

Noncatalytic Alcoholysis Kinetics of Soybean Oil

Mohanprasad A. Dasari, Michael J. Goff, and Galen J. Suppes*

Department of Chemical Engineering, University of Missouri, Columbia, Missouri 65211

ABSTRACT: Reaction kinetics for the alcoholysis of soybean oil with methanol, ethanol, and isopropanol were evaluated in the absence of catalyst. Metal reactor surfaces catalyzed these reactions, so the reactions were conducted in glass capillary tubes at 120, 150, and 180°C. The reactivity of the alcohols increased with decreasing carbon number. Higher temperatures promoted faster reactions. Higher alcohol stoichiometries did not significantly increase reaction rates; this was attributed to the limited solubility of the alcohol in the soybean oil. At less than 20% conversion, the solubility of the alcohol in the oil phase continuously increased, resulting in increased reaction rates. At approximately 20% conversion, the reaction systems became homogeneous until a glycerine phase was formed at high conversions. In addition to their fundamental value, these data provided a basis on which catalytic reactions can be investigated between 100 and 200°C.

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Over the past few years, use of FAME derived from vegetable oils and animal fats as liquid fuel extenders (biodiesel) has received increased attention. Biodiesel cannot replace all the petroleum-based diesel fuels, but it can provide a near-zero sulfur content biodegradable additive that improves the quality of diesel fuel and creates new markets for fats and oils.

Methanol reacts with TG to form methyl esters through mechanisms that include the formation of some DG and MG. Stoichiometry, reaction time, and removal of the glycerine by-product can be used to promote yields of >98% methyl esters.

The most common reaction schemes include the use of alkali catalysts to reduce reaction times to a few hours at atmospheric pressure and methanol reflux temperatures. Acid catalysts are also effective but typically require higher temperatures and/or longer reaction times. In the absence of solvent and with one to three times the stoichiometries of methanol, high conversions result in the formation of a glycerine phase that is immiscible in biodiesel. Although biodiesel can be decanted from the glycerine, removing the catalyst from glycerine is costly and generates a salt waste/by-product.

Reaction schemes based on heterogeneous catalysts or no catalyst could reduce both operating costs and waste generation. A number of kinetic studies examine the transesterification of vegetable oil with alcohols using acid or basic catalysts

(1–3). Few data are available on alcoholysis rates in the absence of catalysts (4,5). Diasakou *et al.* (4) evaluated the alcoholysis of methanol with soybean oil. At 220°C, 67% of methyl esters were obtained in 8 h; at 235°C, 10 h was required to achieve an 85% conversion. These studies were carried out in a 4560 Bench Top series minireactor (Parr Instrument Co., Moline, IL). Saka and Kusdiana (5) evaluated the alcoholysis of rapeseed oil using supercritical methanol. After 240 s, 95% conversion was obtained; however, high temperatures of 350–500°C and high pressures of 45–65 MPa were used. The studies were carried out in a batch-type reactor vessel made of Inconel-625. Data were not reported for the alcoholysis of other simple alcohols or for methanol alcoholysis at lower temperatures. In addition, data were not reported to show the catalytic impact of reactor surfaces on transesterification reaction rates. The present study focused on reaction rates of methanol at 120, 150, and 180°C and reactivity of higher alcohols such as ethanol and isopropanol. The catalytic impact of reactor surface on the transesterification reaction was also investigated.

EXPERIMENTAL PROCEDURES

Materials. Refined soybean oil, Food Club® brand vegetable oil distributed by Topco Associates, Inc. (Skokie, IL), was purchased from a local grocery store. Methanol, ethanol, and isopropanol (all HPLC grade) were purchased from Fisher Scientific Co. (Fairlawn, NJ).

Approximately 150 mL of stock solution soybean oil with 0.01% wt of eicosane (C₂₀H₄₈) was prepared and used in all reactions. Eicosane was used as an internal standard to determine TG conversion to methyl esters.

Reaction conditions. Experiments were designed to determine the conversion of TG into methyl esters. A typical 1:6 molar ratio of oil/alcohol was used in most of the experiments. Ratios of 1:3, 1:9, and 1:12 were also tested to determine the impact of stoichiometry. Reactions were conducted at 120, 150, and 180°C to examine the impact of temperature on conversion.

Apparatus. All of the reactions were carried out in sealed glass capillary tubes (~0.2 mL). Reactions were initiated by placing the sealed tubes in a Fisher Isotemp* Programmable Muffle Furnace (Pittsburgh, PA) capable of programmed dual temperature control from 1 to 1125°C.

Procedure. The glass capillary tubes were sealed at one end and charged with 0.2 mL of soybean oil stock solution and the calculated amount of methanol using a micropipette. The other end of the tube was sealed leaving about 20% of the total internal volume as vapor space to prevent tube breakage due to liquid expansion during heating.

*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

The furnace was preheated to the reaction temperature. Four tubes of each reagent mixture were placed in the oven. After 4, 10, 20, and 32 h, the samples were removed from the oven and allowed to cool to room temperature. Both the heating and cooling times of the tubes were less than 15 min. Therefore, these times had negligible impact on the conversion interpretation. After the allotted reaction time, the tubes were broken and the contents placed in vials. Approximately 0.1 g of the oil phase was placed in 5 mL of hexane. The mixtures were placed in 1 mL GC auto sampler vials. Because the FA derivatives and the internal standard (eicosane) distributed predominantly in the oil phase, variations in dilution prior to GC–MS analysis had minimal impact. Controls conducted in the oil at 180°C showed that eicosane did not react under these conditions.

Method of analysis. Samples were analyzed with a Hewlett-Packard 6890 GC (Wilmington, DE) equipped with a split-splitless injection system. Data collection and analysis were accomplished with Hewlett-Packard Chemstation software. A Restek Corp. (Bellefonte, PA) MXT®WAX 70624 GC column (30 m × 250 μm × 0.5 μm) was used for separation with a Hewlett-Packard 5973 Mass Selective Detector. Samples were diluted in *n*-hexane for injection. About 2 μL of the sample was injected onto the column. The oven temperature program started at 152°C (2 min), ramped at 2.5°C/min to 204°C, and then ramped at 10°C/min to 220°C (1 min). Elution times were as follows: eicosane, 5.6 min; methyl palmitate, 10.1 min; methyl stearate, 16.8 min; methyl linoleate, 18.1 min; methyl linolate, 18.9 min. Standard calibration curves allowed the peak areas of the components divided by the peak area for eicosane to be directly converted into concentration.

GC–MS analysis was used to estimate conversion vs. time. In addition, a first-order linear regression model was used to obtain a least-squares rate constant. This rate constant was then used to calculate the time necessary to achieve 5% conversion.

RESULTS AND DISCUSSION

Effect of alcohol stoichiometry and metal reactor surface.

The noncatalytic alcoholysis reactions of methanol, ethanol, and isopropyl alcohol with soybean oil were evaluated at 120–180°C with oil/alcohol stoichiometries ranging from 1:3 to 1:12. The concentration curve for alcoholysis of soybean oil at 180°C is presented in Figure 1. The rate of formation of methyl esters was compared at three methanol concentrations and in a *ca.* 1-mL 316 stainless-steel (316SS) Swagelok connector (sealed at both ends with a cap) as compared with the glass capillary tube.

The catalytic nature of the 316SS reactor surface was pronounced and attained more than 10% conversion in 4 h, whereas the reaction in glassware achieved approximately 2% conversion in the same time. The catalytic nature of iron and nickel was subsequently confirmed by placing metal shavings into the capillary tube reactor. Fine-mesh 316 stainless steel and nickel increased the reaction rates 30- and 400-fold, respectively, compared with reactions without the fine-mesh metals present.

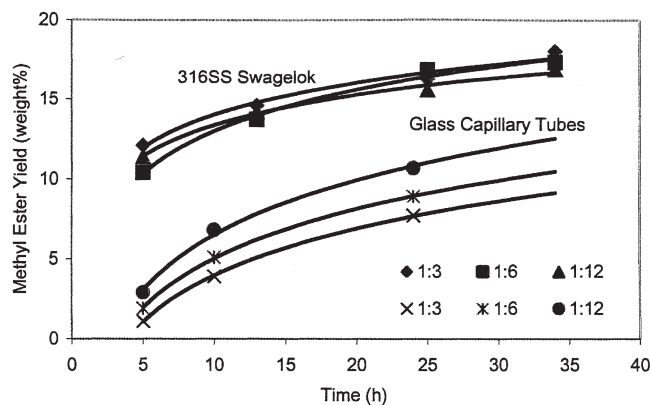


FIG. 1. Effect of reactor surface and time on overall conversion to methyl esters at 180°C. The internal legend shows the soybean oil/methanol stoichiometries.

The oil/alcohol reagent stoichiometries had little impact on reaction rates, primarily owing to the fact that for <20% conversions in these reactions the methanol was predominantly in liquid phase separate from the oil phase. After approximately 20% conversion, the methyl esters, MG, and DG acted as cosolvent, enhancing the solubility of methanol in the oil phase and forming a homogeneous solution.

For a two-phase reaction, the reaction rate can be controlled either by diffusion or by kinetics. Because of the observed relatively slow reaction rates, these reactions were most likely kinetically controlled rather than diffusion controlled. Kinetically controlled mechanisms are possible for two-phase reactions such as these where one of the reagents (methanol) has a moderate solubility in the other (oil). A kinetic expression of the form

$$\text{rate of TG disappearance} = k (\text{TG concentration}) (\text{MeOH concentration}) \quad [1]$$

describes the kinetics and was limited both by rate constant *k* and the concentration of both reagents. During the initial stages of reaction, the methanol concentration was determined by methanol solubility, with the majority of the methanol in the reaction system remaining in the hydrophilic, methanol phase. Kawahara *et al.* (6) report solubility of methanol in fat to be 12–15%, which is consistent with reaction conditions where methanol is sufficient to provide significant oil phase reaction while the reaction remains limited by the solubility of methanol. The reaction is kinetically controlled because methanol is able to diffuse into oil faster than it reacts to form methyl esters. As the reaction proceeds, the intermediates and products increase methanol solubility and thus increase the reaction rate. This increase in reaction rate with conversion is observed for the 120 and 150°C conversion data of Table 1. This mechanism describes the noncatalytic data; however, when catalysts that increase the observed reaction rates constants are employed, the reaction can proceed from a kinetically limited mechanism to a diffusion-limited mechanism.

Evidence that reaction rates are limited by methanol solubility is presented in Table 1. For methanol alcoholysis reac-

TABLE 1
Conversion of Soybean Oil at Different Reaction Conditions^a

Methanol (mol)	Hexane (mol)	Biodiesel (mol)	Temperature (°C)	Yield of methyl ester (weight%)			
				4 h	10 h	20 h	32 h
3			120	0.04	0.05	0.07	0.10
6			120	0.03	0.05	0.11	0.16
12			120	0.03	0.04	0.06	0.07
3			150	0.05	0.13	0.37	0.66
6			150	0.03	0.09	0.17	0.29
12			150	0.02	0.12	0.44	0.85
6	1		150	0.03	0.05	0.07	0.09
6	2		150	0.03	0.08	0.30	0.56
6		0.5	150	0.09	0.26	0.74	1.33
6		1	150	0.13	0.41	1.03	1.78
3			180	1.26	3.92	6.55	10.52
6			180	2.17	5.14	7.73	11.91
12			180	2.82	6.87	9.47	12.41

^aMethanol and solvent concentrations are reported on a basis of 1 mol soybean oil.

tions at 120 and 150°C, the reaction rates increased with time. This increase in reaction rate with increasing time (i.e., conversion) was the result of increased solubility of methanol due to the solvating effect of the methyl ester and glyceride intermediates. These intermediates increased the solubility of methanol and thereby increased the reaction rates.

For the data at 180°C (Fig. 1), the conversion curve began to flatten at higher reaction times (i.e., the reaction rate began to decrease). At this higher temperature, samples with reaction times greater than 10 h were homogeneous when removed from the oven. Hence, the previously described mechanism did not apply. For this reaction, higher temperatures also promoted the formation of a single reaction phase over two phases.

For the noncatalytic reactions at 180°C, the higher methanol stoichiometries led to higher conversions. When increasing the molar ratio of methanol fourfold (1:3 to 1:12), the reaction rate did not increase fourfold because in the absence of solvent the methanol diluted the oil. For the 316SS-catalyzed reactions at 180°C, the impact of methanol stoichiometry was less pronounced, as would be the case where the catalytic surface area dominated the reaction kinetic expression. For reactions at lower temperatures where most of the methanol was in a separate methanol phase, the impact of methanol stoichiometry was again less pronounced.

To test the hypothesis that higher solubility promoted higher reaction rates at 120 and 150°C, we conducted reactions with the initial mixture spiked with 12.5% (0.5 mol) and 25% (1 mol) biodiesel (Table 1; Fig. 2). The presence of biodiesel did promote higher conversions, as would be expected if the conversion rates were limited by the methanol stoichiometry. Increasing amounts of biodiesel increased reaction rates until the system was homogeneous. Methanol was completely miscible in biodiesel at room and higher temperatures.

If biodiesel increased solubility and therefore increased reaction rates, a hydrophobic solvent that decreased the solubility of methanol in the oil phase should have decreased the

alcoholysis rate. When hexane was added to the system, a similar reaction rate was observed. In this case, it was likely that the antisolvent capabilities of hexane were insufficient to have a noticeable impact.

Effect of temperature. Figure 2 summarizes the times necessary to achieve 5% conversion and graphically illustrates the impact of temperature on reaction rate. Figure 2 shows data for reactions with oil/methanol ratio of 1:6. As would be expected for a kinetically controlled process, the reaction rate increased with increasing temperature. Only methanol alcoholysis was evaluated at different temperatures. Under the assumption of a first-order kinetic model, the Arrhenius activation energy was calculated as 1400 K.

The Arrhenius model allowed the reaction rates to be extrapolated to higher temperatures where the reaction rates can be compared with those found in the work of Diasakou *et al.* (4) and Saka and Kusdiana (5). The data from Diasakou *et al.* (4) (Fig. 2) supported the results reported here. At 120 and 150°C, reaction times were higher than predicted by the Arrhenius plot because of limited solubility of methanol at lower temperatures. Using the methyl ester as a solvent (12.5–25% of solution) at 150°C was an effective means to increase reaction rates to values expected for homogeneous reactions where solubility did not limit the reaction rate. This confirms the earlier implication that the noncatalytic alcoholysis was solubility-limited during the initial phase of reaction.

Saka and Kusdiana (5) reported achieving 5% conversion at about 167 s ($k = 0.0003 \text{ s}^{-1}$) at 230°C as compared with the Arrhenius model extrapolation of data in the present paper and the work of Diasakou *et al.* (4) reporting approximately 800 s at 230°C. The reaction time of Saka and Kusdiana (5) was substantially lower. The higher reactions rates were likely due to the catalytic nature of the Inconel-625 reactor surface. Extension of reaction conditions to the supercritical region would possibly exacerbate the reactor wall effects owing to increased diffusivities. When scaling up reactors, care must be taken to ensure that the surface of the reactor

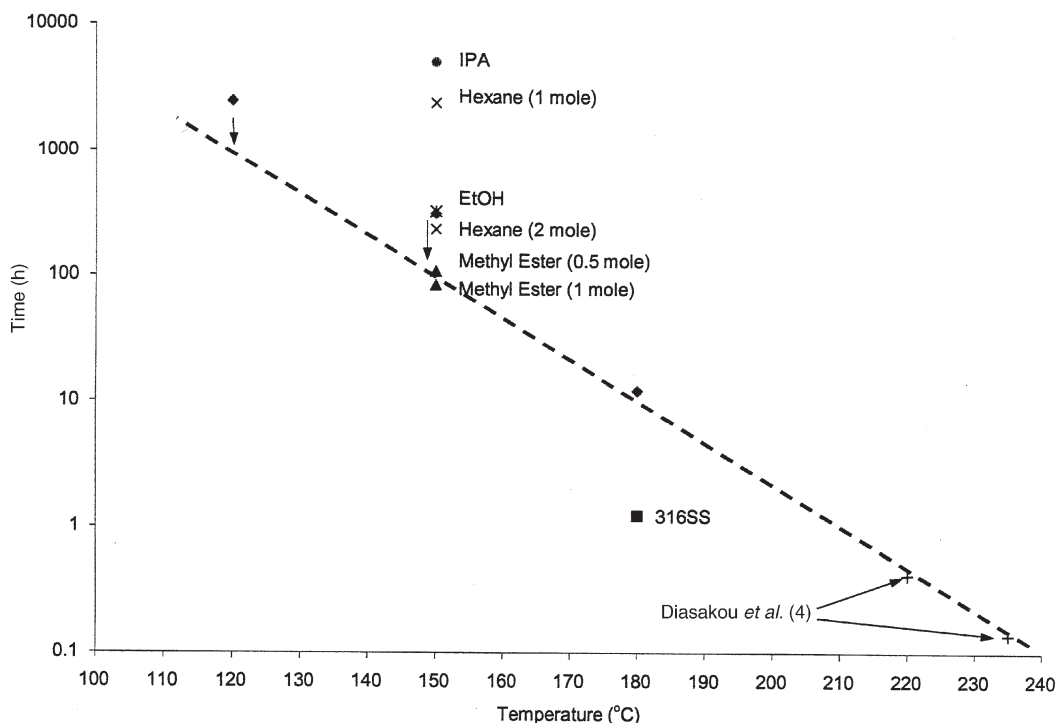


FIG. 2. Time in hours to achieve 5% conversion. \blacklozenge symbols are the average of methanol runs at the indicated temperature without solvent or catalyst; line is the estimate of Arrhenius-type temperature dependence; vertical arrows indicate correction for solubility limitations. IPA, isopropyl alcohol.

does not dominate the observed kinetics, because the ratio of reactor surface area to reactor volume decreases as the reactor size increases.

Reactivity of different alcohols. The alcoholysis reaction rates of methanol, ethanol, and isopropyl alcohol can be readily compared in Figure 2 at 150°C. The reactivity of methanol was similar to that of ethanol and considerably faster than that of isopropanol. The lower reactivity of isopropanol was likely due to the steric hindrance effect, which created repulsion between close groups. Both ethanol and isopropanol were more soluble in the oil reagent. Relative to methanol, the intrinsic reaction rates for ethanol and isopropanol alcoholysis (7) may have been even smaller than indicated by Figure 2. Ethanol likely had a lower intrinsic rate constant but maintained a higher solubility, leading to similar rates at the conditions studied.

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