Standard Biodiesel from Soybean Oil by a Single Chemical Reaction

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ABSTRACT: Laboratory methods are described for producing standard biodiesel from low-acid-number vegetable oils in single-step reactions without distillation of the products. Either sodium hydroxide or methoxide is used as the catalyst. Biodiesel fuel is currently made from vegetable oils using basic catalysts. With this methodology, the oils must be reacted two or three times with methanol, in the presence of sodium methoxide, to make a product that meets the standard for the total chemically bound and unbound glycerol content. Previously it was thought that sodium hydroxide could never be used as the catalyst because it forms soap with the ester, which lowers the yield and makes product isolation difficult. Two of the described methods use sodium hydroxide as the catalyst and the other uses sodium methoxide. These methods rely on the use of oxolane as co-solvent to manipulate phase behavior during the reaction. Reactant molar ratios and base concentrations are also optimized to drive the reactions to the necessary degree of completion.

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KEY WORDS: Biodiesel standards, laboratory methods for biodiesel, one-step reaction.

Biodiesel fuel, in the form of FAME, is now manufactured in many countries. An ASTM standard (1) as well as a unified European standard (2) for biodiesel has now been adopted. The feed material used in Europe for the production of biodiesel has been mainly low-acid-number rapeseed oils, whereas in North America low-acid-number soybean oil is preferred.

In the normal production of biodiesel, the oil, methanol, and sodium methoxide catalyst are mixed together. Mechanical mixing is necessary because the oil and methanol are not miscible. In addition, the sodium methoxide is only soluble in the polar methanol phase. We have proposed that during the mixing, the oil slowly diffuses into the methanol, where the TG that enters the methanol is rapidly converted, first to DG, then to MG, and finally to glycerol, with a molecule of methyl ester being produced in each step. The DG and MG are surfactants, and it is likely that an emulsion exists for a short time, which may improve mass transfer. However, the glycerol by-product is polar, and within a short time a separate glycerol phase appears. This phase selectively extracts the catalysts and, being dense, settles to the bottom of the reaction vessel. Therefore, the reaction essentially stops before it has reached the necessary degree of completion. The upper ester-rich phase must then be reacted with more methanol and catalyst. Sometimes the reaction must be repeated a second time to achieve the allowed levels of chemically bound and free glycerol in the product (3). We have also proposed that because the reaction is initially inhomogeneous, some of the TG does not enter the methanol phase. The consequence is that TG is the dominant unconverted glyceride. In a totally homogeneous reaction, which can only be achieved using a co-solvent, the rate constants for the sequential steps should be similar, so that MG should be the dominant unconverted glyceride. The abnormal kinetics caused by the phase behavior may explain why the European standard includes separate limits for the allowed levels of each of the individual glycerides.

One strategy to overcome the mass transfer limitations of the above reaction would be to make the reaction monophasic (4). We have found that oxolane (THF) is an excellent co-solvent for the methanol/oil systems. When the traditional 6:1 methanol/oil molar ratio is used, the addition of a volume of oxolane 1.25 times that of the methanol results in the reaction mixture being initially monophasic. However, a glycerol phase still appears as the reaction progresses. We refer to this behavior as a pseudo-monophasic reaction. If the methanol/oil molar ratio is raised to approximately 27:1 and the appropriate amount of oxolane is added, then no glycerol separates and the reaction is monophasic throughout (5). At lower molar ratios, a glycerol phase always separates.

Our objective has been to find conditions whereby low acid-number vegetable oils could be converted to standard biodiesel in a single reaction, using sodium hydroxide as catalyst. The key quality parameters are the total glycerol content (free and chemically bound), which is limited to 0.240 and 0.250 wt% by the ASTM and European standards, respectively, and the acid number, which is limited to 0.50 (mg KOH per gram) in both standards.

We have extensively studied the pseudo-monophasic reaction at 23°C with respect to the variables of methanol/oil molar ratio, catalyst concentration, amount of oxolane added, and reaction time. The chemically bound and unbound glycerol content and acid number were the measured parameters. The results indicated the optimal conditions that should be tested as methods to make standard biodiesel using a single chemical reaction only. These conditions were as follows: a methanol/oil

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molar ratio of 14:1, a sodium hydroxide concentration of 1.2 wt% or sodium methoxide concentration of 1.6 wt% (both based on the oil), a methanol/oil volumetric ratio of 1:1, and a reaction time of 10 min at 23°C. Below the 14:1 molar ratio an unacceptable jump in the acid number occurred when the catalyst was added. The catalyst concentrations, which were higher than usually used, were required to drive the glycerides to sufficiently low levels before the acid number exceeded its limit. The methods that were tested in this study are primarily for researchers who need to produce their own biodiesel for engine testing and other research. It also allows researchers to make specialized standard biodiesel from a variety of oils. We believe that these methods are applicable to all low-acid-number vegetable oils.

EXPERIMENTAL PROCEDURES

The soybean oil used for this study was food-grade product purchased from Loblaws Supermarket (President's Choice) Ltd. (Toronto, Ontario, Canada). The following chemicals were supplied by Sigma-Aldrich Chemical Company (Milwaukee, WI): methanol (anhydrous, 99+%); THF (anhydrous, 99+%); oxalic acid (99+%); sodium methoxide in methanol 25 wt% (w/w); sodium chloride (99+%); calcium chloride (–4+30 mesh, technical grade); 2-propanol (anhydrous, 99.5%); toluene (HPLC grade, 99.8%); *p*-naphtholbenzein (indicator grade); 0.1 N aqueous potassium hydroxide (volumetric standard); N-methyl-N-trimethylsilyltrifluoroacetamide (derivatization grade); heptane (anhydrous, 99%); pyridine (anhydrous, 99.8%); tricaprin (C10:0) (99%); mono-olein (C18:1, *cis*-9) (99%); 1,3-diolein (C18:1, *cis*-9) (99%); triolein (C18:1, *cis*-9) (99%); 1,4-butanediol (99+%); glycerol (99.5%); 1,2,4-butanetriol (96+%). A high-temperature guard column (5 m × 0.53 mm) and a DB-5ht fused-silica capillary column with a 5% phenylmethylpolysiloxane bonded and cross-linked phase internal coating were purchased from Chromatographic Specialities Inc. (Brockville, Ontario, Canada). Analytical-grade sodium hydroxide (98%) pellets were obtained from BDH Inc. (Toronto, Ontario, Canada), and anhydrous sodium sulfate was obtained from VWR Inc. (Toronto, Ontario, Canada). The soybean oil had a water content of 107 ppm. The oxolane and methanol were stored over molecular sieves and had water contents of 38 and 30 ppm respectively, as measured by the Karl Fischer method (6).

Method 1. The following method uses a methanol/oil molar ratio of 14:1, an oxolane/methanol volume ratio of approximately 1.0, and a sodium hydroxide concentration of 1.2 wt% (based on the oil). The reaction was carried out at ambient temperature, which in this case was 23°C. Soybean oil (60.0 g) was placed in a 200-mL two-necked round-bottomed flask equipped with a magnetic stirrer, a reflux condenser, and a calcium chloride guard tube. The reflux condenser prevented the evaporation of methanol and oxolane from the reaction mixture and maintained atmospheric pressure. Methanol (30.6 mL) and oxolane (38.4 mL) were then added sequentially. In a 20-mL vial, sodium hydroxide (0.72 g) was dissolved in methanol (8.4 mL). This solution was added all at once to the round-bottomed flask with continuous stirring. Exactly 10 min after this addition the reaction was stopped by the addition of oxalic acid (1.656 g) dissolved in methanol (10 mL). This provided an oxalic acid/sodium hydroxide molar ratio of 1:1. The whole reaction mixture was transferred to a separatory funnel and washed with 10 wt% brine solution (1 × 120 mL, 4 × 150 mL) until the pH of the wash water was 7 and then washed with water (1 × 150 mL). Gentle agitation was used in each washing step to mitigate emulsion formation. The washing removed free glycerol, methanol, oxolane, sodium oxalate, and excess oxalic acid. The water-washed product was dried in a Büchi Rotovapor using a water aspirator at a pressure of approximately 36 mm of Hg, and a water bath at 100°C. The product was then analyzed for glyceride composition by the standard GC reference method ASTM D 6584. The acid number of the product was measured by a manual titration method, ASTM D 974. A typical yield was 58.5 g (96.5%). Yields of methyl ester were limited only by mechanical losses, there being no side reactions, and in all cases exceeded 95%.

Method 2. This method followed the procedure of Method 1 up to and including the addition of the oxalic acid solution. The reaction mixture was then transferred into a round-bottomed flask. The majority of the methanol and oxolane solvents were evaporated in a Büchi Rotovapor by using a water aspirator at a pressure of approximately 36 mm of Hg, and a water bath at 75°C. The removal was considered to be complete in about an hour, after no further condensate was observed. The product was then allowed to cool to room temperature. A glycerol layer separated out at the bottom of the flask. The upper layer was then transferred to a separatory funnel and water-washed with 10 wt% brine solution (5 × 150 mL) until the pH of the wash was 7. In each wash the sample and brine solution were gently agitated to prevent any emulsion formation. The organic layer was collected and dried over sodium sulfate and analyzed for glyceride content and acid number as described in Method 1. The bottom layer in the round-bottomed flask was transferred to two 24-mL vials, with the aid of THF. This glycerol-rich liquid was washed with anhydrous heptane (3–4 × 12 mL) to extract the FA. The vials were centrifuged for approximately 2 min after the addition of heptane each time to enhance clear phase separation. Alternatively, this separation could be carried out in a separatory funnel, particularly if the method has been scaled up. The heptane layer was collected and dried over anhydrous sodium sulfate. The fraction was then evaporated using the Büchi Rotovapor. The acid number of the resulting liquid was measured using the ASTM D 974 method.

Method 3. This method used the same reaction conditions as in Method 1 except that 1.2 wt% of sodium hydroxide was replaced by a molar equivalent (1.6 wt%) of sodium methoxide. The reactants were added to the round-bottomed flask as described in Method 1. Following this, 4 mL of the catalyst solution of sodium methoxide in methanol [25 wt% (w/w); density 0.945 g/mL] was added to the reaction system with continuous stirring. After exactly 10 min the reaction was worked up as described in Method 1, and the glyceride levels and acid number of the product were measured.

RESULTS AND DISCUSSION

The acid numbers; MG, DG, and TG contents; and the chemically bound glycerol (CBG) contents of the biodiesels are shown in Table 1. The values for Method 1 are the means of seven experiments. Three experiments (A, B, and C) were conducted for Method 2, and two experiments (A and B) for Method 3; the values for all of these experiments are shown in the Table. The acid number of the nonpolar phase that was isolated from the glycerol produced by Method 2, Experiment A, is also shown in the Table.

Some comments are necessary on the methods themselves. The first is that the concentration of the basic catalyst that is used in the methods is higher than that normally employed either in industrial processes or laboratory studies. The higher base concentration is necessary to achieve the required chemically bound glycerol content. If the base concentration is reduced from those given in the methods, then the necessary degree of completion is not achieved without exceeding the allowed acid number. In addition, the oil, methanol, and oxolane should be reasonably dry. The soybean oil that was used had a water content of 107 ppm.

Oxalic acid, $HO_2C–CO_2H$, was used to terminate the reactions by neutralizing the catalyst. The use of strong aqueous mineral acids can hydrolyze ester bonds and give erratic results. Oxalic acid is soluble in methanol, so the reactions can be terminated without adding water. In addition, the pK_a for the first dissociation constant of oxalic acid (1.23) is significantly lower than that of most carboxyl groups (~4), so any soap that has been formed is still converted back to FA. Therefore, the increase in acid number from the substrate to the product is a measure of the irreversible attack of hydroxide ion on ester bonds. Both oxalic acid and its salts are very soluble in water and they are easily removed, along with other water-soluble materials such as glycerol, methanol, and oxolane, from the methyl ester by water washing

All the products were washed extensively with brine and/or water, which removed any free glycerol. The CBG concentrations could therefore be used for comparison with the standards. The biodiesels produced by all three methods had CBG concentrations that met both the ASTM and European maximum levels of 0.240 and 0.250 wt%, respectively. Method 2 only differed from Method 1 in that much of the methanol and co-solvent were removed under nonreactive conditions prior to water-washing. Method 1 was repeated seven times. The mean values and 95% confidence intervals for CBG contents and acid number were 0.220 ± 0.018 and 0.459 ± 0.037, respectively. In both cases the upper limits met the ASTM and European standards. The CBG values for all 12 experiments fell within the 95% confidence limits of Method 1. These CBG contents after 10 min of reaction time essentially represented the steady-state conditions. The ASTM and European biodiesel standards differ in that the European standard places individual limitations on MG (0.8 wt%), DG (0.2 wt%), and TG (0.2 wt%) concentrations, and the ASTM standard does not. The limitations cited in the European standard appear to have little scientific basis as acknowledged by ASTM. They may simply exist only because the individual groups of glycerides can be measured. It should be noted that in all 12 experiments, the MG contents of the products exceeded the allowed MG content under the European standard, even though the CBG limit of 0.25 wt% was easily achieved.

Two of the three acid numbers for Method 2 fell below the 95% confidence limit of Method 1, and it did appear that on average, Method 2 produced slightly lower acid numbers for the product. Method 2 is preferred, if only because the excess methanol and oxolane can be kept separate from the water washings, thereby making disposal or recycling easier. In a commercial process the excess methanol and oxolane would have to be removed and recycled prior to any washing steps.

The acid number of the substrate used in this study was 0.06. If the acid number of substrates is closer to 0.10, then products may not meet the standard for acid number when using the hydroxide catalyst and Method 1. In this case Method 3, which uses sodium methoxide, is recommended. Given the results from Methods 1 and 2, we recommend that Method 3 be modified to remove the methanol and oxolane prior to the washing steps, as in Method 2.

When sodium hydroxide was used as the catalyst, the rate of increase in acid number was much lower than expected when compared with the rate of the methylation reaction. This appeared to be due to the presence of the oxolane, which may have influenced the equilibrium between hydroxide and methoxide ions. After 10 min, the reaction, in terms of methyl

TABLE 1
Acid Numbers (mg KOH g^{-1}), Total Chemically Bound Glycerol (CBG, wt%) and Glyceride Contents (wt%) of FAME Obtained from Methods 1 through 3.

Method	Acid number	Total CBG	C16 MG	C18 MG	DG	TG
1 (means of seven expts.)	0.459[a]	0.218[b]	0.104	0.716	0.005	0.054
2 (expt. A)	0.479	0.235	0.111	0.759	0.008	0.090
2 (expt. B)	0.377	0.222	0.113	0.713	0.008	0.075
2 (expt C)	0.407	0.224	0.116	0.718	0.008	0.064
3 (expt. A)	0.123	0.233	0.112	0.767	0.005	0.054
3 (expt. B)	0.162	0.231	0.109	0.752	0.008	0.083
2A (glycerol extract)	0.411	N/A	N/A	N/A	N/A	N/A

[a]95% confidence limits = ±0.037.
[b]95% confidence limits = ±0.018. N/A, not applicable.

ester formation, had essentially reached steady state, whereas the acid number continued to increase. It was therefore necessary to stop the reaction at this time, particularly when sodium hydroxide was the catalyst. When sodium methoxide was used as the catalyst, after 10 min of the reaction, the increase in the acid number from the substrate to the product was reasonably small. This suggests that substrates with acid numbers as high as 0.3 or even greater could be used. Finally, the small amount of nonpolar material that was extracted from the glycerol phase in Method 2 had an acid number similar to that of the methyl ester product. This is consistent with this material actually being methyl ester. It also shows that the low acid number of the methyl ester product is not due to FA removal by glycerol.

The methods that are described here for making standard biodiesel should be applicable to all low-acid-number TG-based vegetable oils. They will allow researchers to make standard biodiesel methyl esters in their own laboratories from a variety of substrates. The commercial application of these methods to standard biodiesel production has not escaped our attention. Importantly, they allow for truly continuous processes in which the substrate has to be reacted only once.

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