Phase Behavior of the Base-Catalyzed Transesterification of Soybean Oil

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ABSTRACT: Biodiesel is made by the transesterification of vegetable oils to form alkyl FA esters. High levels of conversion (>99%) are required to lower the total concentration of free and chemically bound glycerol to that allowed by the ASTM standard (0.240 wt%) for biodiesel. A polar dye was used to visualize the phase behaviors in methanolysis, ethanolysis, and butanolysis. The dye was more strongly colored in more polar phases. Methanolysis and ethanolysis reactions commenced as two phases (alcohol and oil), then formed emulsions, and ended as two phases as glycerol-rich phases separated. Ethanolysis was more easily initiated by mixing than was methanolysis. Ethanolysis also exhibited a much longer emulsion period and slower glycerol separation. The glycerol-rich phase was smaller in volume in ethanolysis than in methanolysis. Butanolysis remained one phase throughout, and no polar phase existed at any time. The results are consistent with the known phase compositions in these reactions. The concentrations of MG, DG, and TG in the products with time in stirred reactions were consistent with the observed phase behavior in the dye experiments.

Paper no. J11376 in *JAOCS 83*, 1041–1045 (December 2006).

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

Biodiesel, a clean-burning, safe, and environmentally friendly transportation fuel, is being used to reduce emissions in many countries. Biodiesel is currently made by the transesterification of vegetable oils (TG) with methanol in the presence of basic catalysts to form FAME, which have significantly lower viscosities than the oils. Transesterification consists of three consecutive, reversible reactions: the TG is converted stepwise to DG, then MG, and finally glycerol, with methyl ester being formed in each step.

Because the combustion of the glycerol moiety in MG, DG, TG, and glycerol can lead to the formation of acrolein, a photochemical smog ingredient, the ASTM standard for biodiesel limits the total glycerol moiety (G_T) in the fuel to 0.240 wt%, as determined by Equation 1, where G, MG, DG, and TG are the weight percentages of glycerol, MG, DG, and TG, respectively.

$$G_T = \text{G} + 0.26\ (\text{MG}) + 0.15\ (\text{DG}) + 0.1\ (\text{TG}) \qquad [1]$$

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As a result, high conversion (>99% of the ester bonds) is required to achieve the glycerol limit set by the standard. However, the necessary conversion is not achievable in one single pass by current processes. In the biodiesel industry, biphasic base-catalyzed transesterification is the most common method for making biodiesel. Methanol and oils are immiscible, and vigorous stirring is required to promote the mass transfer between the oil and methanol phases. The catalyst, usually sodium methoxide, is exclusively in the polar methanol phase. During the transmethylation, the reaction mixture passes from a biphasic (methanol and oil) system to a biphasic (methyl ester-rich and glycerol-rich) system, probably *via* an emulsion. These phase transitions affect the kinetics and steady-state position of the reactions, which are critical for making standard biodiesel fuels.

It has been noted for methanolysis (1–3) that at low base concentrations and with weak mixing regimes there is a lag time, after which the reaction rate speeds up, but then quickly decelerates. As a result, the transesterified products contain significant amounts of unreacted MG, DG, and TG. In particular, in a single-step reaction, the amount of TG often, but not always, exceeds that of MG. This does not conform to the homogeneous kinetic behavior, which can be achieved by using a cosolvent (4–6). Obviously, glycerol separation and emulsion formation can have significant effects on the reaction kinetics. For example, glycerol separation can in theory promote transesterification because the by-product (glycerol) is removed from the system. On the other hand, the catalyst is very soluble in a glycerol-rich phase, which would slow the reaction, as is actually observed.

Methyl esters are currently the only biodiesels sold commercially. However, ethyl esters are attractive for several reasons. Ethanol can be produced from renewable sugars and starches, in which case the biodiesel made from it derives exclusively from renewable materials. Moreover, ethanol is a better solvent than methanol, and therefore it is tempting to use ethanol to overcome the mass-transfer limitation encountered in the methanolysis of TG. However, it is well known that producing ethyl ester from vegetable oils is particularly difficult because of the formation of stable emulsions and the difficulty in isolating the product.

Although the kinetic behavior of methanolysis in a two-phase system has been studied (1–3), there is little available information on the phase behavior of either methanolysis or ethanolysis, and hardly any studies are available on the effect of phase transitions on the multiphase reaction kinetics. One reason for this is that the glycerol-rich phase is relatively small

TABLE 1
Phase Volumes Before and After Transesterification

	Prereaction volumes (mL)		Postreaction volumes (mL)	
	Alcohol	Soybean oil	Glycerol-rich phase	Ester-rich phase
Methylation	16.8	69.0	8.6	77.2
Ethylation	24.0	69.0	6.2	86.8
Propylation	32.4	69.0	5.7	95.7
Butylation	37.5	69.0	NA[a]	NA

[a]NA, not applicable.

and colorless and is difficult to see, particularly in stirred reactions.

Therefore, to characterize the phase behavior during transesterification, we "visualized" the different stages of the transesterification of TG in the form of soybean oil (SBO) by using a polar dye. Like many polar dyes, this exhibited more intense color as the polarity of the dissolving phase increased. We also investigated the effect of the initial mixing time on the phase behavior of transesterification. We also studied butanolysis to investigate further how the chain length of the linear primary alcohol affects the phase behavior of transesterification. The traditional alcohol/oil molar ratio of 6:1 was used, with sodium methoxide as the catalyst (1.0 wt% based on the oil). All experiments were carried out at room temperature, which in all cases was 23°C.

It should be emphasized that in commercial processes stirring is employed. The dye experiments characterized the phases (alcohol, oil, emulsion, glycerol-rich, and ester-rich) that were involved, as well as the sequences in which and the relative rates at which they disappear and appear. Continuously stirred experiments were also performed for methanolysis, ethanolysis, and butanolysis. The glyceride concentrations of the products were measured as a function of reaction times and related to the phase behavior observed in the dye experiments.

EXPERIMENTAL PROCEDURES

Materials. The SBO was purchased from Sunfresh Limited (Toronto, Ontario, Canada). The following chemicals were supplied by Sigma-Aldrich Chemical Company (Milwaukee, WI): methanol (anhydrous, 99+%), ethanol (anhydrous), and sodium methoxide solution in methanol (20%). The dye was a red food colorant in a propylene glycol base and was purchased from McCormick Canada (London, Ontario, Canada). Any polar red food colorant in a similar base would be suitable for this study.

Visualization of transesterification. Base-catalyzed transesterification of SBO with methanol at room temperature was carried out in a cylindrical tube (17 × 3.5 cm i.d.) sealed with a stopper. First, methanol (2.6 mL, containing 0.256 g of reacted sodium metal), more methanol (14.2 mL), and red dye (6 drops) were added to a 250-mL flask and mixed to form a homogeneous solution. SBO (60.0 g) was added to the tube. The above catalyst solution was gently poured down the tube wall to avoid any mixing with the oil. Then the tube was sealed and inverted twice per second manually for a chosen time period. This time period was determined by a scouting experiment to pinpoint how much mixing time was sufficient to form an emulsion. After the chosen mixing time, the agitation was stopped and the tube was returned to the vertical position. The start of agitation of the reaction mixture was recorded as zero time. Digital pictures were taken at various times following time zero. For ethanolysis, propanolysis, and butanolysis, the procedure was the same but the reactant volumes are those listed in Table 1. Sodium metal, as above, was used to provide the appropriate alkoxide. For methanolysis, three experiments were conducted with initial mixing times of 30, 60, and 180 s in order to investigate the effect of initial mixing on the kinetics of transesterification. For ethanolysis and butanolysis, only one experiment was carried with an initial mixing time of 30 s.

Stirred reactions. Methanolysis, ethanolysis, and butanolysis reactions were performed with continuous stirring. The reactions were carried out in 200-mL conical flasks containing a magnetic stir bar. The reactant volumes and catalyst were otherwise identical to those in the experiments above except the dye was not added and the reactions were continuously stirred. Samples were withdrawn at specific time intervals and immediately neutralized with excess methanolic oxalic acid. These were washed with 10% brine solution and then with water until they were neutral. They were then dried over anhydrous sodium sulfate and analyzed for the glycerides by the standard GC reference method, ASTM D 6584 (7). The samples were diluted appropriately with heptane to bring the concentrations of the components into the ranges for which the method is valid.

RESULTS AND DISCUSSION

The initial mixtures. Table 1 contains the volumes of the alcohol and oil used in the methanolysis and ethanolysis reactions. Care was taken not to agitate the two reactants so the volumes also represent the volumes of the two initial phases (the alcohol being the upper phase). Although propanolysis was not subjected to dye experiments, the corresponding reaction was still performed and the volumes of the two initial phases are also given. Butanol and the oil are so miscible that on adding one to the other they form a single phase. The values in Table 1 are the volumes of the oil and alcohol that were mixed. The increasing alcohol volumes on progressing from methanol to butanol are due to the higher molar volumes.

The effect of initial mixing. Because methanol and ethanol are largely immiscible with oil, there is no reaction without mixing. All experiments showed that at time zero, the nonpolar

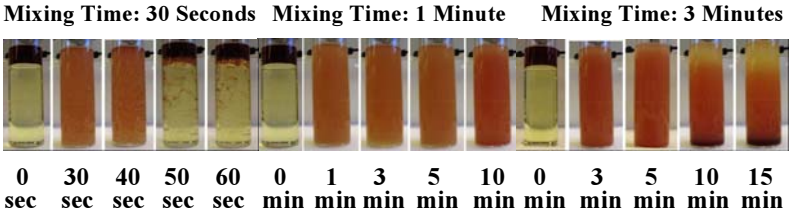
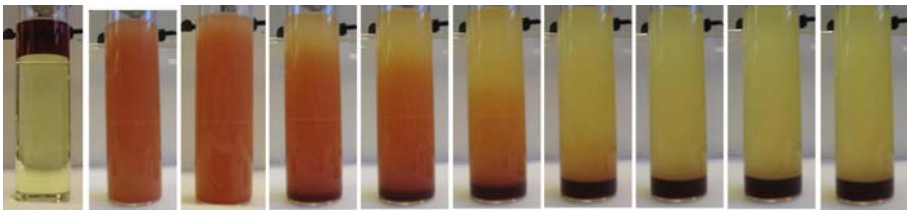


FIG. 1. Mixing time effect on phase behaviors of transmethylation.



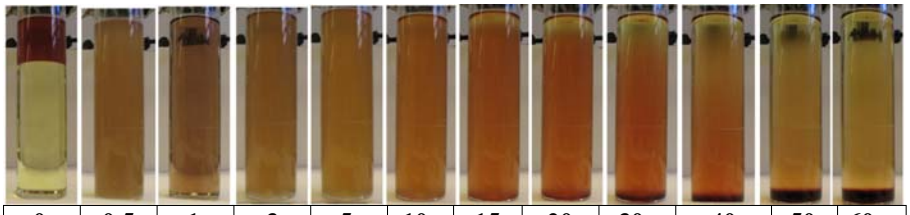
0 min	3 min	5 min	10 min	15 min	20 min	30 min	40 min	50 min	60 min
Two Phases	Glycerol Separation							Two Phases	

FIG. 2. Phase behavior of the methanolysis of soybean oil (mixing time: 3 min).

pale yellow oil phase was at the bottom of the tube, and the polar alcohol phase, where the catalyst and the dye were located, was on top. The dye was intensely colored in the alcohol and in particular was more highly colored in methanol than ethanol. As can be seen from Figure 1, if the initial mixing time was only 30 s, methanol separated from the oil soon after the agitation was stopped, and there was no reaction and no glycerol separation. MG and DG, which are surfactants, are necessary to form an emulsion. Clearly insufficient amounts of them were formed after 30 s of mixing. For methanolysis, the minimum mixing time that was required to achieve a rapid and sustained reaction was approximately 3 min. After this time, the reaction had already passed through any emulsion stage (see below), and a suspended glycerol-rich phase had already appeared, as evidenced by the increase in color intensity. The required time of 3 min was consistent with the lag time reported in the kinetic study of Freedman *et al*. (1,2). When the tube was shaken for only 1 min, sometimes the oil and methanol slowly separated and sometimes the mixture formed an emulsion, followed by the separation of a glycerol layer. Figure 1 shows the images from the latter case. In this case it took twice as much time for a glycerol-rich layer to appear (not shown) at the bottom of the tube as compared with the case when the reaction mixture was shaken for 3 min.

The color intensities show that for a mixing time of 3 min there was clearly a suspended glycerol-rich phase present immediately following the mixing period. In comparison, it took between 5 and 10 min to form a suspended glycerol phase when only 1 min of mixing was carried out, and if the reaction then proceeded (see preceding paragraph). Before that, an emulsion was present as evidenced by the diminished color intensity.

Phase behavior of methanolysis. Figure 2 shows the extended behavior of the methanolysis reaction following 3 min



0 min	0.5 min	1 min	3 min	5 min	10 min	15 min	20 min	30 min	40 min	50 min	60 min
Two Phases	Emulsion				Glycerol Separation					Two Phases	

FIG. 3. Phase behavior of the ethanolysis of soybean oil (mixing time: 30 s).

TABLE 2
Effect of Reaction Time on Product Composition at 23°C Using 6:1 Alcohol/Oil Molar Ratios

Time (min)	Methanolysis (1.0 wt% $NaOCH_3$)[a]			Ethanolysis (1.26 wt% $NaOC_2H_5$)[a]			Butanolysis (1.78 wt% $NaOC_4H_9$)[a]		
	MG	DG	TG	MG	DG	TG	MG	DG	TG
3	1.0	10.6	84.4	10.0	11.6	14.3	10.1	13.4	15.4
6	2.5	12.2	44.9	8.2	8.9	8.4	9.4	11.0	9.6
10	2.5	9.4	26.1	7.0	7.3	5.7	8.6	9.4	7.5
20	1.8	6.2	16.6	5.5	5.3	3.4	7.5	7.4	4.8
30	1.3	4.9	12.7	4.7	4.2	2.4	6.9	6.5	4.0
60	0.8	3.2	7.7	3.2	2.5	1.5	6.5	4.9	3.0

[a]Catalysis concentrations with respect to the oil are the same on a molar basis.

of mixing. The glycerol-rich phase continued to settle resulting in a distinct phase at the bottom of the tube in 10 min. The settling was essentially complete after 40–60 min. The catalyst was a polar species, so it would have dissolved in any suspended or separated glycerol phase that appeared. Parallel studies (8) confirm the preferred solubility of the catalyst in the glycerol phase. In addition, any unreacted glycerides should remain in the ester-rich phase.

Phase behavior of ethanolysis. Figure 3 shows images of the phase behavior of the ethanolysis mixture immediately after a mixing time of 30 s. First it should be noted that, unlike methanolysis, 30 s of mixing was sufficient to cause a reaction. An emulsion appeared to form immediately after mixing, as evidenced by the homogeneity of the reaction mixture and the lack of color. After another 30 s the mixture appeared to exist briefly as either a solution or a microphase, before returning to an emulsion. This existed until a suspended glycerol phase began to appear after approximately 10 min. A separate glycerol phase was seen at the bottom of the tube after 20 min. Separation was complete after 50–60 min.

Korus *et al*. (9) investigated the effect of agitation on the ethanolysis of rapeseed oil in a batch reactor. They concluded that "vigorous" agitation was required until the reaction mixture became homogeneous, but they did not measure the minimum time required to achieve the homogeneity.

Comparison of Figures 2 and 3 shows that ethanolysis formed an emulsion more easily and much faster than methanolysis. For methanolysis, it took more than 30 s to form an emulsion, whereas for ethanolysis, it took only 30 s. Furthermore, ethanolysis briefly passed through a transparent solution or a microphase stage at 1 min, before forming another emulsion. Therefore, the emulsions were much more stable than in methanolysis. After 60 min, the glycerol-rich phase in ethanolysis was visibly smaller than that in methanolysis. A parallel study showed that this was due to more glycerol and more alcohol moving from the glycerol phase to the upper phase (8). Table 2 contains the actual volumes of the glycerol-rich and ester-rich phases for methanolysis, ethanolysis, and propanolysis, which were measured following the settling process. Significantly, the volume of the glycerol-rich phase was smaller in propanolysis compared with that in ethanolysis. A glycerol-rich phase did not appear in butanolysis.

In methanolysis, the glycerol separation was more facile and complete. Glycerol separation occurred in 3 min, and it took less than 40 min for the glycerol to separate completely from the ester phase; whereas for ethanolysis, a strong red color did not appear until 10 min, indicating there was no polar glycerol phase present. Unlike in methanolysis, the ester-rich phase was still slightly red after 60 min. This indicated that the ester-rich phase was more polar than in the case of methanolysis. This was because there was more glycerol, alcohol, MG, and DG in the ester-rich phase after ethanolysis than after methanolysis, and thus the emulsion did not break up completely. In particular, the concentrations of MG and DG were 10 times higher in the ester-rich phase for ethanolysis as compared with methanolysis (8). This comparison suggested that a mixture of methanol and ethanol might be used to optimize phase behavior. Ethanol is a better solvent, and helps to form a prolonged emulsion at the start of the reaction. However, methoxide ion is a better nucleophile than the ethoxide ion, and this helps to push the equilibrium in the required direction. In addition, in methanolysis, more glycerol separates, and this favors the forward reaction.

Phase behavior of butanolysis. The butanolysis reaction was a single phase throughout. The experiment was repeated several times, and in only one case was a very small glycerol phase observed. This emphasized that this reaction was close to forming two phases. The dye was barely colored in this reaction and some of it appeared to precipitate. This was caused by the lack of any strong polar phase as well as the low polarity of the one-phase system.

Extents of alcoholysis. Table 2 shows the glyceride contents of methanolysis, ethanolysis, and butanolysis reactions as a function of time for continuously stirred reactions. It is assumed that the stirred systems exhibit similar phase behavior as the static systems, but without the settling. Mass transfer between phases was promoted by the stirring. In the first 3 min both the ethanolysis and butanolysis reactions occurred at similar rates and were much faster than methanolysis. This suggests that mass transfer in the emulsion period of ethanolysis, coupled with a slightly higher polarity, was as effective as the homogenous system in butanolysis, which was less polar. In both these reactions the TG concentrations fell below those of MG and DG, which was the expected behavior of homogeneous reactions. However, it is obvious that the conversions of

the MG and DG were slower than at the beginning of the reactions. In part this was due to the different equilibrium position of these reactions. For example, butoxide anion is more similar to the glycerol anion than the methoxide anion. As a result, the equilibrium position of this reaction is shifted back toward the alcohol.

In contrast to the other reactions, methanolysis was slow. Freedman *et al.* (2) also showed that the butanolysis in general was faster than methanolysis, but did not comment on the difference in phase behavior. In methanolysis, the MG and DG appeared to be reacting faster than the TG, such that the TG concentration stayed above those of the other two. We propose that the MG and DG, which carry –OH groups, could more easily access the polar glycerol-rich phase, which contained most of the catalyst as well as some methanol. The TG, on the other hand, preferred to be in the less polar ester-rich phase where reaction was negligible. From previous studies (4) on methanolysis it is known that in a truly homogeneous system over 99% of the glyceride bonds are converted at equilibrium at ambient temperatures. Unfortunately, this does not appear to be the case in the biphasic system, even with prolonged stirring. Thus, the phase behaviors observed in the static systems (after stirring) can reasonably explain the kinetics of stirred systems.

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[Received April 6, 2006; accepted September 22, 2006]