

Fast Formation of High-Purity Methyl Esters from Vegetable Oils

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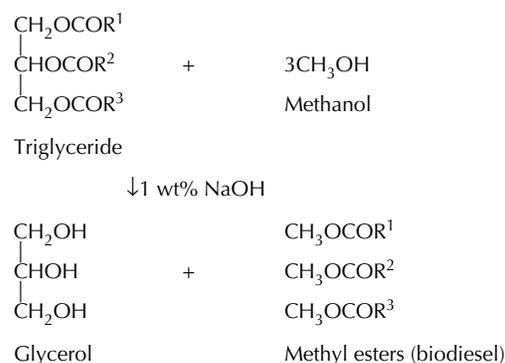
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ABSTRACT: Experiments have confirmed that the base-catalyzed methanolysis of vegetable oils occurs much slower than butanolysis because of the two liquid phases initially present in the former reaction. For the same reason, second-order kinetics are not followed. The use of a cosolvent such as tetrahydrofuran or methyl tertiary butyl ether speeds up methanolysis considerably. However, like one-phase butanolysis, one-phase methanolysis initially exhibits a rapid formation of ester, but then slows drastically. Experiments show that the half-life of the hydroxide catalyst is too long to explain the sudden slowing of the reaction. Similarly, lower rate constants for the methylation of the mono- and diglycerides are not a reasonable explanation. Instead the cause has been identified as the fall in polarity which results from the mixing of the nonpolar oil with the methanol. This lowers the effectiveness of both hydroxide and alkoxide catalysts. Increasing the methanol/oil molar ratio to 27 in the one-phase system raises the polarity such that the methyl ester content of the ester product exceeds 99.4 wt% in 7 min. This has obvious implications for the size of new methyl ester plants as well as the capacity of existing facilities. *JAOCS* 75, 1167–1172 (1998).

KEY WORDS: Base catalyst, coconut oil, methanolysis, methyl esters, methyl *t*-butyl ether, soybean oil, tetrahydrofuran, one-phase transesterification, vegetable oil.

For several years, the transesterification of vegetable oils to form esters, and in particular, methyl esters, has received considerable attention. This is because of the current use of these methyl esters as petrodiesel substitutes. In Europe, environmental concerns and agricultural considerations have resulted in the construction of several fuel methyl ester plants, the largest, in Italy, having a capacity of 250,000 tons per year. The financial incentives for these plants are fuel tax relief and agricultural subsidies for farmers to grow vegetable oil crops, rather than not to grow other crops. Producers in Europe are looking not only to build new plants but also to increase the capacities of older plants. The formation of vegetable oil methyl esters by the base-catalyzed reaction of vegetable oils and methanol as shown in Scheme 1 is fairly slow, and in

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SCHEME 1

some instances stops before completion. In the last 10 yr very little work has been done on the kinetics of the transmethylation of vegetable oils to produce fatty acid methyl esters, presumably because it was believed that the reaction was well understood. Two bench mark papers by Freedman in 1984 (1) and 1986 (2) are probably responsible for this. The work described in the earlier paper established that for the base-catalyzed transmethylation, a 6:1 methanol/oil molar ratio was optimal. This results in greater than 95 wt% methyl esters in the product when 1.0 wt% sodium hydroxide, based on the oil, is used as catalyst. It also maintains the advantage of the natural separation of the glycerol by-product at the bottom of the reactor, whereas when too much methanol is added, the glycerol either does not separate or moves into a methanol-rich upper phase. The use of sodium hydroxide, rather than sodium methoxide, is preferred because of the hazards and inconvenience of using sodium metal to produce the latter. The equilibrium between hydroxide ions and methanol is used to provide the necessary methoxide ions. The later paper by Freedman on the kinetics of the acid- and base-catalyzed transmethylation of soybean oil (SBO) has recently been discussed by us (3). However, for the sake of clarity and completeness of this present study it is first necessary to review our findings. Freedman examined the butanolysis and methanolysis of SBO. Alcohol/oil molar ratios of 6:1 were used along with 1.0 wt% sodium butoxide and 0.5 wt% sodium methoxide. On a molar basis it should be noted that these catalyst concentrations are less than the 1.0 wt% sodium hydroxide referred to above. Figure 1 shows the Freedman

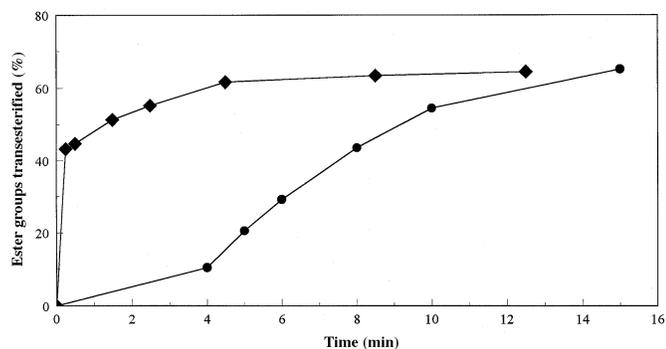


FIG. 1. Change in groups esterified with time for a molar ratio of: (●) MeOH/soybean oil (6:1), 0.5 wt% NaOMe, 40°C; (◆) BuOH/soybean oil (6:1), 1 wt% NaOBu, 30°C. Replotted from data in Reference 2.

data replotted as the percentage of the ester groups converted to methyl esters. Four anomalies were apparent in the original results, and of these the authors noted and commented on the first two. The four anomalies are: (i) whereas butanolysis followed second-order kinetics, methanolysis did not. In particular, the intermediate di- and monoglycerides never built up to the expected concentrations; (ii) the rate constants for the conversion of diglycerides to monoglycerides, and monoglycerides to glycerol, as determined from a computer program, were considerably smaller than that for the conversion of triglycerides to diglycerides; (iii) the methanolysis exhibited a lag time of approximately 4 min before significant amounts of methyl esters appeared; and (iv) butyl ester formation was initially fast but decelerated rapidly, whereas after the lag time, the methyl ester formation proceeded more slowly and uniformly before halting.

In our original discussion of the kinetics paper we explained the first two anomalies on the grounds that, whereas the butanolysis mixture is a single liquid phase, the methanolysis mixture consists of two phases. In addition, the solubility of the oil in the methanol, where the catalyst is located, is low. We also showed that it takes a significant time for the oil to reach saturation levels in the methanol. Therefore, despite the stirring used in the kinetic study, there were significant mass transfer limitations in the methanolysis reaction.

The two-phase reaction is therefore interpreted as follows. When the reaction is started, the concentration of the oil in the methanol is very low. As the concentration increases, the reaction rate increases. It is the slow buildup of the oil concentration that accounts for the lag time. Triglycerides are first converted to diglycerides, and because they are formed in the methanol phase they have a greater chance of reacting there rather than moving back to the oil phase. Therefore, their concentrations, as well as those of the monoglycerides, do not build up to those predicted by second-order kinetics. The reaction is slow compared to butanolysis because, although the methanol concentration is high in the predominantly methanol phase, the oil concentration is very low. It may be noted that the reaction rate remains fairly constant before a sudden deceleration, which is consistent with the rate

being mass transfer-limited. Eventually the reaction passes through an emulsion phase, and under circumstances which favor high conversion, a glycerol layer separates.

Anomaly 4 is partly related to anomaly 2, but in the kinetics paper this anomaly is explained by lower rate constants for the conversion of the di- and monoglycerides to monoglycerides and glycerol, respectively. However, the reactions come to a virtual halt when only 70% of the ester groups have been converted. That is, the reaction may be slowing or stopping for reasons other than lower rate constants for the methylation of mono- and diglycerides.

We have addressed the problem of the mass transfer limitations in methanolysis by the use of nonreactive cosolvents to form a single phase. We are aware of only one previous study of one-phase methanolyses of vegetable oils, although the author did not appear to be aware of the importance of either the cosolvent concept or reactant concentrations in increasing reaction rates. In 1937, Kurz (4) measured the rate of methanolyses at 20°C of several oils such as olive, sesame, linseed, and tung in dilute one-phase systems. He used a large excess of methanol (methanol/oil molar ratio 86:1) and diethyl ether (ether/oil 80:20, vol/vol) which lowered the oil concentration to approximately 11.8% by volume. The concentrations of methanol and base (0.3 wt% KOH based on the oil) were also lowered. As a result of this, the reaction rates were very slow, usually 95% of the available glycerol being liberated in 60 min, and 98% in 48–72 h. Kurz made no attempt to maximize the concentrations of the reactants while maintaining one phase.

We have found that simple ethers in general, such as tetrahydrofuran (THF) and methyl tertiary butyl ether (MTBE), are particularly good cosolvents. THF is the best found so far, approximately 1.25 vol/vol of methanol being required for miscibility at the methanol/oil ratio of 6:1 and a temperature of 23°C. This only causes a modest increase in total volume of the mixture, due to the low molar volumes of methanol and THF as compared to the oil. The oil still accounts for 64% of the volume, a value which is only slightly lower than that in the butanolysis mixture. The one-phase methanolysis occurs considerably faster than the two-phase system, 95 wt% methyl ester being formed in 20 min.

However, the one-phase process still exhibits the dramatic slowing of the reaction as seen in one-phase butanolysis. Ester (68%) is formed in the first minute, but only 77% by the end of the second minute. Significantly lower rate constants for the second and third steps would again be required to fit the result to second-order kinetics. This is not an attractive explanation given the similarities of the required mechanistic steps, and, therefore, we looked for other explanations.

Two possible explanations are: (i) a fall in the catalyst concentration and (ii) a polarity effect caused by the mixing of the methanol with the nonpolar oil. The sudden slowing of the reaction occurs in both alkoxide- and hydroxide-catalyzed reactions, and, therefore, it could be argued that the irreversible formation of soaps by the attack of hydroxide ions on the esters cannot be the reason for the slowing of the reac-

tion. However, it is very difficult to exclude all traces of water from these systems, and, therefore, the hydroxide depletion route is still feasible. Feuge and Gros (5) reported a fall in hydroxide concentration for a number of one-phase hydroxide-catalyzed ethanolsis reactions of peanut oil at 50°C. They found that in each case, 50% or more of the sodium hydroxide was destroyed in the first 15–20 min. They did not measure the hydroxide concentration directly, but derived the fall from the measurement of soap formation. We believed there was a need to measure the change in hydroxide concentration directly in the more important one-phase methanolysis reaction, and at conditions closer to ambient temperatures. This can be accomplished in the one-phase system by quenching it at any time by pouring it into water, whereupon the soap conveniently remains in the upper organic layer, allowing titration of the hydroxide ion in the water phase. In a second study we investigated the polarity effect by a series of experiments including the use of coconut oil and variations in hydroxide and methanol concentrations. The results of this study have led to a method for significantly improving the production of methyl esters.

EXPERIMENTAL PROCEDURES

Materials. The two oils used for this study were food-grade products as follows: SBO (President's Choice, Sunfresh Ltd., Toronto, Ontario, Canada) and coconut oil (Kissan 100% coconut oil; Kissan International Inc., Scarborough, Ontario, Canada). Methanol (anhydrous, 99+%), THF (anhydrous, 99+%), MTBE (anhydrous, 99+%), bis(trimethylsilyl) trifluoroacetamide (BSTFA, 99+%), pyridine (anhydrous, 99+%), and bromothymol blue indicator (pH 6.0–7.6) were supplied by Aldrich Chemical Company (Milwaukee, WI). Analytical grade sodium hydroxide (98%), concentrated hydrochloric acid, and anhydrous sodium sulfate were obtained from BDH Inc. (Toronto, Ontario, Canada).

Gas chromatography (GC) analyses of transesterified methylated products were performed on a Hewlett-Packard (Palo Alto, CA) 5880A series gas chromatograph equipped with an on-column injector, a flame-ionization detector (FID) and a DB-1 fused-silica capillary column (2 m × 0.25 mm i.d.) coated with 0.25 μm film of 100% polymethyl siloxane. The operating parameters were as follows: detector temperature, 320°C; injector temperature, 350°C; temperature program, 2 min at 130°C, heat at a rate of 15°C/min to 350°C; hold for 10 min. Carrier gas (He) velocity was 40 cm/s. The reference standards (purity 99%) were obtained from Sigma (St. Louis, MO) and they were as follows: methyl palmitate, methyl oleate, methyl linoleate, methyl stearate, 1-monopalmitin, 1-monolinolein, 1,3-dipalmitin (1% 1,2-isomer), 1,3-dilinolein (1% 1,2-isomer), tripalmitin, tristearin, and trilinolein.

Methods. Base-catalyzed transesterification reaction of coconut oil was carried out at 23°C using a 1.0 wt% sodium hydroxide catalyst and THF as cosolvent. Coconut oil (20.0 g) was placed in a 150-mL flat-bottom flask equipped with a

magnetic stirrer. Anhydrous THF (6.2 mL) was then added to the flask and the mixture was stirred. Next, sodium hydroxide [0.20 g (1.0 wt% with respect to coconut oil)] solution in methanol [7.1 mL (6:1 methanol-to-oil molar ratio)] was added to the mixture and the stirring was continued for an additional 20 s. Addition of sodium hydroxide solution to the mixture was recorded as zero time. Aliquots of samples (1 mL) were taken at 30 s and 1 min through to 10 min and quenched immediately to 20-mL vials containing 1 N HCl solution (1 mL). The organic layer of each sample was collected from the aqueous layer and transferred to 2-mL vials. Anhydrous sodium sulfate was added to each of the vials to absorb the trace amount of moisture. The samples were then derivatized for GC analyses. The derivatization of the organic material was necessary in order to determine the amount of mono- and diglycerides present in the final product by GC. Mono- and diglycerides are not volatile enough for GC analysis; the addition of BSTFA reagent made them more volatile so that they could be detected by the GC.

For derivatization, anhydrous pyridine (0.4 mL) and BSTFA reagent (0.2 mL) were added to each 20-mL vial containing transesterified product (100 mg). The vials were then capped, shaken, and placed on a water bath at 65°C for 20 min, with occasional stirring. After heating, the samples were removed from the water bath and cooled to room temperature and diluted using THF (4.4 mL). The samples were then injected onto the gas chromatograph to obtain a profile of the conversion of methyl ester with respect to time.

The change in hydroxide concentration in the one-phase methanolysis reaction was measured directly at room temperature (23°C). SBO (100.0 g) and anhydrous THF (45 mL) were placed in a 500-mL flat-bottom flask equipped with a magnetic stirrer and the mixture was stirred. Next, sodium hydroxide [1.0 g (1.0 wt% with respect to SBO)] solution in methanol [28 mL (6:1 methanol-to-oil molar ratio)] was then added and the stirring was continued for an additional 20 s. Samples of the reaction mixture were taken at 3, 5, 10, 20, 30, 60, and 120 min and quenched immediately into 125-mL Erlenmeyer flasks containing water (20 mL). The soap remained in the upper organic layer in the reaction mixture, thus allowing titration of the hydroxide ion in the water phase. For titration of each of the samples containing hydroxide ions, 5 drops of bromothymol blue were added to the mixture as an indicator. The sample was then titrated with 0.507 M sulfuric acid. From the amount of sulfuric acid added to the sample, the percentage depletion of hydroxide ions could be calculated.

A number of transesterification reactions were carried out using SBO, methanol, and four different but slightly higher concentrations than the conventional 1.0 wt% sodium hydroxide catalyst (1.1, 1.3, 1.4, and 2.0 wt%) in order to improve the reaction rate in less time. All other experimental conditions including the methanol-to-SBO molar ratio (6:1) were the same as described above.

A number of experiments were also conducted using higher methanol-to-SBO molar ratio (25:1, 27:1, 28:1, 35:1, and 40:1) than the conventional 6:1 ratio and 1.0 wt% sodium

hydroxide catalyst to study the polarity effect of the reaction mixture and to obtain high conversion of methyl esters in less time. The amount of THF needed to make the mixture one phase in different methanol-to-oil molar ratio combinations was determined by a cloud point method (6).

RESULTS

A typical hydroxide depletion curve for the one-phase methanolysis of SBO at 23°C (6:1 methanol/oil molar ratio and 1.0 wt% sodium hydroxide based on the oil) is shown in Figure 2. Methyl ester production for both SBO and coconut oil (conditions as above) are shown in Figure 3. Results for SBO in which 1.3 wt% sodium hydroxide was used are also shown in Figure 3. Figure 4 shows results in which extra methanol was added during the methanolysis of SBO. The volumes of methanol and THF used to make the mixture one phase for different molar ratios of methanol to SBO are shown in Table 1. Table 2 illustrates the results from transesterification reactions of SBO involving higher methanol-to-oil molar ratio than the conventional 6:1 ratio.

DISCUSSION

It can be clearly seen from Figure 2 that the half-life for the depletion of the hydroxide ion in the one-phase methanolysis of SBO was approximately 12 min. In contrast, the reaction rate had already slowed down after only 3 min. After 1 h, the transesterification reaction was essentially complete when the depletion of the hydroxide ion was in the range of 86–94% (see Figs. 2 and 3). Therefore, the half-life of the hydroxide catalyst is too long to explain the sudden reduction of the reaction rate. Feuge and Gros (5) reported a fall in hydroxide ion concentration during the ethanolysis of peanut oil at 50°C. They investigated a number of ethanolysis reactions which involved one equivalent of oil, one or two equivalents of ethanol, and three different concentrations of sodium hydroxide catalyst (0.2, 0.4, and 0.8 wt%). In all cases the ethanolysis mixture was one-phase. They reported that, in each case, 50% or more of the catalyst was destroyed in the first 15–20

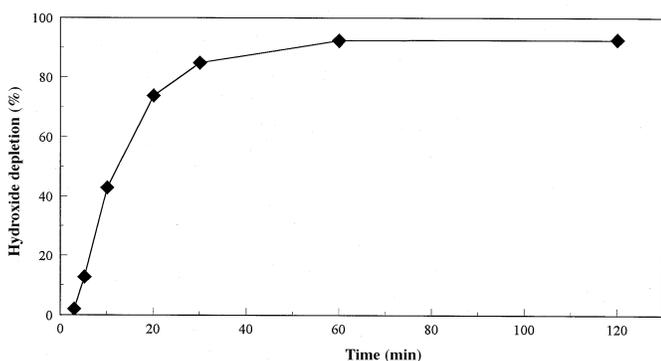


FIG. 2. Percentage of depletion of hydroxide ion concentration with time during methanolysis of soybean oil (6:1 methanol/oil molar ratio) using 1 wt% NaOH catalyst and tetrahydrofuran (THF) as cosolvent.

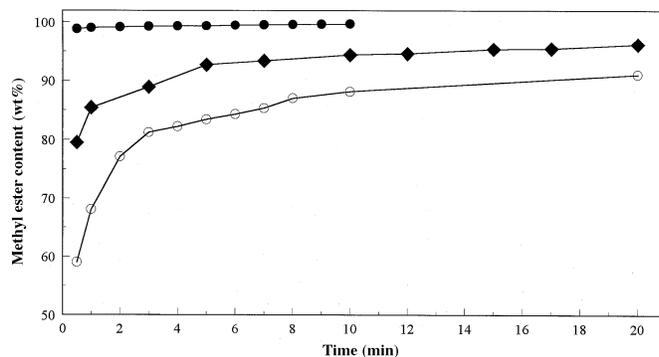


FIG. 3. One-phase methanolysis of: (●) coconut oil with 1 wt% NaOH; (○) soybean oil with 1 wt% NaOH; (◆) soybean oil with 1.3 wt% NaOH. Each experiment was conducted using 6:1 methanol/oil molar ratio and THF as cosolvent. See Figure 2 for abbreviation.

min at 50°C. For base-catalyzed one-phase methanolysis of SBO at 23°C, 67–83% of the hydroxide ions are depleted in about the same time. Feuge and Gros (5) did not measure the hydroxide concentration directly, but calculated the fall of hydroxide concentration from the measurement of soap formation. Our results suggest that the indirect measurement of hydroxide ion is reasonable.

Transesterification reactions were also carried out using SBO, methanol, and different concentrations of sodium hydroxide catalyst. The ester contents after 1 min for 1.1, 1.3, 1.4, and 2.0 wt% sodium hydroxide were 82.5, 85, 87, and 96.2%, respectively. Results indicated that the hydroxide concentration can be increased up to 1.3 wt%, resulting in 95 wt% methyl ester after 15 min. A dramatic increase in reaction rate was accomplished by increasing the hydroxide concentration from 1.0 to 2.0 wt% which resulted in a 98.8% ester content in only 3 min. Substantial amounts of glycerol appeared almost immediately after the start of the reaction, and in a few minutes a significant amount of precipitate accumulated in the reaction mixture. This precipitate immediately dissolved when dilute hydrochloric acid was added, which suggests that it was sodium hydroxide and not soap. We believe that as the reactants mix, the medium around the sodium

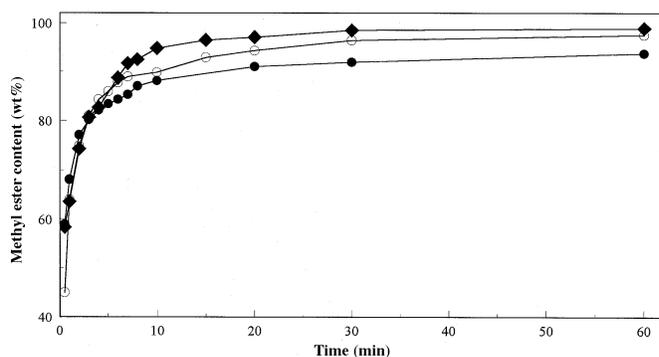


FIG. 4. One-phase methanolysis of soybean oil with 1 wt% NaOH and methanol/oil molar ratio: (●) 6:1; (○) 8:1; (◆) 6:1 + methanol (at 5 min) to 8:1. Each experiment was conducted using THF as cosolvent. See Figure 2 for abbreviation.

TABLE 1
Volumes of Methanol and Tetrahydrofuran (THF) Used for Different Molar Ratios of Methanol to Soybean Oil^a

Molar ratio	Volume of methanol (mL)	Volume of THF (mL)
25:1	23.3	20.0
27:1	25.2	22.0
28:1	26.2	25.0
35:1	32.8	26.0
40:1	37.3	28.0

^aVolume of oil is 23 mL in all cases.

hydroxide falls in polarity, thereby causing the precipitation. These results show that high conversions can be achieved at higher hydroxide concentrations. However, this must be balanced against the soap formation which occurs by attack of hydroxide on the esters. The results suggest that one way to achieve high conversion and high yield is to perform the reaction using close to 2.0 wt% hydroxide, and add neutralizing acid after 4 to 5 min. Only a small amount of precipitate was formed at the end of 4 h when 1.0 wt% sodium hydroxide was used. The ester compositions for the reactions catalyzed by 1.0 and 2.0 wt% sodium hydroxide were very similar after 4 h. The ester contents for the various reactions after 20 h were indistinguishable, thus, given sufficient time, transesterification occurred to the same extent. However, soap formation would be higher when more base was used.

In order to study the polarity effect, the transesterification of coconut oil and methanol was investigated under the same experimental condition as described above for SBO. Coconut oil has shorter alkyl side chains than SBO and therefore has a higher polarity and lower molar volume.

For coconut oil, the THF/methanol volume ratio required to achieve miscibility is only 0.87—less cosolvent is required to achieve miscibility compared to other oils such as SBO and canola oil, which have longer alkyl side chains. The total volume of the reactants only increases by 21% because the coconut oil accounts for a relatively large volume fraction of the mixture. This shows that the relative mass contents of the nonpolar chains and the polar ester linkages in the oils are important in determining the amount of required cosolvent. For

TABLE 2
Composition of Methyl Esters in the Products Obtained from Transesterification Reactions of Soybean Oil with Methanol Using Different Methanol/Oil Molar Ratios and 1.0 wt% NaOH Catalyst

Time (min)	Methyl esters (%) at different methanol/oil molar ratios				
	25:1	27:1	28:1	35:1	40:1
1	83.3	82.0	80.6	75.6	63.7
2	89.3	90.9	89.5	88.2	79.7
3	90.2	95.3	95.1	91.8	86.2
4	91.3	98.2	97.1	95.7	95.5
5	94.7	98.3	98.0	96.2	95.0
7	NA ^a	99.4	99.2	NA	NA

^aNA = Not available.

one-phase methanolysis of coconut oil, using 1.0 wt% sodium hydroxide catalyst and THF as cosolvent, the methyl ester content of the ester product was over 99 wt% in 1 min (see Fig. 3). This result confirms that polarity does indeed play an important role in the reaction.

Another way to counteract the polarity effect would be to use more methanol at the beginning of the reaction or add more methanol later. A reaction using 1.0 wt% sodium hydroxide and a starting methanol/SBO molar ratio of 8:1 was carried out. This reaction is compared to the reaction carried out at a starting methanol/SBO molar ratio of 6:1 with the same catalyst as shown in Figure 4. There is obviously more methanolysis for the 8:1 molar ratio reaction than for the 6:1 ratio; the ester contents after 1 h were 97.5 and 93.7 wt% for the 8:1 and 6:1 molar ratio reaction, respectively, whereas after 4 h the ester contents were essentially the same. It could be argued that, although the hydroxide and oil were diluted 12.5% by the addition of the extra cosolvent and methanol, the concentration of the latter increased by almost 30%, and this alone could account for the faster reaction. Therefore, a reaction was performed in which the extra methanol required to bring the ratio to 8:1 was added after 5 min. An advantage of doing this is that no extra cosolvent is required. This addition caused a surge in the reaction rate which was sufficient to cause a greater conversion after 10 min than when all the methanol was added at the beginning of the reaction. This increase in rate is probably due to incomplete mixing, which results in regions of higher polarity where the ionization of the sodium hydroxide is better. The rate of reaction decreases again as the methanol is blended into the mixture. The ester content before and after the addition of extra methanol was 82.7 (at 4 min) and 88.7 (at 6 min) wt%, respectively, but increased by only 3 wt% in the next minute. At 20 min and 1 h, the methyl ester contents were 98.1 and 98.9 wt%, respectively. Another way to address the polarity problem is to add more methanol at the beginning of the reaction. If polarity of the reaction mixture is a factor, then the addition of more methanol should improve reaction rates up to a point where dilution effects then take over. Experiments were therefore carried out using different methanol/oil molar ratios.

The results (Table 2) show that the highest methyl ester content after 5 min occurred at a methanol-to-oil molar ratio of approximately 27:1. A dilution effect appeared above a molar ratio of 28:1. At a 40:1 methanol-to-SBO molar ratio, the contribution of the methyl ester was only 95 wt% after 5 min. At the molar ratio of 27:1 the Austrian Standard of 99.4 wt% methyl ester was achieved in only 7 min. The monoglyceride content was about 0.6 wt%, and no di- and triglycerides were detected.

These results show that methyl ester contents which meet fuel standards can be achieved rapidly in one pass. In those cases where extra methanol and cosolvent are used, there are costs associated with extra distillation. However, the rapid reactions can be used in smaller, continuous plants. The excess methanol and cosolvent are flashed off and recycled. Separation

tion of the glycerol followed by water washing and distillation yields high-purity methyl ester.

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