Ethyl Esters from the Single-Phase Base-Catalyzed Ethanolysis of Vegetable Oils

Weiyang Zhou, Samir K. Konar, and David G.B. Boocock*

Department of Chemical Engineering and Applied Chemistry, University of Toronto, Toronto, Ontario, Canada, M5S 3E5

ABSTRACT: The effects of alcohol/oil molar ratio, base concentration, and temperature on the single-phase base-catalyzed ethanolyses of sunflower and canola oils were determined. The use of tetrahydrofuran as co-solvent, as well as higher than usual alcohol/substrate molar ratios, prevented glycerol separation. This allowed each reaction to reach equilibrium rather than just steady-state conditions. High conversions of oil lowered the concentrations of MG and DG surfactants in the products, and thereby mitigated the formation of emulsions usually associated with ethanolysis reactions. An alcohol/oil molar ratio of 25:1, together with the necessary amount of cosolvent, gave optimal results. At this molar ratio, despite equilibrium being achieved, ethanolysis, unlike methanolysis, did not quite produce biodiesel-standard material, the MG content being approximately 1.5 mass%. For methanolysis and 1-butanolysis, the corresponding values were 0.6 and 2.0 mass%, respectively. The use of 1.4 mass% KOH (equivalent to 1.0 mass% NaOH) led to ethanolysis equilibrium within 6–7 min at 23°C rather than 15 min when only 1.0 mass% was used. At 60°C, equilibrium was reached within only 2 min. Soybean and canola oils behaved the same.

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KEY WORDS: Base-catalyzed ethanolysis, biodiesel standards, canola and sunflower oils, one-phase transesterification.

The base-catalyzed formation of methyl and ethyl esters (EE) of FA from vegetable oils (TG) is important for several reasons. For many years, these esters have been commercially available in several European countries as renewable diesel fuel substitutes. In the year 2000, these esters were designated as allowable substitute fuels under the U.S. Energy Policy Act (EPACT). Although it is easier to make methyl esters, in some jurisdictions, it may be more desirable to make ethyl esters because the ethanol can be derived from renewable starch sources such as corn.

The base-catalyzed formation of ethyl esters is difficult compared to the production of methyl esters. Specifically, the formation of stable emulsions during ethanolysis is a problem (1). Methanol and ethanol are not miscible with TG at ambient temperatures, and the reaction mixtures are usually mechanically stirred to enhance mass transfer. During the course of these reactions, emulsions usually form. In the case of methanolysis, these emulsions quickly and easily break down to form a lower glycerol-rich layer and an upper methyl ester-rich layer. In ethanolysis, these emulsions are much more stable and severely complicate separation and purification of the ester. The emulsions are caused in part by the formation of the intermediate MG and DG, which have both polar hydroxyl groups and nonpolar hydrocarbon chains. Therefore, these intermediates are strong surface-active agents and are used as such in the food industry as emulsifiers. In alcoholysis reactions, the catalyst, usually either sodium or potassium hydroxide, is dissolved in the polar alcohol phase, into which TG must transfer in order to react. Therefore, the reaction is initially mass-transfer controlled and does not conform to expected homogeneous kinetics. When the concentrations of these intermediates reach a critical level, emulsions form. The larger nonpolar group in ethanol, relative to methanol, is assumed to be the critical factor in stabilizing the emulsions. However, if the concentrations of the MG and DG are very low, then the emulsions become unstable. This emphasizes the necessity for the reaction to be as complete as possible, thereby reducing the concentrations of the MG and DG. This is also consistent with the current ASTM standard for biodiesel, which limits the total bound and unbound glycerol (G_T) in the fuel to 0.24 mass%, as determined by Equation 1,

$$G_T = G + 0.25(MG) + 0.15(DG) + 0.1(TG) \qquad [1]$$

in which G, MG, DG, and TG are the mass percentages of glycerol, MG, DG, and TG, respectively, in the product. However, the ASTM limitation is designed to mitigate the formation of acrolein (propenal) from glycerol moieties when the fuel is combusted, and has nothing to do with the process by which the fuel is made. If the methyl ester is reasonably pure, then its glycerol content is not usually a problem, because the esters and glycerol are sufficiently insoluble in each other. Therefore, the concentrations of the MG and DG become dominant in Equation 1. In the case of ethanolysis, ASTM standards will not be met, and the emulsion problem will prevail if the reactions do not approach completion.

Freedman *et al.* studied the transmethylation and transbutylation of soybean oil (2,3). Unfortunately, these studies did not recognize the importance and limitations of the two-phase nature of the reaction between methanol and soybean oil. The nonconformity to second-order kinetics was explained in terms of

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*To whom correspondence should be addressed.
E-mail: boocock@chem-eng.utoronto.ca

a dubious mechanism, which involved the simultaneous attack of more than one methanol molecule on the TG. The observed reaction kinetics were typical of mass transfer-controlled reactions (4,5) in which normal mechanisms prevail. We have shown that the use of an inert cosolvent, such as THF, can produce a single phase between vegetable oils and methanol, thereby causing the reactions to speed up dramatically (4).

At the lower alcohol/molar ratios used by Freedman *et al.* (2,3), even in the presence of a cosolvent, a glycerol-rich phase still formed as the reactions proceeded. It has been assumed that the formation of this glycerol layer is beneficial in shifting the equilibrium in the required direction. However, a significant deleterious effect is associated with the separation of the glycerol. The catalyst is very soluble in glycerol, and once the separation occurs, the reactions either stop or slow to the point of being commercially unusable. We have shown that if more methanol and a nonreactive cosolvent are used in methanolysis, then ASTM product can easily be achieved at ambient temperatures in only 7 min. (4,5).

The present study was designed to investigate the effects of alcohol/oil molar ratio, base concentration, and temperature on the equilibrium position of the ethanolysis of vegetable oils. A comparison was made with alcoholysis using methanol and 1-butanol.

EXPERIMENTAL PROCEDURES

Materials. The sunflower and canola oils used were food-grade products purchased from Unico Inc. (Concord, Ontario, Canada). The major FA components of the sunflower oil TG are: 7% palmitic acid (16:0), 4% stearic acid (18:0), 25% oleic acid (18:1), and 64% linoleic acid (18:2). From this composition, an average molecular mass of 876 was determined (6). For canola oil, the major FA components are: 5% palmitic acid, 25% oleic acid, 60% linoleic acid, and 10% linolenic acid (18:3) (7). Accordingly, the averaged molecular mass of canola oils was calculated to be 877. The following chemicals were supplied by Sigma-Aldrich Chemical Company (Milwaukee, WI): ethanol (anhydrous, denatured), 1-propanol (anhydrous, 99.7+%), 1-butanol (anhydrous, 99.9+%), THF (anhydrous, 99+%), *N,O* bis(trimethylsilyl)trifluoroacetamide (BSTFA, 99+%), pyridine (anhydrous, 99+%), and molecular sieves 4A (8–12 mesh). Analytical-grade potassium hydroxide (98%), concentrated hydrochloric acid, and anhydrous sodium sulfate were obtained from BDH Inc. (Toronto, Ontario, Canada).

Analyses. The exact compositions of the transesterified products were determined by a GC method (8). The samples were analyzed on a Hewlett-Packard (Palo Alto, Ca) 5880A series gas chromatograph equipped with an on-column injector, FID, and a 2 m × 0.25 mm DB-1 (J&W Scientific Inc., Folsom, CA) fused-silica capillary column coated with a 0.25-μm film of 100% polymethyl siloxane. The operating parameters were as follows: injector temperature, 350°C; detector temperature, 320°C; and temperature program, 2 min at 130°C, heating at a rate of 15°C/min to 350°C, and holding for 10 min. Average linear velocity of carrier gas (He) was 40 cm/s. Reference standards were purchased from Sigma Chemical Company (St. Louis, MO) and were chromatographically pure (>99%). These standards included: methyl linoleate, 1-monolinolein, 1,3-dilinolein (1% 1,2 isomer), and trilinolein.

Methods. The base-catalyzed transesterification reaction of sunflower oil at room temperature was performed in a 150-mL flat-bottomed flask equipped with a magnetic stirrer, using 20.0 g sunflower oil, KOH catalyst, and THF cosolvent. KOH was used instead of NaOH because it dissolves faster in alcohol. We have shown that on a molar basis, the two hydroxides are equally effective in the one-phase system (9). KOH at 1.4 mass% is equivalent to 1.0 mass% NaOH on a molar basis. The catalyst was first weighed in a 20-mL vial, and then dissolved in ethanol (4 mL), which represented the stoichiometric amount required for transesterification. Sunflower oil (20.0 g) was placed in the flask, followed by adding appropriate amounts of anhydrous THF and ethanol, and then the mixture was stirred. The KOH solution in ethanol was added to the mixture, and the stirring was continued for an additional 20 s. Addition of KOH solution to the mixture was recorded as zero time. Samples of approximately 1.5 mL of the reaction mixture were pipetted out at various times during the course of 2 h. The samples were quenched immediately into 4-mL vials containing 2 mL 1 N HCl acid solution to neutralize the catalyst. The samples were allowed to stand overnight, during which time the ester separation was complete. The organic layer of each sample was collected and transferred to 2-mL vials. Since ethyl ester has a high tendency to form an emulsion on contact with water, care must be taken to maintain low levels of agitation during quenching and collecting samples, especially when ester conversion is low. Anhydrous sodium sulfate was added to absorb trace amounts of moisture. The samples were then derivatized for GC.

Base-catalyzed transesterification reactions of sunflower oil at elevated temperature were carried out in a 200-mL three-necked flask equipped with a magnetic stirrer, a reflux condenser, a thermometer, and a sampling port. The flask was immersed in a constant-temperature oil bath equipped with a temperature controller capable of maintaining the temperature within ±1°C. The catalyst was first weighed in a 20-mL vial and then dissolved in 4 mL of ethanol, which represented the stoichiometric amount required for transesterification, and heated separately to the desired temperature. Sunflower oil (20.0 g) was placed in the flask, followed by adding appropriate amounts of anhydrous THF and ethanol. Then the mixture was stirred and heated to the desired temperature. Next, KOH solution in ethanol was added to the mixture, and stirring was continued for an additional 20 s. Addition of KOH solution to the mixture was recorded as zero time. All other conditions and subsequent treatments were the same as described above.

For derivatization of the MG and DG, anhydrous pyridine (0.4 mL) and BSTFA reagent (0.2 mL) were added to a 20-mL vial containing transesterified product (100 mg). The vial

TABLE 1
Reaction Conditions for One-Phase Transethanolysis

Reaction run #	THF (mL)	Ethanol (mL)	Temperature (°C)	Ethanol/oil molar ratio	Catalyst (mass%, based on oil)
1	8.5	33.2	23	25:1	1.4
2	8.5	33.2	40	25:1	1.4
3	8.5	33.2	60	25:1	1.4
4	2.0	8.0	23	6:1	1.4
5	7.4	26.6	23	20:1	1.4
6	8.5	33.2	23	25:1	1.4
7	9.5	40.0	23	30:1	1.4
8	8.5	33.2	23	25:1	0.5
9	8.5	33.2	23	25:1	1.0
10	8.5	33.2	23	25:1	1.4

TABLE 2
Volumes of Ethanol, Oil, and THF Used for Molar Ratios of Ethanol to Sunflower Oil

	Volume (mL)			Volume percentage (%)		
Molar ratio	Ethanol	Oil	THF	Ethanol	Oil	THF
6:1	8.0	22.0	2.0	25.0	68.8	6.2
20:1	26.6	22.0	7.4	47.5	39.3	13.2
25:1	33.2	22.0	8.5	52.2	34.5	13.3
30:1	40.0	22.0	9.5	55.9	30.8	13.3

was capped, shaken, and placed in a water bath at 65°C for 20 min with occasional stirring. It was then removed from the water bath and cooled to room temperature. The sample was then diluted to 5 mL with THF for GC analysis.

Experiments were carried out to determine the optimal conditions for converting sunflower oil into ethyl ester by transesterification. Experimental variables included reaction temperature (23, 40, and 60°C), molar ratio of ethanol to sunflower oil (6:1, 20:1, 25:1, and 30:1), and concentration of catalyst (0.5, 1.0, and 1.4 mass%).

The scope of the transesterification experiments is outlined in Table 1. All were carried out at atmospheric pressure. In all cases, 20.0 g of sunflower oil was used. The amounts of THF needed to convert different alcohol/oil molar ratios into a single phase were determined by a "cloud point" method (10), and the volumes used are included in Tables 2 and 3.

A number of experiments were conducted to study the transesterification of sunflower oil with 1-butanol at room temperature, using 25:1 alcohol/oil molar ratio and 1.4 mass% KOH. Experiments were also carried out to study the transesterification of canola oil with ethanol. All experimental conditions were the same as described above. Each kinetic experiment was conducted three times and the results averaged.

TABLE 3
Volumes of THF Used to Achieve Miscibility[a]

Alcohol	Volume of alcohol (mL)	Volume of THF (mL)
Methanol	23.3	20.0
Ethanol	33.2	8.5
1-Butanol	52.0	0

[a] Molar ratio of alcohol/oil is 25:1 in all cases.

RESULTS AND DISCUSSION

Results are presented only for sunflower oil, because we found no significant difference between behaviors of sunflower and canola oils. A chromatogram of a typical transesterified sunflower oil reaction mixture is shown in Figure 1. Although the mass percentages of methyl ester, MG, DG, and TG in the derivatized samples were measured for all runs, for simplicity, only the methyl ester concentrations are shown in Tables 5–7. These values were calculated by subtracting the summed concentrations of the three glyceride components from 100, and therefore are normalized with respect to all esters. Because of small amounts of other components in the starting material, this method slightly overstates the methyl ester concentration. At high conversions it may be assumed that MG is the only glyceride that is present. This is important because the ASTM standard limits only the glyceride content and says nothing about the ester content.

Table 4 shows results for four ethanol/oil molar ratios in the ethanolysis of sunflower oil at 23°C using 1.4 mass% of potassium hydroxide. Table 5 shows results for the ethanolysis of sunflower oil to ethyl ester for an ethanol/oil molar ratio of 25:1 at temperatures of 23, 40, and 60°C. Table 6 shows results for KOH concentrations of 0.5, 1.0, and 1.4 mass% with respect to the oils at 23°C and an ethanol/oil molar ratio of 25:1. Table 7 compares results for the alcoholysis of sunflower oil using methanol, ethanol, and 1-butanol.

The data in Table 4 indicate that at ethanol/oil molar ratios of 20, 25, and 30:1, equilibrium was reached in 6 to 10 min at 23°C when 1.4 mass% of KOH was used. The more detailed results in Table 7 show that 6 to 7 min was required at a molar ratio of 25:1. At the classical molar ratio of 6:1, equilibrium

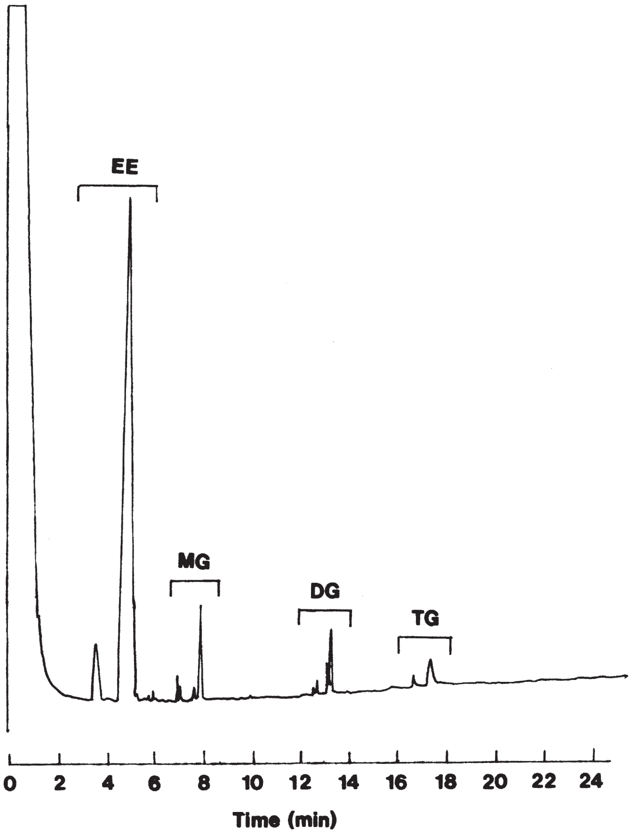

FIG. 1. Chromatogram of reaction mixture from transesterification of sunflower oil with ethanol (molar ratio 6:1, 23°C, 1.4 mass% KOH, THF, 1-min sample).

was not reached after 30 min. The equilibrium position shifted toward the ester as the molar ratio increased, but the difference for the range of molar ratios from 25:1 to 20:1 was small. However this region is rather critical for meeting the Biodiesel standards. To achieve the G_T limit of 0.24 mass%, the alcohol/oil molar ratio would have to be increased considerably above 30:1. The optimal alcohol/oil molar ratio in the case of soybean and canola oils is approximately 27:1. We have subsequently concluded that this ratio essentially coincides with the conditions under which glycerol does not separate. Coconut oil, which contains over 50% of the shorter lauric acid chains (major components: 51% lauric acid, 18.5% myristic acid, 10.5% palmitic acid, and 8.2% oleic acid) (7), has a smaller molar volume than most oils; therefore, the same effect can be achieved at a 6:1 molar ratio. The product contains 0.5 mass% MG or less. It is clear that in methanolysis, the separation of the glycerol is not required, and that equilibrium alone will produce ASTM glyceride standards in the product.

TABLE 4
Effect of Ethanol/Oil Molar Ratio on Conversion, 1.4 mass% KOH Catalyst, 23°C

Time	Ethyl ester (mass%)			
(min)	6:1	20:1	25:1	30:1
1	86.2	91.3	92.6	90.9
3	86.3	94.5	97.4	97.7
6	86.5	96.0	98.4	98.4
10	87.6	97.0	98.6	98.7
15	89.2	96.9	98.5	99.0
20	89.4	97.1	98.6	98.9
30	90.0	96.9	98.5	98.8

TABLE 5
Effect of Reaction Temperature on Conversion, 1.4 mass% KOH Catalyst, 25:1 Ethanol/Oil Molar Ratio

Time	Ethyl ester (mass%)		
(min)	23°C	40°C	60°C
0	0	0	0
1	92.6	97.2	98.5
2	95.7	97.5	98.8
3	97.4	98.0	98.8
4	97.5	98.1	98.6
5	98.1	98.2	98.5
6	98.4	98.4	98.6
7	98.4	98.4	98.6

The results in Table 5 show that, as expected, an increase in temperature causes faster reactions, with equilibrium being reached earlier. At 60°C, equilibrium is reached within 2 min. The transethanolysis is only slightly exothermic, which probably explains the similarity in the equilibrium positions for the three temperatures.

Table 6 shows that, as expected, the catalyst concentration affects the rate of the reaction. Hydroxide ion produces methoxide ion by equilibrium with methanol, so if all other parameters are kept constant, the rate of the reaction should be proportional to the hydroxide concentration. In all three cases the reaction was so fast at ambient temperatures that the initial rates of the reactions could not be measured by usual means. For all three base concentrations, the same equilibrium position was reached. This occurred at about 7 min for the highest base concentration (1.4 mass%).

Table 7 compares the results for three different alcohols. The only difference in reaction conditions is the amount of

TABLE 6
Effect of Catalyst Concentration on Conversion, 23°C, 25:1 Ethanol/Oil Molar Ratio

Time	Ethyl ester (mass%)		
(min)	0.5 mass%	1.0 mass%	1.4 mass%
1	55.4	86.1	92.6
2	67.8	92.9	95.7
3	79.3	94.8	97.4
4	87.5	94.9	97.5
5	91.8	95.1	98.1
6	92.0	96.5	98.4
7	92.3	96.9	98.4
8	92.7	97.1	98.4
9	93.8	97.2	98.5
10	94.1	97.4	98.6
12	95.0	97.9	98.6
15	96.7	98.3	98.5
20	97.1	98.6	98.6
30	98.1	98.7	98.5

TABLE 7
Effect of Alcohol Type on Conversion, 1.4 mass% KOH, 23°C, 25:1 Alcohol/Oil Molar Ratio

Time	Ester (mass%)		
(min)	Methanol	Ethanol	Butanol
1	97.8	92.6	87.7
2	98.6	95.7	91.1
3	99.3	97.4	91.8
4	99.4	97.5	93.6
5	99.2	98.1	93.8
6	99.4	98.4	94.0
7	99.4	98.4	94.4
8	99.4	98.4	95.0
9	99.4	98.5	95.3
10	99.4	98.6	95.7
15	99.4	98.5	96.6
20	99.4	98.6	97.3
30	99.4	98.5	98.0

cosolvent required to achieve miscibility for each alcohol. Only in the case of methanol can biodiesel standard product be obtained at the alcohol/oil molar ratio of 25:1. After methanol, ethanol is probably the only other alcohol that, realistically, would be used in a commercial process. Therefore, some method must be found to lower the MG content. Advantage may be taken of the polar hydroxyl group in the MG. Many adsorbents are capable of selectively removing some of the MG. Dissolving the product in a nonpolar solvent, such as hexane, facilitates this process but adds distillation costs. In a continuous ethanolysis reaction, the catalyst would be neutralized after equilibrium is reached. The excess ethanol and cosolvent would be codistilled and recycled to the front end of the reaction.

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