Acid-Catalyzed Alcoholysis of Soybean Oil

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ABSTRACT: In an effort to increase utilization of fats and oils with high concentrations of FFA, acid catalysts were investigated at elevated temperatures to determine their efficacy under various operating conditions. Acid-catalyzed alcoholysis of soybean oil using sulfuric, hydrochloric, formic, acetic, and nitric acids was evaluated at 0.1 and 1 wt% loadings at temperatures of 100 and 120°C in sealed ampules, but only sulfuric acid was effective. Kinetic studies at 100°C, 0.5 wt% sulfuric acid catalyst, and nine times methanol stoichiometry provided >99 wt% conversion of TG in 8 h and less than 0.8 wt% FFA concentrations at less than 4 h. Reaction conditions near 100°C at 0.1 to 0.5 wt% were identified as providing the necessary conversions in a 24-h batch cycle while not darkening the product as is typical with high temperatures and catalyst loadings. The oxygen/air contained in the reaction ampules at the onset of the reaction was not sufficient to color the product, but the product darkened if atmospheric air contacted the reacting mixture. The presence of small amounts of stainless steel significantly decreased conversions.

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Acid-catalyzed alcoholysis of TG can be used to produce alkyl esters for a variety of traditional applications and for potentially large markets in the biodiesel fuel industry and phase change material market (1). As the U.S. biodiesel industry gains momentum, there has been an increased interest in the development of catalysts that overcome some of the shortcomings of traditional base catalysis for producing alkyl esters. A significant disadvantage of base catalysts is their inability to esterifiy FFA. These FFA are present at about 0.3 wt% in refined soybean oil and at significantly higher concentrations in waste grease due to hydrolysis of the oil with water to produce FFA. FFA react with soluble bases to form soaps through the saponification reaction mechanism. This soap forms emulsions and makes recovery of the methyl esters (ME) difficult. Saponification consumes the base catalyst and reduces product yields. Use of alkaline catalysts requires that the oil reagent be dry and contain less than about 0.3 wt% FFA (2,3). Acid catalysts are robust and can handle large amounts of FFA and higher concentrations of water. Throughout this paper, alcoholysis refers to the transesterification between an alcohol and the FA of TG, whereas esterification refers to the reaction between alcohol and FFA.

Base-catalyzed alcoholysis yields about 95 wt% ME in 1 h (4,5) at temperatures between 40 and 65°C at atmospheric pressure. Knothe *et al.* (6) report that optimal conditions of 1 wt% KOH catalyst at 69°C and a 7:1 alcohol/vegetable oil molar ratio provide 97.7% conversion in 18 min and that KOH under the given conditions is the preferred catalyst when used on high-purity feedstocks. However, when considering the entire process, acid catalysts offer significant advantages. These include reduced removal costs and the ability to utilize less expensive feedstocks.

Many are researching the use of heterogeneous catalysts for alcoholysis reactions (7,8). No heterogeneous catalysts are commercially viable in the 45–65°C range. Some may be viable at 100–150°C; however, reactor residence times are in excess of 4 h, requiring large amounts of catalysts. At greater than 100–150°C, the high pressures needed to keep the methanol in the liquid phase can significantly increase equipment costs (9). Although heterogeneous catalysts are typically preferred over homogeneous catalysts operating at the same temperatures and pressures, a homogeneous catalyst may be preferred if it is equally effective at lower loadings. Lower homogeneous catalyst loadings reduce catalyst costs and reduce waste generation. In addition, homogeneous catalysts tend to be more robust because a fresh charge of catalyst is used each time, thus avoiding deactivation problems possible with reused heterogeneous catalysts. When heterogeneous catalysts and homogeneous catalysts allow similar batch times, the homogeneous catalyst can avoid the often expensive costs of the heterogeneous catalysts.

Acid catalysts can handle large amounts of FFA and are commonly used to esterify FFA in a fat or oil feedstock prior to base-catalyzed alcoholysis to ME (10,11). This approach effectively solves the FFA problem but adds an additional reaction and cleanup step that increase batch times, catalyst costs, and waste generation. Although acid catalysts are active in the esterification of FA, there is still a considerable amount of FA present after reaction completion (12). ME yields of 97–98 wt% are obtained for esterification with 2 wt% sulfuric acid and excess alcohol in about 4 h under reflux conditions (12). Examination of the alcoholysis reaction kinetics presented reveals that reaction times of 24 h are

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*To whom correspondence should be addressed at Department of Chemical Engineering, W2028 Engineering Bldg. East, University of Missouri, Columbia, MO 65211. E-mail: suppesg@missouri.edu necessary to decrease the FFA concentration to an acceptable concentration of 0.4 wt%, to a point where most of the TG are converted to ME. Using acid catalysts throughout the entire reaction process for both esterification and transesterification eliminates washing steps compared with the two-step process of acid catalysis followed by base catalysis, eliminates waste streams, and permits handling of high amounts of FFA in the oil.

Acid-catalyzed alcoholysis of TG has been studied. Methanolysis studies were carried out at temperatures at or below that of methanol reflux (65°C) and required reaction times on the order of days to achieve satisfactory conversions. Schwab *et al.* (13) and Liu (14) compared acid and base catalysts and determined that, although base catalysts perform well at the lower temperatures, higher temperatures are required when using acid catalysts (13). Freedman *et al.* (15) and Liu (14) investigated the influence of acid and base catalysts on yield and purity of the product and suggested that an acid catalyst will be more effective for alcoholysis if the vegetable oil contains more than 1 wt% FFA. For alcoholysis with butanol, higher reaction temperatures were possible at reflux conditions (117°C) where high conversions were achieved in 3 h (15). Haas *et al.* (16) demonstrated good conversions of TG in acid oil using acid catalysis; however, the lower reaction temperatures (65°C) limited conversion of TG, resulting in TG concentrations near 1 wt% at 24 h.

The purpose of this study was to investigate the transesterification of soybean oil with acid catalysts at higher temperatures in order to increase reaction rates and provide competent alternatives over base catalysts. Acids investigated in this study were sulfuric, hydrochloric, formic, acetic, and nitric. The inorganic acids were selected because they can be neutralized to form insoluble salts, allowing for easy removal from biodiesel. Formic and acetic acids were selected because of their high pK_a values and because they could be readily removed through evaporative distillation at mild conditions. Organosulfonic acids would be expected to be good catalysts; however, they were not investigated because of the difficulty of their removal due to their lower vapor pressures and formation of soluble salts. The kinetics of soybean oil transesterification were examined at 100°C with sulfuric acid as catalyst to determine reaction rates.

Pressure vessels are required to contain the acid-catalyzed alcoholysis reactions at higher reaction temperatures. At 100°C, the vapor pressure of methanol is 3.5 bar (52 psia). For the alcoholysis reaction, the partial pressure of methanol deviates only slightly from 3.5 bar at 100°C due to the high activity coefficients of methanol in fats, oils, and alkyl esters of FA. Pressure vessel requirements are the primary disadvantage of acid catalysis at these higher temperatures.

Potential benefits of acid catalysis include the following: (i) The catalyst remains active in the presence of FFA; (ii) esterification of the FFA and alcoholysis of the TG occur simultaneously; (iii) catalyst loadings can be reduced to levels lower than are possible with base catalysis since FFA do not neutralize the catalyst; and (iv) lower catalyst loadings can simplify product cleanup and result in a glycerin co-product that is easier to upgrade. These benefits can give acid catalysis a distinct advantage over base catalysis when considering the process as a whole.

EXPERIMENTAL PROCEDURES

Materials. Refined soybean oil, Food Club® brand vegetable oil distributed by Topco Associate, Inc. (Skokie, IL) was purchased from a local grocery store. Methanol (HPLC grade), sulfuric acid (ACS grade, 95.4% assay), nitric acid (ACS grade, 69.5% assay), acetic acid (ACS grade, 99.7% assay), and formic acid (ACS grade, 88%) were all purchased from Fisher Scientific (Fairlawn, NJ). Hydrochloric acid (37%) was from J.T.Baker, Inc. (Paris, KY).

Reaction conditions. Screening reactions were designed to evaluate several different acid catalysts at a typical molar ratio of methanol to oil of 9:1, 1 wt% catalyst, 120°C, and 24 h residence times. Catalyst (wt%) is relative to the total weight of oil plus alcohol prior to reaction. Kinetic studies were carried out using sulfuric acid catalyst at 0.1 and 0.5 wt% loadings at a 9:1 ratio at 100°C.

Apparatus. All of the reactions were conducted in sealed 1-mL glass ampules (actual volume was 2 mL) from Fisher. Reactions were initiated by placing the sealed tubes in a Fisher Isotemp programmable muffle furnace (Pittsburgh, PA) capable of programmed dual temperature control from 30 to 1125°C. Baseline studies on the homogeneous reactions in these ampules were reported elsewhere (17).

Procedure. Catalysts were mixed with methanol in the calculated proportion to achieve the desired catalyst loading. The methanol/catalyst solution was transferred with a micropipette in the calculated volume to the ampule containing 1 mL soybean oil measured with a syringe. The ampules were sealed to prevent methanol from escaping and to keep oxygen out of the system. Three ampules of each reaction were prepared and the resulting analyses averaged to reduce errors associated with charging the ampules and in conversion analysis. SD associated with the experiment were <1.5%. Reaction was initiated by placing the ampules inside a preheated Fisher Isotemp® muffle furnace. Heating and cooling times of the ampules in the oven were less than 10 min each, a short time when considering the length of reaction times investigated. Reactions were run concurrently in the oven. After reaction, the ampules were broken and the contents placed in test tubes and diluted with chloroform containing eicosane as an internal standard. The contents were placed in 1 mL HPLC autosampler vials.

Method of analysis. Samples were analyzed on a Hewlett-Packard 1100 high-performance liquid chromatograph (Wilmington, DE) using an Alltech Apollo 5 µm silica column, 250 × 4.6 mm, and an Alltech (Deerfield, IL) 500 ELSD (evaporative light-scattering detector). The mobile phase consisted of a chloroform/methanol mixture, with a solvent gradient going from pure chloroform to 50 vol% methanol at 15 min. A flow rate of 1 mL/min was used at ambient temperature. Analysis of chromatogram areas was done using Hewlett-Packard Chemstation software. Concentrations of ampule products were determined by construction of a calibration curve and using the least squares method for a linear fit. Analysis of DG was performed after the initial kinetic studies by repeating select experiments, determining the DG reaction profile, and subtracting this from the FA/DG peak to give both FA and DG compositions. These additional studies were necessary because the initial HPLC method resulted in overlapping peaks for the FA and DG. The overlapping peaks were separated by replacing the old column with a new one, i.e., the same Alltech column just described.

RESULTS AND DISCUSSION

Impact of acid catalyst and water. Screening studies were performed to distinguish between the efficacy of sulfuric, hydrochloric, formic, acetic, and nitric acids. The results of these screening studies are summarized in Table 1. Sulfuric acid was the only catalyst that showed significant activity; hydrochloric, formic, acetic, and nitric acids all had conversions less than 0.7%. Nitric and hydrochloric acids darkened the product. Although sulfuric acid caused the product to have a yellow tint, this was easily controlled (discussed later) to maintain good product quality.

Acids investigated in this study (hydrochloric, sulfuric, nitric, formic, and acetic) have pK_a values (18) of –6.1, –3, –1.38, 3.8, and 4.8, respectively. It was quantitatively determined that sulfuric acid was the only active catalyst for the alcoholysis of soybean oil. These data indicate that pK_a alone is not a good indication of the catalytic ability of an acid for alcoholysis. In the case of hydrochloric acid, experiments were repeated several times to make sure the results were not anomalous. The literature indicated that hydrochloric acid catalyzed the alcoholysis reaction; however, this study determined that hydrochloric acid severely darkens the product at the higher temperatures investigated (12).

Water in the system is a major concern when using a base catalyst, and many investigators have noted that more than 0.5 wt% water in the system significantly reduces reaction rates in base-catalyzed reactions (3,5). Water was added to systems containing 0.1 and 0.5 wt% sulfuric acid catalyst and 9:1 methanol/TG mole ratios. Whereas controls with <0.1 wt% water achieved conversions of 40% and >90% for the respective catalyst loadings after 2 h of reaction, samples with 1 wt% water had conversions of 21 and 66% after 2 h of reaction, respectively. These higher water concentrations resulted in significantly lower ME yields, probably due to the water inducing a second phase (at higher conversions, methanol alone would not induce this phase) that extracted methanol and catalyst from the oil.

Table 2 shows the effect of the water content of the acid catalyst on yields of ME—the amount of water in the acid in our experiments was much lower than the higher levels evaluated above with 1 wt% water. Acid purity was determined to have a negligible effect on reaction kinetics. For reaction times of 24 h at 120°C, no detectable TG remained.

Impact of air on product quality. When performing acid-catalyzed alcoholysis, care must be taken not to oxidize the FA and produce a dark product. Experiments were conducted to determine the effect of air in the system by sealing the ampules under a nitrogen blanket to prevent air from entering the system. The reactions were carried out with 1 wt% sulfuric acid with a 9:1 molar ratio of methanol/soybean oil at 120°C for 19 h, an amount of time sufficient to yield >99% conversion. These conditions are also more conducive to product oxidation, providing better conditions for studying the effects of oxygen. Reactions carried out under a nitrogen blanket were qualitatively compared with those sealed under atmospheric air. Analysis revealed no change in color of the products during reaction in either case.

However, acid-catalyzed alcoholysis reactions occasionally produced dark products. For this reason, the effect of air was evaluated by varying the volume of air in the reaction ampule. This was done by adjusting the volume of reactants loaded in the ampule to obtain air volumes of 20 or 80%. The reactions were carried out with 1 wt% sulfuric acid with a 9:1 molar ratio of methanol/soybean oil at 120°C for 19 h. Table 2 reveals that there was essentially no difference in ME yield with varying amounts of air present in the ampule at the onset of reaction. Air-to-liquid volume ratios up to 4:1 had no impact on yields or product color. Significant degradation was noted, as evidenced by a dark product, only when the ampules were not sealed properly and the ampule was open to the surroundings. Loss of vessel containment not only allows air to enter the system but also allows methanol to escape from the system at the elevated ampule temperatures. Kulkarni *et al.* (19) report that sulfuric acid colors the product owing to the

TABLE 1
Screening Studies on the Efficacy of Catalysts and Impact of Water Content[a]

Acid catalyst	Conversion (%)	Product methanol phase	Product glycerin phase	Color
Sulfuric acid	>99	No	Yes	Yellow to brown
Nitric acid	<0.7	Yes	No	Orange to brown
Hydrochloric acid	<0.7	Yes	No	Yellow to light orange
Formic acid	<0.7	Yes	No	SBO yellow
Acetic acid	<0.7	Yes	No	SBO yellow

[a] Reactions are at 120°C, 1 wt% acid catalyst, and 9:1 methanol/TG molar ratio. Reactions were conducted for >20 h. A "No" in the product glycerin phase column indicates that no glycerin phase was formed anytime during the reaction. A "Yes" in the methanol phase column indicates that methanol phase was present throughout the experiment. SBO, soybean oil.

TABLE 2
Effect of Water and Air Volume on Yields for Sulfuric Acid-Catalyzed Alcoholysis of Soybean Oil Reacted at 120°C, 1 wt% Acid Catalyst, and a 9:1 Methanol/TG Molar Ratio

Acid quality (wt% acid in water)	Air volume in ampule (%)	Reaction time (h)	Mass fraction in product (%)		
			ME[a]	TG	MG
95.4	50	28	95.9	0.0	0.4
70	50	28	96.0	0.0	0.4
95.4	20	28	96.5	0.0	0.0
95.4	80	28	95.0	0.0	1.0
95.4	20	28	96.5	0.0	0.0

[a]Methyl ester.

formation of sulfones and sultones. The results of this work indicate that additional mechanisms also promote darkening of the product and that the problem can be controlled with proper sealing of the ampule contents and by using sulfuric acid concentrations of 0.5% or less.

Effect of stainless steel on conversion. All reactions in this study were carried out in glass ampules to eliminate any interactions between the stainless steel typically used in acid catalyst and the reactor wall. To determine the effect of reactor materials on the reaction, metal shavings of stainless steel 316 were added to the glass ampule at 0, 0.2, 0.5, and 1 weight percentages. The ampules were loaded with 0.5% catalyst, a 9:1 molar ratio of methanol/TG, at 100°C for 8 h. ME conversions for the reaction were 96, 90, 85, and 51%, respectively. As the surface/volume ratio for the reactor decreases, the effect of a stainless steel reactor wall will be reduced.

Conversion profiles. Figures 1 and 2 show the reaction profiles at 100°C for the alcoholysis of a refined soybean oil product having an initial FFA content of about 0.3 wt% and 24 wt% methanol (9 times molar stoichiometry). A 0.5 wt% sulfuric acid catalyst loading led to considerably better conversions than the system having a 0.1 wt% loading. The FFA content of the 0.5 wt% catalyzed system was 0.71 wt% at 3.5 h and 0.41 wt% at 24 h. The presence of TG was undetectable after 13 h. These data illustrate that low FFA contents can be attained, with equilibrium limitations possibly being a greater obstacle than the reaction kinetics.

At a 0.5 wt% catalyst loading and a 9:1 methanol/TG molar ratio, the pseudo first-order rate constant (methanol concentration nearly constant) for the conversion of TG was 0.6 h^{-1} (based on observed half life). At approximately 40% conversion of TG, the DG had a maximal concentration of about 15%. This indicates that the reactivity of the DG was about 2.3 times greater than that of the TG with an assumed pseudo first-order rate constant of 1.4 h^{-1}.

As summarized by the reaction profiles of Figures 1 and 2, the FFA react quickly to form ME, with the rate-determining step being the conversion of glycerides. The product mixture cleanly separates into a glycerin phase and an ME phase. The reaction profile for the 0.1 wt% catalyst loading (Fig. 1) suggests that the reaction is substantially quenched at about 75% conversion of the TG; this is likely due to insufficient catalyst remaining in the ME phase once the glycerin phase is formed. Agitation of the reaction mixture will increase conversion by preventing formation of the second phase. Agitation will both enhance kinetics and increase conversion at the end of the reaction when the glycerin phase pulls out much of

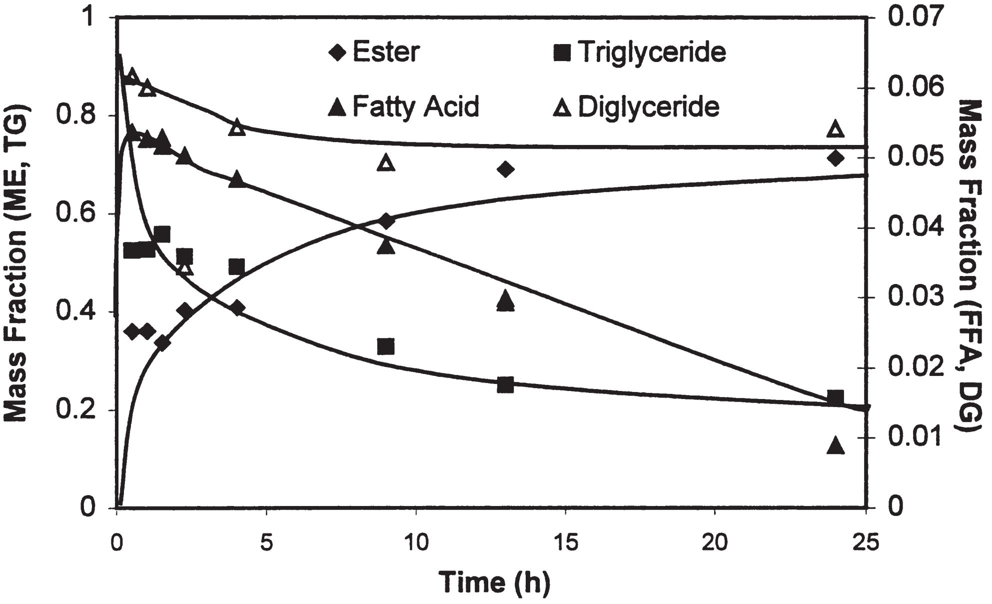

FIG. 1. Kinetics of 0.1 wt% sulfuric acid catalyst at 100°C and a 9:1 methanol/TG molar ratio. ME, methyl ester.

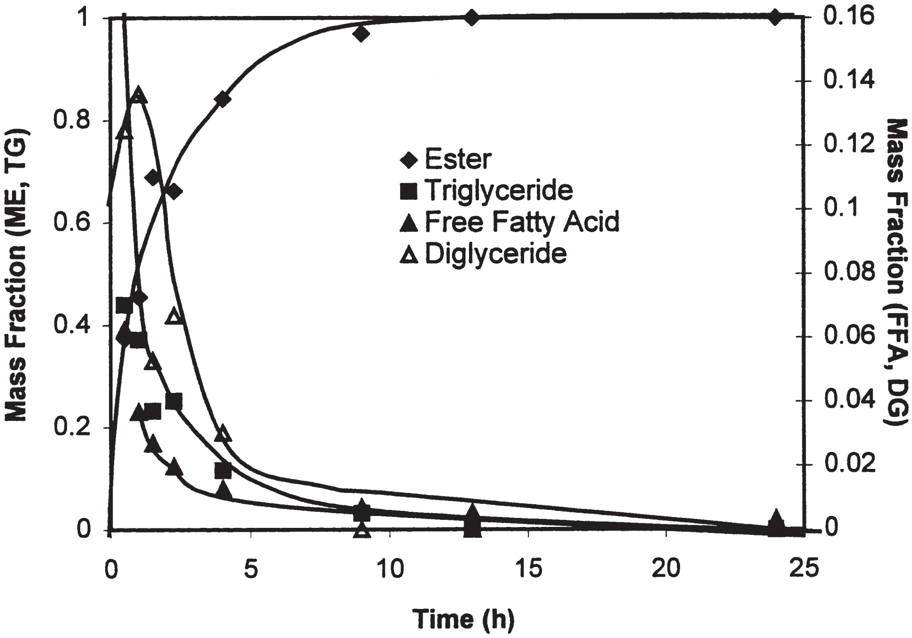

FIG. 2. Kinetics of 0.5 wt% sulfuric acid catalyst at 100°C and a 9:1 methanol/TG molar ratio. ME, methyl ester.

the alcohol and catalyst. Decanting of the glycerin phase and even a small loading of catalyst (0.02–0.1 wt%) should achieve desired conversions of greater than 98%.

Conversions for the transesterification of TG with different alcohols are not presented in this paper; however, our laboratory often synthesizes ethyl, propyl, isopropyl, butyl, and isobutyl esters *via* alcoholysis at conversions greater than 95% in 24 h at 100°C at a 9:1 molar ratio of alcohol to oil with 1 wt% sulfuric acid. In view of the butanol conversions of Freedman *et al.* (15) and the results presented in this paper, sulfuric acid catalysis at 100–120°C and pressures as necessary to maintain liquid phases provides an effective means to produce alkyl esters without the disadvantages associated with base catalysts.

For sulfuric acid catalysis of this reaction, a very limited limited range of temperatures and acid concentrations conditions provides >98% at reaction times of less than 24 h without substantial darkening of the product. Screening studies conducted prior to the experiments of Tables 1 and 2 indicated that higher sulfuric acid (>1%) concentrations and higher temperatures (>120°C) lead to product degradation. This narrow range of acceptable reaction conditions is not obvious based on previously published work on acid catalysis. Similar conversions are not possible in one-step esterification with methanol. Water is not formed as a by-product of alcoholysis, as compared to esterification where water is formed. The absence of water formation allows for high conversions of small amounts of FFA that may be present in the TG feedstock. As the FFA concentration of the feedstock increases, the amount of FFA in the final product will also increase.

The preferred conditions are near 100°C, a methanol/TG molar ratio of 9:1, and a sulfuric acid concentration between 0.2 and 0.5 wt%. The resulting system pressure is about 3.5 bar and requires pressure vessel containment. Low sulfuric acid concentrations are preferred because lower concentrations lead to less waste generation during product cleanup and increase the practicality of adsorption or ion-exchange processes for removing the acid remaining in the ME phase after the glycerin phase is drained from the reactor.

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