The Pseudo-Single-Phase, Base-Catalyzed Transmethylation of Soybean Oil

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ABSTRACT: The base-catalyzed transmethylation of soybean oil has been studied under conditions whereby the reaction starts as a single phase, but later becomes two phases as glycerol separates. Methanol/oil molar ratios of 6:1 were used at 23°C. The catalysts were sodium hydroxide (0.5, 1.0, and 2.0 wt%), potassium hydroxide (1.0 and 1.4 wt%), and sodium methoxide (0.5, 1.0, and 1.35 wt%), all concentrations being with respect to the oil. Oxolane (tetrahydrofuran) was used to form a single reaction phase. The reactions deviated from homogeneous kinetics as glycerol separated, taking with it most of the catalyst. When 1.0 wt% sodium hydroxide was used, the methyl ester content reached 97.5 wt% after 4 h, compared with 85–90 wt% in the two-phase reaction. Sodium hydroxide (1.0 wt%), sodium methoxide (1.35 wt%), and potassium hydroxide (1.4 wt%) gave similar results, presumably because the same number of moles was used. The ASTM biodiesel specification for chemically bound glycerol was achieved after only 3 min when 2.0 wt% sodium hydroxide was used. However, the standard was not achieved after 4 h when 1.0 wt% sodium hydroxide was used, the MG content being 1.1–1.6 wt%. The use of 2.0 wt% catalyst is commercially impractical.

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FA methyl esters (ME) have become important, given the increasing use of these esters as renewable diesel fuels. Although the term "biodiesel" has been adopted for all lower alkyl ester fuels, it is the ME that are used exclusively. These fuels have been available for several years in some European countries and are now available on a limited basis in North America. Production volumes in Europe and the United States were approximately 1.45 billion and 0.13 billion liters, respectively, in 2003. Although biodiesel standards have existed in many European countries for a number of years, a common European standard was adopted only in 2003. An ASTM standard for a blended biodiesel was adopted in 2001 (1). Researchers and producers now face the challenge of making ME that meet these standards. In Europe the fuel is produced predominantly from purified rapeseed oil. In North America, purified soybean oil (SBO) is the preferred feedstock, although waste fats and oils, which contain both FA and TG, are the cheapest starting material.

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The process for the formation of ME involves the base-catalyzed transmethylation of TG in the oils, with glycerol (G) being a by-product,

$$TG + 3CH_3OH \rightarrow 3CH_3O{\cdot}CO{\cdot}R + G \quad [1]$$

where R is usually either a C_{15} or C_{17} alkyl or alkenyl chain. TG are converted to glycerol sequentially *via* DG and MG, with an ME molecule being formed at each step:

$$TG \rightarrow (ME) + DG \rightarrow (ME) + MG \rightarrow (ME) + G \quad [2]$$

Both the ASTM and European standards limit the levels of certain components in the fuel, such as acids, free glycerol, and bound glycerol in the form of glycerides. The chemically bound and unbound glycerol, G_T, is limited to 0.24 and 0.25 wt% by the ASTM and European standards, respectively. The formula for calculating this value is approximately

$$G_T = G + (0.25)MG + (0.15)DG + (0.10)TG \quad [3]$$

in which G, MG, DG, and TG are now the weight percentages of the corresponding glycerol and glycerides in the product. The numerical factors in the equation account for the fraction of glycerol moiety in each species. The free glycerol content is itself limited to 0.02 wt% by both standards, but even if none were present, then either just over 99% of the ester bonds must be converted to ME in order to meet the standard or else residual glycerides must be removed after the process. If the MG account for all the residual glyceride moieties in the biodiesel, then their concentration is limited to approximately 0.96 wt%.

The catalyst concentrations, in terms of sodium hydroxide, that are used in the reactions are usually 1.0 wt% or less with respect to the oil. A methanol/oil molar ratio of 6:1 is typically employed, because Freedman *et al.* (2) claimed on the basis of their studies that there was no significant increase in yields when using higher molar ratios. However, no biodiesel standards existed at that time, and the analytical methods available, namely, TLC coupled to FID, would not have provided the necessary degree of analytical accuracy.

The methylation reactions typically produce 85–98% of the theoretical amount of ME at equilibrium, the balance being glycerides. For example, Darnoko and Cheryan (3) found that the methylation of palm oil reached equilibrium after 60 min at 50°C: The content of TG was 0.54 wt%.

Unfortunately, they gave no numerical values for the MG and DG contents, but it is clear that unless glycerides were removed, the product would not meet the ASTM glycerol specification, even though the content of ME would lie at the high end of the range quoted above. For these reasons, commercial processes use two and sometimes three successive reactions with the base in order to achieve standard biodiesel product.

The methylation reactions do not follow homogeneous kinetics and are characterized by a sudden reduction in the reaction rate after a few minutes. The concentrations of TG throughout the reactions are higher than those that are predicted from homogeneous kinetics, and the concentrations of MG and DG never reach the predicted maximum values (4). Special models have been developed to fit the kinetic data (3). We have identified that the esterification reaction is limited at the beginning because methanol and the oils are immiscible (5,6). Therefore, homogeneous reaction kinetics are not applicable. TG that enter the methanol phase initially are rapidly converted sequentially to esters. TG that do not enter this phase have difficulty reacting later because of glycerol separation. The mass-transfer limitations, which Freedman *et al.* (4) did not note, slow down the reaction at the beginning as compared with the butanolysis reaction, in which the reaction mixture is one phase. The subsequent separation of glycerol and, along with it, the catalyst then either stops the reaction altogether or slows it to the point of being impractical for a commercial one-step process. Darnoko and Cheryan (3) noted that the rate constants for the conversion of MG to ME were significantly greater than those for the conversions of the DG to MG, and TG to DG. We suggest this is because the MG are more soluble in the glycerol phase, where the catalyst is located.

We have shown that certain inert co-solvents, such as oxolane (tetrahydrofuran, THF), can convert the methanol/oil system to a single phase, thereby removing the limitations of mass transfer at the commencement of the reaction (6). We also have shown that if the methanol/oil molar ratio is raised to approximately 24:1 and higher and the appropriate amount of co-solvent is added, then glycerol separation can be prevented, thereby eliminating mass-transfer limitations throughout the reaction. At a methanol/oil molar ratio of 27:1, biodiesel product that meets the glycerol standard for biodiesel can be formed in only 7 min at ambient temperature, showing that achievement of the glycerol standard is not limited by the equilibrium of the reaction (6). At lower methanol/oil molar ratios, a glycerol-rich phase still separates from the one-phase system as the reaction progresses. We refer to this as the pseudo-single-phase system or reaction. This study examined the pseudo-single-phase reaction of SBO at the traditional methanol/oil molar ratio of 6:1. The glycerol phase was allowed to separate under nonstirring conditions to mimic commercial practices. The reactions also compared sodium hydroxide, sodium methoxide, and potassium hydroxide as catalysts in this system. The aim of this study was to find out whether use of the traditional 6:1 methanol/oil molar ratio would result in standard biodiesel product in terms of chemically bound glycerol when the reaction starts as a single phase. The study also compared the pseudo-single-phase reaction with both the two-phase reaction and the total single-phase reaction. The acid numbers of the products were not measured and are the subject of a future study.

MATERIALS AND METHODS

Materials. Commercial brand (President's Choice; Loblaw's, Toronto, Canada) edible-grade SBO was used. The following chemicals were supplied by the Aldrich Chemical Company (Milwaukee, WI): anhydrous grade methanol and THF (purity >99%, water content <0.005 wt%); *N,O*-bis(trimethylsilyl)-trifluoroacetamide (BSTFA); glycerol (99.5% spectrophotometric grade); anhydrous pyridine (purity >99%, water content <0.005 wt%); analytical grade sodium hydroxide (98 wt% pure). Concentrated hydrochloric acid and anhydrous sodium sulfate were obtained from BDH Inc. (Toronto, Canada). Metallic sodium (Fisher Scientific, Fair Lawn, NJ) was used to prepare sodium methoxide. ME standards including MG and DG were obtained from Sigma Chemical Co. (St. Louis, MO).

Preparation of catalyst solutions. Sodium or potassium hydroxide catalyst solutions were prepared by dissolving the required weights in the appropriate amounts of methanol (5.6 mL). The sodium methoxide solution was prepared in a dry two-necked flask equipped with a calcium chloride drying tube. The oxide layer was first removed from the metallic sodium under kerosene oil. Anhydrous methanol (the stoichiometric amount required for reaction with the methanol plus the amount required in the reaction) was placed in the flask. The necessary amount of sodium was weighed and immediately transferred to the flask. After the reaction, the methoxide solution was cooled to room temperature before use. The 100 mg of sodium methoxide required 42.6 mg of sodium and 59.3 mg of methanol.

Methylation of SBO. All the glassware was heated in an oven (100°C) overnight to dry before use. For each experiment, the SBO (20 g) and THF (9.0 mL) were mixed in a 100-mL round-bottomed flask equipped with a magnetic bar stirrer. The catalyst solution (5.6 mL) was added quickly, this being the zero time point of the reaction. Stirring was discontinued after 15 s. Samples (approximately 0.5-mL aliquots) were removed from the upper layer of the reaction mixture at appropriate times up to 4 h, and a final sample was taken after 20 h. All samples were quenched in 1.0 M HCl (0.5 mL), with gentle agitation to neutralize the base. The upper layers of the quenched samples were separated and dried over anhydrous sodium sulfate. To a portion (100 mg) of each sample was added stock tridecanoin solution (0.01 mL of 20 mg/mL in THF). Most of the THF was then removed with a dry stream of nitrogen. Pyridine (0.4 mL) and BSTFA (0.2 mL) were then added. The mixture was shaken for 30 s and then heated to 70°C for 15 min and cooled to room temperature. Each sample was then diluted to 5.0 mL with THF before GC

analysis. All kinetic runs were performed three times and the results were averaged.

Calibration of the gas chromatograph. The four component types (ME, MG, DG, and TG) were calibrated using stock solutions in THF of methyl linoleate (ML, 50 mg mL^{-1}), 1-monolinolein (MoL, 5.0 mg mL^{-1}), 1.3-dilinolein (DiL, 5.0 mg mL^{-1}), and trilinolein (TL, 5.0 mg mL^{-1}). A stock solution of tridecanoin (TD, 20 mg mL^{-1}) was used to establish the internal standard because it has a significantly different retention time from the ester and glycerides. Appropriate amounts of ML, MoL, DiL, and TL were measured from the stock solutions into separate sampling vials. To each was added stock solution of TD (0.10 mL). Before injection into the gas chromatograph, the samples for ML and TL were diluted to 5.0 mL with THF. In the cases of of MoL and DiL, virtually all of the small amount of THF present in each sample was removed in a stream of dry nitrogen. Pyridine (0.4 mL) and BSTFA (0.2 mL) were added to each sample, and the same procedure was followed as for the kinetic samples before GC injection. The concentrations of the standard solutions ranged from 2 to 20 mg mL^{-1} for ML and from 0.04 to 6.0 mg mL^{-1} for MoL, DiL, and TL. The concentration of TD was constant at 0.4 mg mL^{-1} in all standard solutions. The response factors, which were determined from the slopes of the linear calibration graphs (*R* values in brackets) were 0.51 (0.998), 0.55 (0.999), 1.13 (0.996), and 1.52 (0.984) for ML, MoL, DiL, and TL, respectively. The *R* value for TL was lower than the other *R* values because of deviation from linearity at the lowest concentrations.

Gas chromatograph operating conditions. Analyses were performed on a Hewlett-Packard model 5880A chromatograph equipped with an on-column injector, an FID, and a DB-1 fused-silica capillary column (2 m × 0.25 i.d.) coated with a 0.25-μm film of 100% polymethylsiloxane (J&W Scientific, Folsom, CA). Operating conditions were injector and detector temperatures of 350 and 320°C, respectively; helium carrier gas flow rate of 3 mL min^{-1} with makeup gas total of 55 mL min^{-1}. Air and hydrogen flow rates for the FID were 310 and 34 mL min^{-1}, respectively. Samples (0.5 μL) were manually injected at an oven temperature of 130°C, which was held for 2 min and then increased at a rate of 15°C min^{-1} to 350°C and held for 8 min. The total run time for each sample was 24.6 min.

RESULTS

The results are shown in Tables 1–3 and Figure 1. The values in the tables are averages of three runs for each set of conditions. The values for each run all lay within ±2.5% of the mean value for a particular data point. The results are normalized with respect to the ME and three glyceride components only. Because of other minor constituents in the product, this slightly overvalues the four components, but not sufficiently to change conclusions related to achievement of the ASTM glycerol specification. Table 1 shows the results for sodium hydroxide concentrations of 0.5, 1.0, and 2.0 wt%, all with respect to the oil. Table 2 shows results for 1.0 and 1.4 wt% potassium hydroxide. Table 3 shows results for 0.5, 1.0, and 1.35 wt% sodium methoxide. The results for a reaction that used 1.0 wt% sodium hydroxide and a methanol/oil molar ratio of 8:1 are not shown, because the results were very similar to those for the corresponding run in which the 6:1 molar ratio was used. Figure 1 contains plots of the increase in ME content and the decrease in the glyceride content in the first 10 min when 1.0 wt% sodium hydroxide was used as catalyst. It is included to give a visual idea of the slowing of the reactions. Graphical plots are not presented for the other data because they do not show, in detail, the critical regions related to the ASTM bound and unbound glycerol specification.

TABLE 1
Effects of Time and Sodium Hydroxide Concentration[a] on Ester and Glyceride Contents[b,c]

	0.5 wt% NaOH				1.0 wt% NaOH				2.0 wt% NaOH			
Time (min)	ME	MG	DG	TG	ME	MG	DG	TG	ME	MG	DG	TG
0	0	0	0	100	0.0	0.0	0.0	100	0.0	0.0	0.0	100
0.5	48.2	9.1	18.7	24.0	72.4	6.9	10.9	9.7	92.0	2.2	3.9	1.9
1	60.1	12.3	15.1	12.5	79.3	6.1	6.9	7.6	97.9	0.6	0.5	1.0
2	69.3	9.1	12.5	9.1	85.5	5.1	5.9	3.5	99.1	0.5	0.3	0.2
3	72.5	8.3	11.1	8.1	87.4	4.9	5.1	2.6	99.3	0.4	0.2	0.1
4	75.2	7.8	10.1	6.9	88.7	4.7	4.2	2.4	99.2	0.6	0.2	0.1
5	77.8	7.3	9.1	5.7	89.5	4.5	3.8	2.2	99.3	0.5	0.2	0.0
6	80.4	6.9	7.7	5.1	90.0	4.4	3.5	2.1	99.2	0.6	0.2	0.0
7	—	—	—	—	90.7	4.2	3.4	1.8	—	—	—	—
8	83.0	6.3	6.6	4.2	91.7	3.9	2.8	1.6	—	—	—	—
10	84.4	6.0	6.1	3.5	92.4	3.6	2.6	1.4	99.6	0.4	0.1	0.0
20	87.2	5.6	5.1	2.2	94.2	3.2	2.0	0.6	99.6	0.4	0.1	0.0
30	88.5	5.0	4.6	1.9	94.7	3.0	1.9	0.4	99.4	0.6	0.1	0.0
60	90.9	4.3	3.3	1.5	96.0	2.2	1.6	0.3	99.2	0.7	0.1	0.0
120	92.9	3.5	2.4	1.2	97.5	1.6	0.7	0.2	99.2	0.7	0.1	0.0
240	92.8	3.9	2.1	1.1	98.3	1.3	0.4	0.0	99.2	0.8	0.1	0.0

[a]wt% are based on oil.
[b]wt% are expressed with respect to the sum of methyl esters (ME), MG, DG, and TG only.
[c]6:1 methanol/oil molar ratio, 23°C, 1.6:1 tetrahydrofuran (THF)/methanol volumetric ratio.

TABLE 2
Effects of Time and Potassium Hydroxide Concentration[a] on Ester and Glyceride Contents[b,c]

	1.0 wt% KOH				1.4 wt% KOH			
Time (min)	ME	MG	DG	TG	ME	MG	DG	TG
0	0.0	0.0	0.0	100	0.0	0.0	0.0	100
0.5	60.3	12.3	14.2	13.2	67.2	9.3	8.6	15.0
1	70.4	8.6	11.5	9.4	75.9	7.8	7.5	8.8
2	75.5	6.6	10.3	7.6	81.8	6.5	6.7	5.0
3	79.9	6.1	7.9	6.1	85.8	5.5	6.0	2.7
4	82.7	5.5	7.2	4.6	87.5	5.1	5.0	2.4
5	84.7	5.3	6.3	3.8	88.7	4.9	4.4	2.0
6	85.4	5.0	6.1	3.6	90.4	4.5	3.4	1.6
8	87.1	4.7	5.2	2.9	92.4	3.3	2.8	1.5
10	89.3	4.5	4.8	1.4	93.6	3.0	2.2	1.3
15	—	—	—	—	94.7	2.5	1.7	1.1
20	90.9	4.0	4.4	0.7	95.9	2.2	1.1	0.8
30	92.0	3.7	3.6	0.6	96.2	1.9	1.1	0.8
60	93.5	3.3	2.8	0.5	97.0	1.7	0.7	0.6
120	94.9	3.0	1.7	0.4	97.5	1.4	0.6	0.5
240	96.1	2.2	1.5	0.2	98.2	1.1	0.3	0.4

[a]wt% are based on the oil.
[b]wt% are expressed with respect to sum of ME, MG, DG, and TG only.
[c]6:1 methanol/oil molar ratio, 23°C, 1.6:1 THF/methanol volumetric ratio. For abbreviations see Table 1.

TABLE 3
Effects of Time and Sodium Methoxide Concentration[a] on Ester and Glyceride Contents[b,c]

	0.5 wt% $NaOCH_3$				1.0 wt% $NaOCH_3$				1.35 wt% $NaOCH_3$			
Time (min)	ME	MG	DG	TG	ME	MG	DG	TG	ME	MG	DG	TG
0	0.0	0.0	0.0	100	0.0	0.0	0.0	100	0.0	0.0	0.0	100
0.5	46.7	8.7	21.7	23.0	73.8	6.4	13.9	5.9	80.0	6.3	7.9	5.8
1	55.8	10.2	17.1	16.9	81.1	6.6	9.7	2.7	83.4	5.9	6.9	3.7
2	61.0	11.9	13.3	13.7	87.6	5.1	5.8	1.5	86.5	5.4	5.6	2.5
3	67.4	10.3	11.6	10.7	88.6	4.7	4.7	2.0	90.7	4.4	3.8	1.1
4	69.7	9.4	11.0	9.9	89.7	4.1	4.5	1.7	91.5	4.2	3.3	1.0
5	72.5	8.6	10.0	8.8	90.1	4.2	4.1	1.6	91.9	4.2	3.1	0.8
6	73.8	8.4	9.6	8.2	—	—	—	—	92.8	3.9	2.7	0.7
7	76.4	8.1	8.6	6.9	—	—	—	—	—	—	—	—
8	78.6	7.7	7.5	6.2	91.6	3.7	3.6	1.1	95.1	2.5	1.9	0.5
10	80.6	7.4	6.5	5.4	93.8	3.2	2.4	0.6	95.8	2.3	1.5	0.5
20	82.7	7.0	5.6	4.7	95.6	2.6	1.5	0.3	96.5	2.1	1.1	0.3
30	83.9	6.7	5.5	3.9	96.2	2.3	1.2	0.2	97.0	1.8	1.0	0.2
60	87.2	6.5	3.9	2.4	97.3	1.7	1.0	0.0	98.0	1.5	0.4	0.1
120	89.2	5.0	4.0	1.8	97.9	1.6	0.5	0.0	98.3	1.3	0.3	0.0
240	92.8	4.0	2.0	1.2	98.5	1.3	0.3	0.0	99.1	0.9	0.1	0.0

[a]wt% are based on oil.
[b]wt% are with respect to the sum of ME, MG, DG, and TG.
[c]6:1 methanol/oil molar ratio, 23°C, 1.6:1 THF/methanol volumetric ratio. For abbreviations see Table 1.

DISCUSSION

The most important feature of all the results is the fast rate at which the reactions took place in the first minute, compared with later (see Fig. 1). There was a sudden slowing of all reactions, which we attribute to the formation of the glycerol phase in which the catalyst is preferentially soluble. In the first instance, this may have been in the form of a microphase, but it appeared that this was sufficient to dissolve most of the catalyst, thereby slowing the reactions. Only when 2.0 wt% sodium hydroxide was used did the reaction yield glyceride concentrations (after 2 to 3 min) that would satisfy the allowed biodiesel glycerol specification. However, the sodium hydroxide concentrations in excess of the 1.0 wt% identified by Freedman *et al.* (2) as being optimal are generally considered impractical. At higher concentrations, the potential to form soap irreversibly (and indirectly FA) and thereby exceed the biodiesel ASTM acid number of 0.8 is significantly increased. The extra base would also add significantly to the cost of a commercial process. As shown previously, if conditions are created that prevent the separation of the glycerol phase, then the biodiesel ASTM glycerol specification can be reached using 1.0 wt% sodium hydroxide in approximately 7 min. This entails raising the methanol/oil ratio to 25:1 or more for most oils. However, in the case of coconut oil, which has a significantly lower molar volume than other oils, biodiesel

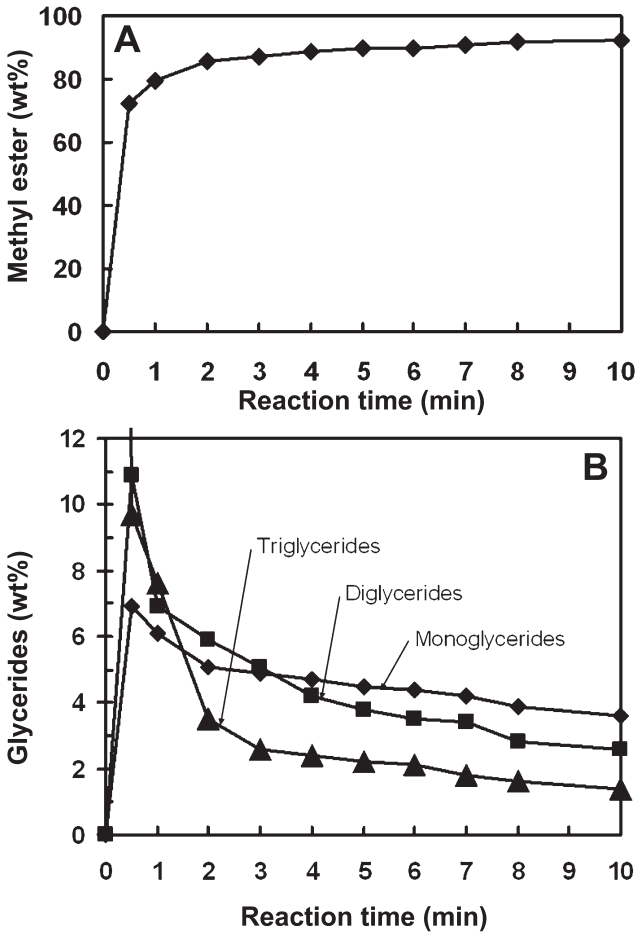

FIG. 1. Effects of reaction time on the contents (expressed as wt% of the sum of ME, TG, DG, and MG only) of the methyl ester (ME) and glyceride components at 23°C. Molar ratio of methanol/oil = 6.0, catalyst = 1.0 wt% NaOH with respect to oil.

standard material was formed in less than 1 min at the 6:1 methanol/oil molar ratio (6). The lower molar volume of the nonpolar coconut oil raised the polarity of the reaction mixture such that the glycerol did not separate at this molar ratio. Therefore, contrary to common belief, the glycerol did not have to separate to drive the reaction to the necessary degree of completion. The results from the homogeneous systems also demonstrated that, in the case of methylation, the ASTM biodiesel glycerol specification could be achieved solely by the equilibrium position of the reaction and did not require glycerol separation.

A second general feature of the results is that the concentration of TG eventually falls below the concentrations of the DG and MG. This is the expected behavior of a homogeneous reaction. In the two-phase reaction, some TG are initially excluded from the methanol phase and later are excluded from the glycerol phase, which in both cases is where the catalyst is located (3). The result is that the concentration of TG is higher than those of the MG and DG at the end of the reaction.

Some form of a glycerol phase must form rather quickly. This was seen in the reaction in which 1.0 wt% sodium hydroxide was used as catalyst (also see Fig. 1). The concentration of TG fell 84% in the first 30 s and only another 3% in the following 30 s. This deceleration of the reaction may be due in part to the reduction in the methanol concentration, but catalyst removal is the major contributor.

As expected, the data in all three tables show that an increase in base concentration leads to faster reaction rates, as well as higher ME and lower MG concentrations after 2 h. The concentrations of 1.0 wt% sodium hydroxide, 1.35 wt% sodium methoxide, and 1.4 wt% potassium hydroxide were all the same on a molar basis. The methoxide ion was the actual species that attacked the TG in methylation, and in the case of the hydroxides this was formed by the equilibrium between the methanol and hydroxide ions. Therefore, the concentrations of methoxide ions in the equimolar solutions of sodium and potassium hydroxide should have been the same. The results obtained with the two catalysts were very similar, with values at 5, 10, and 240 min being good examples. These were consistent with previous results obtained in our laboratory (7). The sodium methoxide catalyst appeared to be slightly better in terms of initial reaction rates as well as final glyceride contents. This may have reflected that the above hydroxide equilibrium produced water, whereas no such equilibrium existed in the case of sodium methoxide and methanol.

Finally, sets of experiments were carried out using a methanol/oil molar ratio of 8:1 and catalyst concentration of 1.0 wt% sodium hydroxide. These reactions occurred a little slower within the first few minutes than in the case of 6:1, reflecting the dilution of the catalyst, which was presumed to be the limiting kinetic species. However, as the methanol was consumed, the reaction rate became a little faster than in the case of 6:1, probably reflecting the higher polarity resulting from the higher concentration of residual methanol. This, in turn, favored more catalyst in the reacting phase due to the partitioning with the separated glycerol. Despite these observations, the results after 2 h were not significantly different from the experiments using the methanol/oil molar ratio of 6:1.

This study shows that, unless a subsequent purification step, such as distillation, is used, it is not possible to produce ME that meet biodiesel glycerol specifications in a single-step reaction that starts as a single phase but otherwise uses the traditional reaction conditions. The same conclusion prevails when the same molar quantities of potassium hydroxide and sodium methoxide are used. Elevation of the catalyst concentration may not be an option in the case of hydroxide catalysts, because the formation of soap is increased. For this reason, sodium methoxide is used as the catalyst for making ME from vegetable oils in all commercial multistep processes, such as that proposed by the Lurgi Corporation (8).

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