J Amer Oil Chem Soc (2007) 84:189–195
DOI 10.1007/s11746-006-1023-3

ORIGINAL PAPER

Variables Affecting the Production of Standard Biodiesel

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Received: 30 August 2006 / Accepted: 1 November 2006 / Published online: 10 January 2007

Abstract Biodiesel is composed of fatty acid methyl esters, currently made from vegetable oils using basic catalysts. The oils must be reacted two or three times with methanol, in the presence of sodium methoxide to make products which meet the ASTM and European biodiesel standards. It is also believed that sodium hydroxide can never be used as the catalyst because it causes soap formation, which either lowers the yield or raises the acid number and makes product isolation difficult. Methods for producing standard biodiesel from low-acid-number soybean oil, in one chemical reaction using sodium hydroxide and a cosolvent, were recently reported. This study reports the effects of variables on the acid numbers and chemically bound glycerol contents of the products which led to the methods. These variables were the molar ratio of alcohol to oil, catalyst concentration, cosolvent volume, and reaction time. The alcohol-to-oil molar ratio must be at least 14, and the sodium hydroxide concentration should be at least 1.2 wt% (based on oil), to meet the necessary acid number and glycerol contents of the biodiesel. The volume of tetrahydrofuran cosolvent used must be 90–130% of that required to just create complete miscibility at the beginning of the reactions.

Keywords Biodiesel standards · One-step reaction · Molar ratio · Catalyst concentration · Cosolvent volume

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Introduction

Biodiesel is composed of fatty acid methyl esters that are produced by the reaction of low-acid-number vegetable oils in the presence of a basic catalyst. Presently, many countries are establishing biodiesel as an alternative fuel. Biodiesel is currently made by the base-catalyzed methylation of triglycerides, which by attack of methoxide ion are sequentially converted via diglycerides and monoglycerides to glycerol, with a molecule of methyl ester being formed in each step as follows:

$$\mathrm{TG} + \mathrm{MI} \rightleftharpoons \mathrm{ME} + \mathrm{DG}, \quad \mathrm{DG} + \mathrm{MI} \rightleftharpoons \mathrm{ME} + \mathrm{MG},$$
$$\mathrm{MG} + \mathrm{MI} \rightleftharpoons \mathrm{ME} + \mathrm{G},$$

where TG represents triglycerides, MI methoxide ion, DG diglycerides, MG monoglycerides, G glycerol, and ME methyl ester.

It should be noted that the attacking species is methoxide ion and not methanol. It should also be noted that the glycerides on the right-hand side of each equation are initially formed as their anions, which then are rapidly converted to their neutral forms by abstraction of protons from methanol, thereby regenerating methoxide ions. Also in those cases where hydroxide catalysts are used, the methoxide ions are generated by equilibration of hydroxide ions with methanol:

$$\mathrm{CH_3OH} + {}^{-}\mathrm{OH} \rightleftharpoons \mathrm{CH_3O^-} + \mathrm{H_2O}.$$

Finally, it should be pointed out that, whereas the reactions of methoxide ions with glyceride bonds reversibly form methyl ester, the reactions of hydroxide ions with all ester bonds (including those in methyl ester) irreversibly form soap. This soap, if acidified, forms fatty acids, which then increase the acid number (see below) of the methyl ester.

In order to increase the commercial viability of biodiesel, standards for fuel quality and control have been instituted. Of these, the ASTM and European standards are the most prominent [1, 2]. The two critical quality parameters in the standards, with respect to the process chemistry, are the acid number and the total glycerol content. Acid number, which is an indirect measure of the free fatty acid (FFA) content in the biodiesel, is numerically the number of milligrams of KOH required to neutralize the FFAs in 1 g of sample. To a first approximation, this value is numerically twice that of the fatty acid content (oleic acid equivalent in weight percent). Thus, the acid number limit of 0.50 set by the ASTM and European standards corresponds to a fatty acid content of approximately 0.25 wt%. The total glycerol content in the system is the sum of the free glycerol and chemically bound glycerol (CBG) in the following manner:

$$G_{\text{total}} = G + [(\text{MG} \times 0.2591) + (\text{DG} \times 0.1488) + (\text{TG} \times 0.1044)] = G + \text{CBG},$$

where G, MG, DG, and TG are, for the purpose of this equation only, the weight percentages of glycerol, monoglycerides, diglycerides, and triglycerides in the product. The numerical factors are those cited in the ASTM reference method for measuring glycerol and glycerides [3]. They are the fractions of glycerol moiety in each glyceride.

The (G + CBG) value is limited in the ASTM and European biodiesel standards to 0.240 and 0.250 wt%, respectively. All current processes wash out the free glycerol from the biodiesel with water, in which case the CBG value becomes the critical value.

Many researchers have been able to produce some kind of biodiesel from the reaction of various oils and alcohols; however, it is a much greater challenge to make biodiesel which meets either the ASTM or the European standards. This can be attributed to the two major problems inherent in the reaction between methanol and vegetable oils. First, the oil is essentially immiscible with the methanol, which is currently the only alcohol (apart from ethanol) used for making commercial biodiesel; therefore, the reaction is initially mass transfer limited. Second, as the reaction time is increased, the CBG content of the biodiesel decreases, but the acid number increases owing to the reaction with hydroxide ions, which are present because of the inevitable moisture in the system. This makes the reaction time and temperature very critical.

The problem of immiscible phases has been addressed by using a cosolvent such as tetrahydrofuran (THF) to create a monophasic system for the reaction [4], which enables the system to overcome the initial mass transfer resistance and greatly increases the reaction rate.

We have already published methods for producing standard biodiesel from low-acid-number vegetable oils in a single-step reaction using either sodium hydroxide or methoxide [5]. For the methanol-to-oil molar ratios that were used, these methods commence as one phase but become biphasic as a glycerol-rich phase separates. The study described here on soybean oil (SBO) provided the data on which those methods are based. More specifically, it measured the variability of CBG contents and acid numbers of the products as affected by the critical parameters such as alcohol-to-oil molar ratio, catalyst type and concentration, cosolvent volume, and reaction time. Higher methanol-to-oil molar ratios that together with THF give monophasic reactions throughout were not studied.

Experimental Procedures

Materials

The SBO used for this study was food-grade product purchased from Loblaws Supermarket (President's Choice; Toronto, ON, Canada). All the following chemicals were supplied by Sigma-Aldrich Chemical Company (Milwaukee, WI, USA): methanol (anhydrous, 99+%); THF (anhydrous, 99+%); oxalic acid (99+%); calcium chloride (–4+30 mesh, technical grade) sodium chloride (99+%); sodium methoxide (25 wt%); palmitic acid (99%); 2-propanol (anhydrous, 99.5%); toluene (high-performance liquid chromatography grade, 99.8%); *p*-naphtholbenzein (indicator grade); sulfuric acid (volumetric standard, 0.0995 N solution in water); 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%); monoolein (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 (Brockville, ON, Canada). Analytical grade sodium hydroxide (98%) pellets were obtained from BDH (Toronto, ON, Canada) and anhydrous sodium sulfate was obtained from VWR (Toronto, ON, Canada).

Methods

To determine the volume of cosolvent that was required for the creation of one phase at the beginning of each reaction, SBO (60.0 g) was placed in a round-bottom flask. The amount of methanol specific to the desired molar ratio (alcohol to oil) was added. THF was added slowly to this mixture, followed by thorough shaking of the flask. The amount of THF that transformed the milky, nonhomogenous solution to a clear, homogenous one over a period of 30–40 min was noted. This procedure was repeated at different molar ratios (methanol to oil), and the volume of THF that was used to achieve miscibility, as defined above, was recorded in each case.

The reactions were conducted at ambient temperature, which in this case was 23 °C. SBO (60.0 g) was weighed in a 200-mL round-bottom flask equipped with a magnetic stirrer, condenser, and a calcium chloride guard tube. The reflux condenser/drying tube prevented the evaporation of methanol and THF from the reaction mixture and maintained atmospheric pressure and prevented the ingress of water.

The calculated amount of methanol for the required molar ratio of alcohol to oil, less 8.4 mL (3 mol) for catalyst preparation, was poured in the flask. The predetermined volume of THF that was required for the creation of one phase was then added to the system.

For the preparation of the catalyst, the appropriate weight of NaOH pellets was taken in a 20-mL vial and then dissolved in methanol (the 8.4 mL left aside). The time of addition of the catalyst solution to the reaction mixture was considered as time zero. The reaction mixture was stirred continuously using a magnetic stirrer. For reactions using sodium methoxide as the catalyst, molar equivalents of the sodium hydroxide weight were used. Samples (12 mL) were taken at desired time intervals and quenched in 24-mL vials containing 1 mL methanolic oxalic acid of desired strength (1 mol of oxalic acid per mole of NaOH required for neutralization). The workup procedure involved washing the samples with aqueous brine solution (10% by weight) (4 × 12 mL) until the resultant wash was almost neutral. This removed THF and excess methanol, as well as oxalate salts and the residual oxalic acid. Gentle agitation was used in each washing step to mitigate emulsion formation. The CBG contents and acid numbers were then determined for the samples using methods ASTM D 6584 [3] and ASTM D 974 [6], respectively. The reaction was studied extensively with respect to the variables of methanol-to-oil molar ratio, catalyst concentration, amount of THF added, and reaction time.

Results and Discussion

Cosolvent

The solubility of SBO in methanol is very low. It is approximately 7.5 g/L at 30 °C, which is only attained after vigorous stirring for several minutes [7]; therefore, the catalyst, which is present in the methanol, is immediately unavailable for the bulk SBO to react with. The oil that does diffuse into the methanol is rapidly converted via diglycerides and monoglycerides. These glyceride intermediates act as emulsifiers and for a short time an emulsion may form. However, the appearance of a separate glycerol-rich phase soon dominates. This removes the catalyst and the reaction slows or essentially stops. If sufficient THF is used as a cosolvent, the reaction can be made monophasic from the beginning, in which case it occurs faster. In this study, as the molar ratio of methanol to oil increased, the volume of THF (relative to that of methanol) that was required for the creation of one phase at the beginning of the reaction decreased. The required THF-to-methanol volume ratios for the various methanol-to-oil molar ratios were as follows: 0.80 at 6:1; 0.91 at 9:1; 0.94 at 12:1; 0.98 at 13:1; 1.02 at 14:1; 1.03 at 15:1; and 1.06 at 18:1.

Neutralizing Acid

Oxalic acid, $HO_2C–CO_2H$, was used to terminate the reactions by neutralizing the catalyst. The use of strong aqueous mineral acids can cause hydrolysis of ester bonds and give erratic results. Oxalic acid is soluble in methanol, so the reactions could 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 (approximately 4), so any soap which was formed was converted back to fatty acids. Therefore, any increase in acid number from the substrate to the product was a measure of the irreversible attack of hydroxide ion on ester bonds. Both oxalic acid and its salts are very soluble in water, and were easily removed from the methyl ester by water-washing along with other water-soluble materials such as glycerol, methanol, and oxolane.

Experimental Matrix

Previous research had demonstrated that the transesterification, being an equilibrium reaction, requires excess alcohol to proceed towards completion; therefore, alcohol-to-oil molar ratios that were in excess of the traditional 6:1 were chosen for this study [8]. Beyond an alcohol-to-oil molar ratio of 18:1, the system (with THF) gets very close to being monophasic throughout, so higher molar ratios were not studied.

The catalyst concentration was varied in the range 1.0–1.5 wt%. Initially, the use of such a high catalyst concentration was not anticipated; however, preliminary experiments using base concentrations lower than this range did not result in sufficiently low glyceride contents for the products to meet the standards in a reasonable time. Catalyst concentrations above 1.5 wt% were not considered practical as they were close to solubility limits.

Temperatures higher than ambient make the reactions more difficult to control. In addition, it has also been reported that at higher temperatures soap formation is accelerated more than ester formation [9]. This would lead to products with higher acid number. On the other hand, lowering the temperature would promote phase separation of the THF/methanol/SBO system. Therefore, ambient temperature (23 °C) was chosen for this reaction.

Finally, after narrowing down the possible conditions for meeting the standards, the variation in cosolvent (THF) volume was investigated. The volume of THF in the system was varied in the range 90–130% of that which was required for the creation of one phase at the beginning of the reaction. Lower THF volumes (below 90%) were not investigated because the creation of one phase was greatly delayed by the lack of THF, which affected the conversion. In addition, the lack of THF caused emulsion formation in the workup of the samples. No significant effects on acid number and CBG content were observed within this range of THF volumes cited above.

Physical Nature of Reactions

The reaction mixture started as a two-phase system (just after the catalyst was added), because even though there was sufficient THF to create one phase, physical mixing of 15–20 s was required before one phase developed. Subsequently, as glycerol separated (90–120 s) the mixture became hazy, and darkened, after which the original SBO color (pale yellow) appeared as the reaction progressed.

Acid Number

In the absence of THF, the two important reactions, the formation of methyl ester and the formation of soap, were essentially mass transfer limited throughout. It should be emphasized that the workup procedure transformed all the soap that was formed back to fatty acid, which then moved into the ester phase to be measured as the acid number. The presence of THF in sufficient amounts to form a single phase at the beginning accelerated the two important reactions. As expected, the acid numbers of the products increased as the reaction times were extended, while the CBG contents decreased.

Figure 1 shows that for all alcohol-to-oil molar ratios there was a jump in the acid number (soap formation) immediately after the catalyst was added. Samples were taken at 1 and 5 min for each run, so it was not possible to identify exactly when the rate of increase decreased in this time period. For this reason, the data points in Fig. 1 for 0, 1, and 5 min have been joined with straight lines. The initial jump in the acid number was mitigated by the addition of more methanol and THF. This can be explained by equilibrium and dilution effects. The addition of more methanol lowered the number of hydroxide ions and increased the number of methoxide ions by the equilibrium process. The hydroxide ion concentration would have been lowered further by dilution with both the extra methanol and the extra THF. This latter effect is not as great as might be anticipated because of the low molar volumes of methanol and THF compared with the volume of the oil.

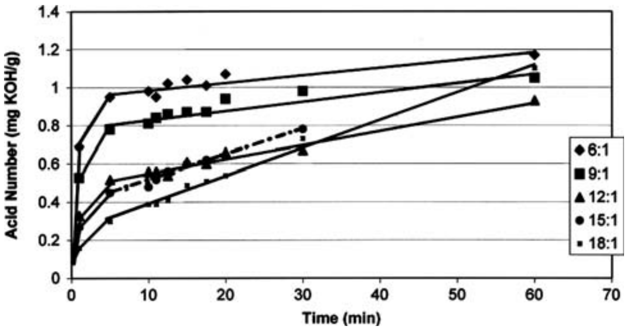

Fig. 1 Effect of methanol-to-oil molar ratio on acid number (1.3 wt% NaOH). Data points are means from duplicate runs, except for that at 10 min for a molar ratio of 12:1, which is a mean of seven runs (95% confidence limits, ±0.0137). R^2 values for linear sections of ‘‘curves’’ are as follows: 6:1, 0.828; 9:1, 0.863; 12:1, 0.967; 15:1, 0.970; 18:1, 0.991

At the methanol-to-oil molar ratio of 18:1, the initial surge in acid number diminished significantly. Despite this, the increase in acid number at the highest molar ratio, when sodium hydroxide was used as the catalyst, was still much lower than expected. It was calculated that for an alcohol-to-oil molar ratio of 18:1, when 99% of the ester bonds have been converted, the acid number of the product should be at least 3.2. The actual value was considerably lower (0.39). The calculation assumed that the methoxide ion/hydroxide ion equilibrium constant was 1.0, and that the hydroxide and methoxide ions had the same nucleophilicity during the reactions. The calculation ignored the fact that during the initial period of the reaction the number of ester bonds available for attack by hydroxide ions remained constant, whereas the number of glyceride bonds available for attack by methoxide ions to form methyl ester fell dramatically. If this is allowed for, then the predicted acid number when 99% of the glyceride bonds had been converted should have been in excess of 8. Therefore, either the apparent concentration of hydroxide ions or their nucleophilic abilities were much lower than expected. In practice, methoxide ions are more nucleophilic than hydroxide ion, although the difference is not large. We thus conclude that the presence of THF either lowered the activity coefficient of the hydroxide ions or raised the activity coefficient of the water that was formed in the equilibrium. We are currently investigating this phenomenon in transmethylation reactions that remain monophasic throughout.

Figure 1 shows that at all molar ratios there was a linear increase of acid number with time following the initial abrupt increase. We attribute this to the establishment of a glycerol-rich phase, which would have contained most of the catalyst. Mass transfer between the two phases therefore controlled this period of the reaction. Figure 1 also shows that the linear rate increased as the methanol-to-oil molar ratio increased. At the higher molar ratios, the two phases were becoming more similar in composition, which would have increased mass transfer and hence the reaction rate. This trend, if continued, suggests that when the alcohol-to-oil molar ratio reached a level at which the reaction could be made monophasic throughout (approximately 24:1), the rate of acid number increase might be linear throughout. Finally, an increase in catalyst concentration at the same methanol-to-oil molar ratio led to an increase in acid number (Fig. 2). This increase was again consistent with the expected increase in hydroxide ion concentrations.

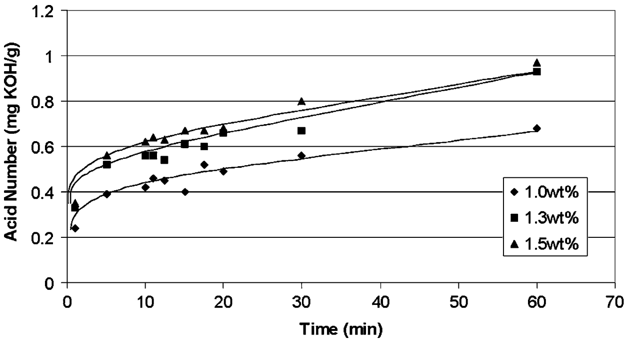

Fig. 2 Effect of NaOH concentration on acid number at a methanol-to-oil molar ratio of 12:1. Data points are means of duplicate runs, except for that at 10 min (1.3 wt%), which is the mean of seven runs (95% confidence limits, ±0.037). Acid number at time zero was 0.06

Methyl Ester Formation

It was observed (results not shown) that at lower alcohol-to-oil molar ratios such as 9:1 the CBG content eventually met the ASTM standard (0.240), at reaction times greater than 20 min. In fact, there appeared to be a better conversion than that achieved at higher methanol-to-oil molar ratios of 15:1 and 18:1 (results not shown). However, the conversion was fairly slow and by the time the CBG content met the ASTM and European standards, the acid number of the methyl ester exceeded the limit of 0.50. Also at methanol-to-oil molar ratios of 15:1 and 18:1, the CBG content appeared to increase slightly after a reaction time of approximately 30 min. This reversal was presumably due to the re-formation of monoglycerides resulting from a reequilibration between the methyl ester and the glycerol dissolved in the methyl ester rich phase as

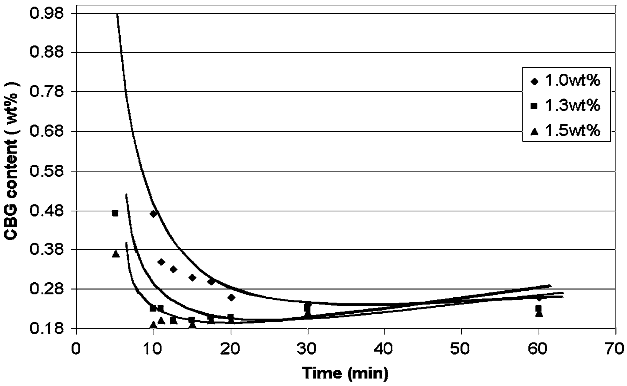

Fig. 3 Effect of NaOH concentration (with respect to oil) on chemically bound glycerol (*CBG*) content for a methanol-to-oil molar ratio of 12:1. Data points are means of triplicate runs. CBG content at time zero was 10.4 wt%

Table 1 Progress of reaction at a methanol-to-oil molar ratio of 14:1, 1.2 wt% catalyst (NaOH) at 23 °C (all glyceride and chemically bound glycerol contents in weight percent)

Time (min)	Acid no.	CBG	C16 MG	C18 MG	DG	TG
1	0.261	NA	NA	NA	NA	NA
5	0.417	0.321[b]	0.150	1.003	0.031	0.279
10	0.461[a]	0.219[b]	0.116	0.744	0.006	0.027
11	0.551	0.210[b]	0.112	0.719	0.005	0.020
12.5	0.561	0.216[b]	0.131	0.725	0.004	0.017
15	0.584	0.209[b]	0.111	0.718	0.004	0.012
17.5	0.648	0.184[b]	0.098	0.630	0.004	0.012
20	0.689	0.207[b]	0.110	0.711	0.004	0.014
30	0.830	0.215[b]	0.116	0.736	0.004	0.014
60	1.166	0.243[b]	0.130	0.832	0.004	0.013

Data are means of seven runs

CBG chemically bound glycerol, *MG* monoglycerides, *DG* diglycerides, *TG* triglycerides, *NA* not available

[a] 95% confidence limits, ±0.037

[b] 95% confidence limits, ±0.02 (rounded to two decimal places to cover all results)

a consequence of its higher polarity. This reversal was not observed either at lower methanol-to-oil molar ratios or when using lower catalyst concentrations because the reactions did not proceed to a sufficient degree of conversion in the first place.

Figure 3 illustrates another unexpected result of this study, which was that raising the sodium hydroxide concentration from 1 to 1.3 wt% drove the methyl ester formation reaction not only faster, but further. In particular, at a methanol-to-oil molar ratio of 12:1 the CBG level of 0.240 wt% was achieved before the acid number of 0.50 was exceeded (Fig. 1). We initially proposed that it was important to drive the ester-formation reaction to the necessary degree of completion before the glycerol-rich phase was clearly established; however, preliminary evidence indicates that the same phenomenon is seen in the totally monophasic reactions. If this is verified, the concentration of the hydroxide ions was playing a role in the equilibrium position of this reaction. In theory, catalysts should not influence the equilibrium of a reaction, only the rate at which it is achieved. Further studies are continuing on the monophasic system.

Optimum Conditions

Based on a desire to keep the catalyst concentration and costs as low as possible (the catalyst is not recovered in either commercial or laboratory operations), we concluded that the catalyst concentration could be lowered to 1.2 wt% if the methanol-to-oil molar ratio was raised from 12:1 to 14:1. The results for this system are shown in Table 1. After 10 min the acid number was 0.461, while the CBG content was 0.219 wt%, thereby meeting the biodiesel standards. The results showed that it is critical to terminate the reaction as soon as 10 min has elapsed, and also emphasized the need to control the temperature. It should be noted that the European biodiesel standard includes separate limits on the individual glycerides. The limit set for monoglyceride is 0.80 wt%. This level was always exceeded in these studies when the acid number and CBG content requirements were met.

Catalyst Type

It is generally believed that methoxides are better catalysts for transmethylation than hydroxides, because in the absence of water they prevent soap formation; however, owing to its low cost and ease of use, sodium hydroxide is the preferred catalyst if it yields standard biodiesel. The use of sodium methoxide was nevertheless examined at the reaction conditions of 14:1 methanol-to-oil molar ratio, and at a molar concentration equivalent to 1.2 wt% of NaOH. The results agreed strongly with the expected behavior. The acid numbers for reaction products using $NaOCH_3$ were significantly lower than those using NaOH [2], while the CBG content remained similar. $NaOCH_3$ should be used as the catalyst in those cases where the use of NaOH gives products in which the acid numbers are too high.

The methods for making standard biodiesel that arose from this study are for researchers who require standard biodiesel for engine studies and other research activities; however, it is fairly obvious that such methods could be adapted to commercial processes.

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