of the catalyst, and the reaction becomes limited by mass transfer. A true thermodynamic

equilibrium is not reached even with mixing of the two phases, and the necessary conversion to meet biodiesel standards is not achieved in one reaction.

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