

# Calcium Carbonate Catalyzed Alcoholysis of Fats and Oils

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**ABSTRACT:** Several alcoholysis catalysts, known to be effective for reactions between simple alcohols and soybean oil, were evaluated and found to be ineffective toward alcoholysis of ethylene glycol with soybean oil under traditional reaction conditions. An initial survey of alternative catalysts revealed that organometallic tin complexes were effective but unsatisfactory due to toxicity and difficulty in recovering the catalyst. Satisfactory performance for several alcoholysis reactions was achieved with calcium carbonate catalysts even though at higher temperatures, typically greater than 200°C. Higher reaction temperatures are not considered to be a problem for flow reactors where heat exchangers can be readily used to minimize energy costs. Free fatty acids were esterified by the calcium carbonate and did not appear to inhibit the catalyst. Reaction times of 18 min provided essentially complete conversion. No decrease in the activity of calcium carbonate was observed after weeks of utilization. The robust structure is suitable for use in packed-bed reactors. The catalyst used for the flow reactors was pulverized limestone. Limestone from two locations was tested and found to be effective. Catalyst removal requires only a screening process at the reactor discharge.

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**KEY WORDS:** Alcoholysis, biodiesel, calcium carbonate, catalyst, ester, glycerin, heterogeneous catalysis, soybean, tallow, transesterification.

Ester formation constitutes one of the most important classes of reactions in value-added processing of animal fats and vegetable oils. Typical schemes for ester formation include reactions of (i) an alcohol with an acid (esterification), (ii) an ester with an alcohol (alcoholysis), (iii) two different esters (transesterification), and (iv) an ester with an acid (acidolysis). Of these reaction schemes, esterification and alcoholysis are by far the most important to the fat and oil industry since these make use of the fatty acid components that comprise most of fats and oils.

Conversion of fats and oils into monoglyceride and glycol esters has often been performed through hydrolysis followed by esterification. Although this multistep scheme can be accomplished in one pot, the process (i) produces an aqueous waste stream containing both the hydrolysis catalyst and oil's/fat's natural glycerin, (ii) requires drying of the alco-

hol-acid mixture to drive equilibrium toward ester formation,

and (iii) requires the removal of the homogeneous catalyst from the product.

Alcoholysis schemes have the advantage of requiring only one reaction step. Simple Brønsted bases like NaOH and KOH are widely used for alcoholysis of agricultural triglycerides with simple alcohols like methanol. This is the most common method for converting a triglyceride to a monoester (1–4). While this process works well for monoalcohols such as methanol and ethanol, we have found that little or no conversion occurs when using glycols as the transesterifying alcohol.

The catalytic activity of strong Lewis acids such as titanium (IV) alkoxides  $Ti(OR)_4$  (5,6) can provide effective alternatives to traditional Brønsted base catalysts. However, many of these catalysts suffer from problems of cost, toxicity, and difficulty of removal from the product. Specifically, the active early transition metal catalysts tend to be poisoned by water, while the heavy metal catalysts are more durable, but quite toxic (7).

For many industrial applications, heterogeneous catalysts (two-phase catalysts) offer several advantages over homogeneous catalysts (one-phase catalysts), the largest being ease of separation from products. This alone provides sufficient motivation to investigate solid-phase materials capable of catalyzing these reactions.

Calcium oxide is one of the few heterogeneous alcoholysis catalysts that is in common use (7) for monoglyceride production at temperatures of 200 to 220°C with reaction times of 1 to 4 h. While the calcium oxide is largely a solid catalyst, the reaction mixture forms a slurry that requires a solid-liquid separation process. Phosphoric acid is often used to neutralize residual basicity. This type of catalyst was of specific interest for the research of this paper.

Alkaline earth metal compounds are effective catalysts for certain ester formation or interchange reactions. Calcium and barium carbonates, acetates, oxides, and hydroxides are active catalysts for the production of sorbitol esters from free fatty acids (1). Other catalysts also have been studied for these alcoholysis reactions. Zinc oxide supported on alumina promotes alcoholysis reactions of alcohols higher than methanol (8). Another recent patent expanded on the use of the acetates of calcium and barium to the application of the alcoholysis of triglycerides with methanol at 200–250°C (9). Certain carbonate systems also promote glycerolysis (1,4);

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however, no data have been reported concerning alcoholysis with other alcohols.

## EXPERIMENTAL PROCEDURES

Alcoholysis reactions were conducted using two general methods: (i) controlled batch-reactor studies in 50- and 250-mL reactors and (ii) flow-reactor studies.

*Batch-reactor studies.* For the 50-mL batch-reactor studies, a 50-mL three-necked round-bottom flask was charged with 1–2 g of soybean oil, 1–2 mL of ethylene glycol, and *ca.* 0.25 g of catalyst. Stirring was maintained throughout the reaction by use of a magnetic stirrer. The reactions were run for up to 24 h at temperatures of 100–150°C. After the contents of the flask had cooled to near room temperature, the product was extracted into diethyl ether and washed with saturated NaCl. The ether layer was dried with anhydrous sodium sulfate and filtered. The solvent was removed by rotary evaporation.

For the ion-exchange resin-based 250-mL batch-reactor studies, a 250-mL three-necked round-bottom flask was charged with 13.5 g of soybean oil, 59 g of ethylene glycol, and 2.8 g dry acidified resin. The contents were purged with oxygen-free, dry N<sub>2</sub> for 10 min prior to heating under a N<sub>2</sub> atmosphere. Stirring was maintained throughout the reaction by use of a magnetic stirrer. The mixture was allowed to react for 48 h at 120°C. The product was isolated by extraction into diethyl ether. The ether layer was washed with saturated NaCl, dried with anhydrous sodium sulfate, and filtered. The solvent was removed by rotary evaporation.

For the carbonate-based 250-mL batch-reactor studies, a 250-mL three-necked round-bottom flask was charged with 30.0 g of oil or fat, a variable amount of glycol, and 2.0 g of catalyst. The contents were purged with oxygen-free, dry N<sub>2</sub> for 10 min prior to heating under a N<sub>2</sub> atmosphere. Stirring was maintained throughout the reaction by use of a magnetic stirrer. The temperature was allowed to increase to a maximum of 195–225°C and was held at around 210°C for 2.5–3 h. After the contents of the flask cooled to near room temperature, the product oil was extracted into diethyl ether. The ether was washed four times with 1 N HCl (to remove the carbonate catalyst) and twice with distilled water. The ether layer was dried with anhydrous sodium sulfate and filtered. The solvent was removed by rotary evaporation.

*Flow-reactor studies.* For flow-reactor studies, a 9-mL reactor was packed with 16–60 mesh calcium carbonate obtained by pulverizing limestone rock found locally. The results are generally reproducible with sieved calcium carbonate (14–20 mesh) obtained from the Iowa Limestone Co. (Des Moines, IA). All liquid reactants were premixed and stirred, if required, to prevent the mixtures from separating. A high-performance liquid chromatography (HPLC) pump capable of metering flow at set points between 0.5 and 10 mL/min pumped the mixture through about 0.9 m of 1.6-mm tubing that rapidly brought the contents to reaction temperature in-

side a furnace that contained the reactor and coiled tubing for preheating the mixture. A Camile control system (Camile Products, LLC, Indianapolis, IN) maintained the reactor at temperature within a 1–2°C range. After the reactor, the 1.6-mm tubing proceeded through a water quench at room temperature. The pressure of the reactor system was maintained using an Autoclave (Autoclave Engineering, Erie, PA) micrometering valve located after the quench operated by a Vexta stepping motor (available from Alzanti, Blackwater, United Kingdom).

Effluent was collected in 100-mL vials. Reactor flow was continued over at least four residence times prior to the collection of samples for analysis. The same packing was used for a multitude of different triglyceride reactions, as well as oxidation reactions in supercritical water. Within a set of experiments run with a particular catalyst packing, no deterioration in performance was observed over the course of about 200 h of reactions. Reactor pressure was maintained at 30 to 200 bar to maintain a single liquid phase—liquid phase reactions tend to be relatively insensitive to moderate changes in pressure. At 220°C, equal masses of alcohol and fat/oil have bubble-point pressures calculated to be 0.11, 1.5, and 35 bars for glycerin, ethylene glycol, and ethanol, respectively. Pressures between 30 and 200 bar were chosen with the intent of avoiding formation of vapor phases in the reactor.

*Characterization methods.* Infrared (IR) spectra of samples were obtained on thin films sandwiched between salt plates. The spectra were taken either on a Nicolet (Madison, WI) Avatar 320 FT-IR connected to a personal computer (PC) running Omnic 5.1b or on a Nicolet Impact 410 FT-IR connected to a PC running Omnic 2.1. Gas chromatography/mass spectrometry (GC/MS) chromatograms were obtained on a DB-5MS column (J&W Scientific, Inc., Folsom, CA) with a Hewlett-Packard HP 6890 Series GC System (Palo Alto, CA) equipped with a mass selective detector connected to a PC running Enhanced ChemStation G1701BA Version B.00.00 (Agilent, Palo Alto, CA).

Samples of methyl esters of the starting soybean oil and beef tallow used for GC/MS analysis were prepared according to standard procedures described earlier (4). Acetate ester samples were prepared by standard procedures described by Bettelheim and Landesberg (10). The temperature program used for GC/MS included: (i) initial temperature of 80°C, (ii) temperature ramp from 80 to 150°C at 80°C/min, (iii) temperature ramp from 150 to 175°C at 5°C/min, (iv) temperature hold at 175°C for 30 min, (v) temperature ramp from 175 to 300°C at 80°C/min, and (vi) temperature hold at 300°C for 30 to 60 min. Mole percentages of the fatty acids (C<sub>12:0</sub>, C<sub>14:0</sub>, C<sub>15:0</sub>, C<sub>16:0</sub>, C<sub>16:1</sub>, C<sub>17:0</sub>, C<sub>18:0</sub>, C<sub>18:1</sub>, C<sub>18:2</sub>, C<sub>18:3</sub>, C<sub>20:0</sub>, and C<sub>22:0</sub>) for soybean oil and beef tallow used for ester-forming reactions were 0, 0, 0, 11.86, 0, 0, 4.55, 27.23, 50.24, 5.54, 0.30, and 0.30; and 0.67, 3.19, 0.59, 24.38, 3.26, 2.22, 19.05, 44.29, 2.22, 0, 0.11, and 0, respectively. GC/MS data were obtained from dilute solutions of samples in ether. The flow rate was held constant at 1 mL/min.

The DEG acetate ester program was (i) initial temperature

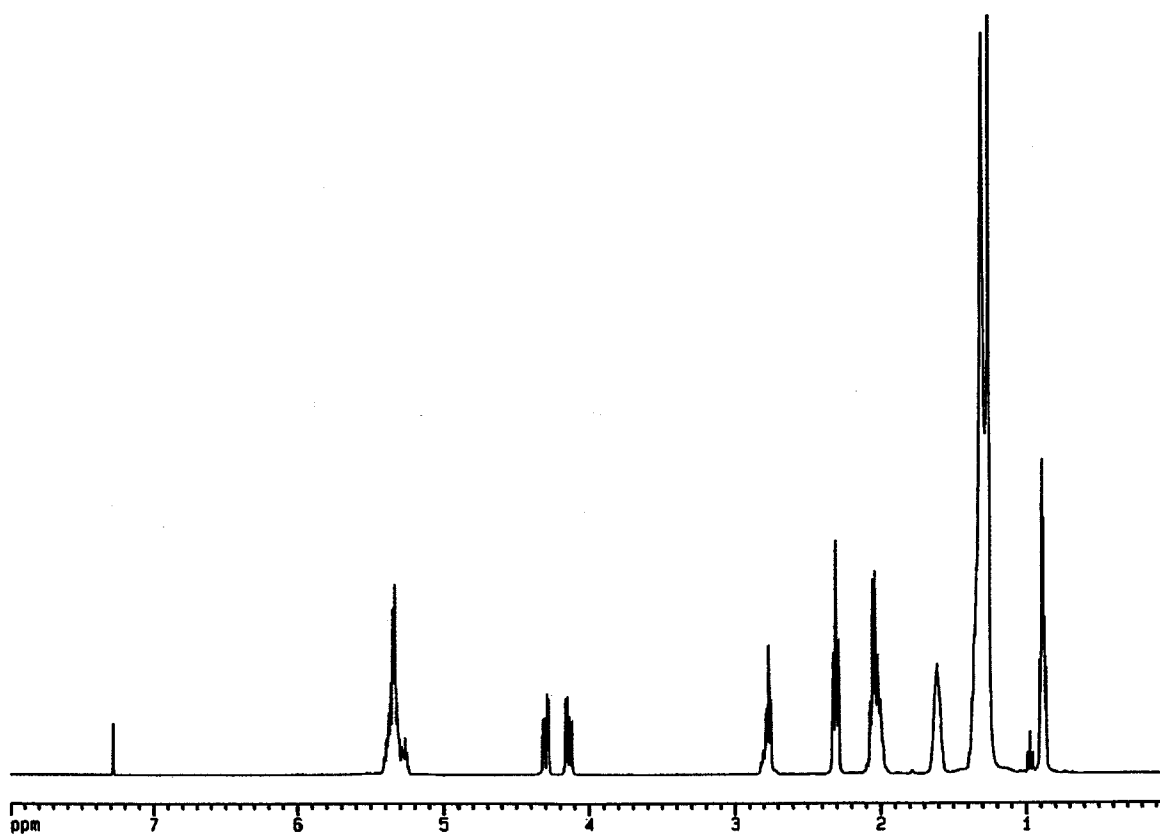


FIG. 1.  $^1\text{H}$  nuclear magnetic resonance (NMR) spectrum of soybean oil.

80°C, (ii) temperature ramp 80–150°C at 80°C/min, (iii) temperature ramp 150–165°C at 5°C/min, (iv) temperature ramp 165–230°C at 80°C/min, (v) temperature hold 230°C for 35 min, (vi) temperature ramp 230–280°C at 80°C/min, (vii) temperature hold 280°C for 10 min, (viii) temperature ramp 280–300°C at 80°C/min, and (ix) temperature hold 300°C for 30 min.

Reaction conversion was quantified by comparing integrations of  $^1\text{H}$  nuclear magnetic resonances (NMR) that were characteristic of the starting oil/fat and the desired product ester. All  $^1\text{H}$  NMR spectra were taken in  $\text{CDCl}_3$  (99.8% D) purchased from Cambridge Isotope Laboratories, Inc. (Andover, MA). Individual spectra were obtained using a Bruker (Billerica, MA) 400 MHz NMR. Figures 1 and 2 show representative spectra for the oil before and after alcoholysis with diethylene glycol.

GC/MS analysis of the various reaction products was compared to the product distributions obtained by  $^1\text{H}$  NMR analysis. For the fatty acid methyl esters, integration of the  $^1\text{H}$  resonances from the olefin group compared to the integrations of the methoxy group gave the average degree of unsaturation. Comparison of the average degree of unsaturation obtained from  $^1\text{H}$  NMR to that obtained from GC/MS gave 1.487 to 1.443 for soybean oil and 0.552 to 0.520 for tallow. For the diethylene glycol (DEG) alcoholysis reaction product distribution, data were obtained on the acetate ester derivative of the product. Integration of the  $^1\text{H}$  resonances from the glycol methylene protons compared to the glyceride protons

gave the ratio of glycol to glyceride products. For reactions in which a large excess of DEG was used,  $^1\text{H}$  NMR data showed that the product consisted of 93.4% glycol-containing species as compared to 96.4% by GC/MS analysis. Total glyceride products were found to be 6.6% by  $^1\text{H}$  NMR but only 3.6% by GC/MS. When only 2 mol of DEG were used,  $^1\text{H}$  NMR data showed the product to consist of 76.3% glycol-containing species as compared to 79.6% by GC/MS analysis. Total glyceride products were found to be 23.7% by  $^1\text{H}$  NMR and 20.4% by GC/MS.

*Reagents.* Bis(tri-*n*-butyltin)oxide, anhydrous ethylene glycol, DEG, and triethylene glycol were purchased from Aldrich (Milwaukee, WI). The glycols (reported purity of 99%) were used without further purification. Soybean oil, Food Club brand vegetable oil that is distributed by Topco Associates, Inc. (Skokie, IL), was purchased from a local grocery store. The reported composition for the soybean oil was 64% polyunsaturated fats, 21% monounsaturated fats, and 14% saturated fats. Beef tallow was supplied by Inland Products, Inc. (Columbus, OH). Anhydrous sodium sulfate (certified ACS grade), sodium carbonate, potassium carbonate, glycerin (certified ACS grade), and methanol (HPLC grade) were purchased from Fisher Scientific (Fair Lawn, NJ). Zinc carbonate (Baker analyzed reagent grade) was purchased from J.T. Baker Chemical Co. (Phillipsburg, NJ). Approximately 100 mesh calcium carbonate and calcium oxide used for batch reactor studies were obtained from Lancaster (Windham, NH).

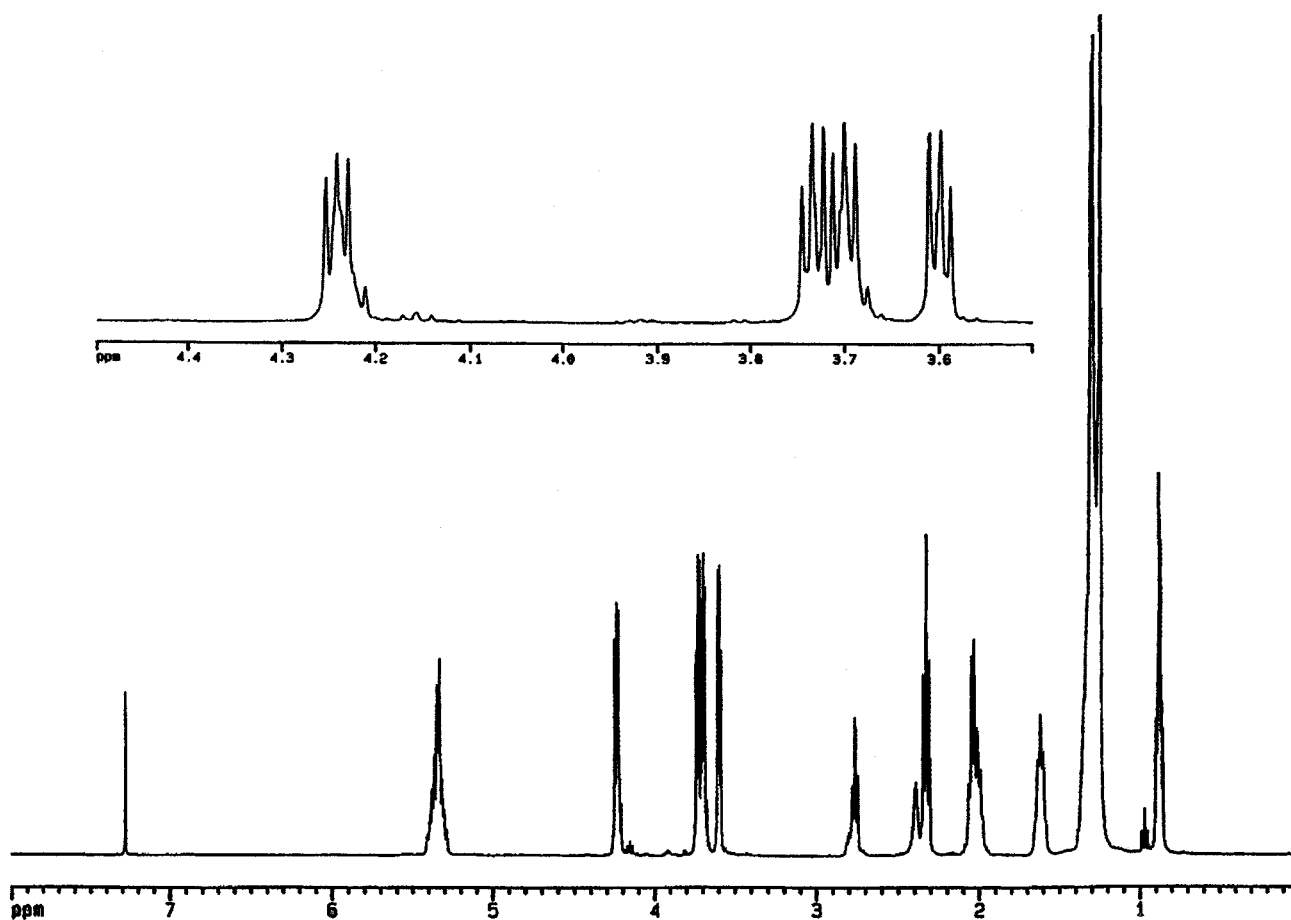


FIG. 2.  $^1\text{H}$  NMR spectrum of diethylene glycol monoester of soybean oil. See Figure 1 for abbreviation.

Dowex 50W-X8 ion-exchange resin was purchased from Sigma (St. Louis, MO). All reagents were used without further purification. All other solvents and reagent grade materials were purchased from Fisher Scientific.

## RESULTS AND DISCUSSION

Our research team focuses on producing derivatives of triglycerides suitable for use as cetane improver additives for diesel fuel. Monoglycol esters of fatty acids are convenient

**TABLE 1**  
Batch Reactor Studies on Alcoholysis of Soybean Oil and Beef Tallow

Reactor size (mL)	Fat/oil	Alcohol <sup>a</sup>	Catalyst	Molar ratio (lipid:ROH:cat.)	Time (h)	Temperature (°C)	Yield (g)	Conversion (%)
250	Soybean oil	DEG	None	1.72:14.2:1.0	2.5	205	N/A	<5
250	Beef tallow	DEG	None	1.75:14.2:1.0	2.5	205	N/A	<5
50	Soybean oil	EG	NaOH	0.92:9.16:1.0	24.0	150	N/A	<5
50	Soybean oil	EG	H <sub>2</sub> SO <sub>4</sub>	10:20:1 <sup>b</sup>	8.0	90	N/A	<5
250	Soybean oil	EG	Dowex 50W-X8	1.00:61.8:2.8 <sup>c</sup>	48.0	120	N/A	<5
50	Soybean oil	EG	(C <sub>12</sub> H <sub>27</sub> Sn) <sub>2</sub> O	62.0:1660:1.0	24.0	100	—	>95
250	Soybean oil	GLY	CaO	0.96:10.4:1.0	2.5	210	—	>95
250	Soybean oil	GLY	CaCO <sub>3</sub>	1.73:17.9:1.0	2.5	210	15	>95
250	Soybean oil	DEG	CaCO <sub>3</sub>	1.73:18.9:1.0	2.0	210	20.8	>95
250	Beef tallow	DEG	CaCO <sub>3</sub>	1.75:16.5:1.0	3.0	210	30.5	>95
250	Soybean oil	DEG	Na <sub>2</sub> CO <sub>3</sub>	1.81:14.9:1.0	2.0	210	—	>95
250	Soybean oil	DEG	K <sub>2</sub> CO <sub>3</sub>	2.37:19.5:1.0	2.0	210	—	>95
250	Soybean oil	DEG	ZnCO <sub>3</sub>	3.27:27.0:1.0	2.0	210	29.6	>95
250	Soybean oil	DEG	MgCO <sub>3</sub>	1.01:11.8:1.0	2.0	210	—	>95
250	Beef tallow	TriEG	ZnCO <sub>3</sub>	3.33:27.0:1.0	2.5	210	34.9	>95

<sup>a</sup> DEG = diethylene glycol, EG = ethylene glycol, GLY = glycerin, TriEG = triethylene glycol; N/A, not applicable.

<sup>b</sup> Approximate reaction conditions.

<sup>c</sup> 2.8 g of the resin was used.

precursors for production of these additives since they contain primary hydroxyl groups suitable for nitration. Suppes *et al.* (11,12) have described the performance of nitrates of some monoglycol esters as cetane improvers. However, these monoglycol esters were produced through a two-step synthetic route involving hydrolysis followed by esterification.

**Batch-reactor studies.** In an attempt to convert the starting triglycerides directly to the mono(ethylene glycol) esters, various common alcoholysis catalysts were tested. Table 1 summarizes the conditions used for these attempted reactions. In cases where no catalyst was employed or where NaOH, H<sub>2</sub>SO<sub>4</sub>, or acidified ion exchange resin was used as catalyst, only the starting triglyceride was recovered as determined by the IR and <sup>1</sup>H NMR spectra.

After these failed attempts, a bis(tri-*n*-butyltin)oxide catalyst was tested. As is shown in Table 1, it proved to be an effective catalyst for this transesterification reaction at 100°C when used in catalytic quantities (1 mol catalyst to 60 mol soybean oil). After a period of 12 h, no triglycerides were present in the reaction mixture. After extraction into ether and repeated water washes, both the mono-fatty glycol and di-fatty glycol esters were recovered. Formation of the diester could be suppressed by utilizing a 30–50 molar excess of ethylene glycol. However, this catalyst is soluble in the fatty esters, and MS analysis of the transesterified products revealed appreciable amounts of catalyst after repeated attempts at purification. Concerns about catalyst cost and toxicity associated with the difficulty of catalyst recovery limited our interest toward pursuing further development of these organometallic catalysts.

Screening tests were performed to evaluate the catalytic activity of both calcium oxide and calcium carbonate toward the alcoholysis of soybean oil with glycerin. The <sup>1</sup>H NMR spectra of the products obtained from the screening tests showed conversion of the starting triglyceride to mostly monoglyceride products. Comparison of the changes in the glyceride resonances ( $\delta$  3.5–5.0) of the products of the screening tests revealed that the products obtained in each case were identical.

Upon determination that the soybean oil could be converted into the monoglyceride product, a series of alcoholysis reactions was performed using di- or triethylene glycol, soybean oil, or beef tallow and a carbonate-based catalyst (Table 1). Three hours at about 200°C was sufficient to completely convert the triglyceride into the monoglycol product. As is shown in Table 1, calcium, zinc, and magnesium carbonates all show good catalytic activity, producing a clean monoglycol product. Sodium and potassium carbonate, although active alcoholysis catalysts, were found to promote surprising side reactions. The IR spectra of the products of these catalysts show the presence of a new carbonyl peak around 1710 cm<sup>-1</sup> and a broad hydroxyl peak characteristic of a carboxylic acid. This negative hydrolysis side-reaction is a drawback to using these catalysts. The <sup>1</sup>H NMR spectra also show another interesting side-reaction. The olefinic protons

for fatty acid esters typically appear as a broad multiplet centered around 5.3 ppm (Figs. 1 and 2). However, in the products obtained from the alkali carbonate reactions, additional peaks in the <sup>1</sup>H NMR spectra appear at  $\delta$  6.40,  $\delta$  6.15, and  $\delta$  5.75 downfield of the broad olefin multiplet. The position of these new olefin resonances strongly suggests that the double bonds are migrating into conjugation with the carbonyl group.

**Commercial development.** Of the systems listed in Table 1, catalysis over calcium carbonate is of the greatest interest since calcium carbonate has extremely low solubilities in fats/oils, is readily available at low costs, and has a structure robust enough for use in flow reactors. Thus, further studies of these conversions were conducted in a 9-mL packed-bed flow reactor. Table 2 summarizes the flow-reactor reactions and conversions.

By comparing batch-reactor data to flow-reactor data for alcoholysis with DEG, the flow reactor is observed to enhance higher reactivity. This is due to the higher catalyst loading (the ratio of grams catalyst to liquid reactants in reactor) in the flow reactor and the improved contact with the catalyst created by flow through the packed-bed configuration. Qualitatively, the batch-reactor studies are in good agreement with the packed-bed reactor studies with the calcium carbonate becoming highly active toward this reaction at about 210°C.

Generally, reaction rates increased with increasing temperatures and increasing residence times. The exception to this is the first set of data on reactions with glycerin at 240°C in Table 2. For this first set of data, the impact of increased temperatures and residence times was counterintuitive with lower conversions at 240°C as compared to 200°C. Because of these unusual trends, the data were repeated. Higher conversions were achieved when the experiment was repeated at 240°C. The second set of reaction data with glycerin is consistent with an extrapolation of the initial data point of 17% conversion at 4 min and 200°C.

The reactor and catalyst packing used for these studies were also used to evaluate the impact of calcium carbonate on the supercritical water oxidation of phenol with hydrogen peroxide. Hundreds of hours of operation were logged without decreasing reactivity; if anything, the reactivity could have increased with time. After several weeks of operation, the catalyst packing was replaced. Some of the packing at the reactor exit had been crushed to a finer particle size. It is believed that the crushing of the catalyst was due to the pressure drop across the reactor. The pressure drop was not measured.

The first nine reactions of Table 2 were conducted with limestone prepared by crushing rock obtained locally. The remaining experiments were conducted with sieved, crushed limestone from Iowa Limestone Company (Des Moines, IA). The inconsistencies of trends of the glycolysis reactions of Table 2 could be attributed to different sources of the limestone; however, insufficient data are available to identify definitively the cause of the inconsistencies. Useful temperature ranges for calcium carbonate catalyzed alcoholysis were between 210 and 280°C. Below 210°C, the reaction was too slow while above 300°C polymerization dominated.

**TABLE 2**  
**Summary of Flow Reactor Studies Over Calcium Carbonate Catalyst**

	Temperature (°C)	Residence time (min)	Soybean oil conversion (%)
Equal masses			
Soybean oil/glycerin	200	4	17
Soybean oil/glycerin	240	4	<5
Soybean oil/glycerin	240	18	18
Soybean oil/ethanol	200	18	<1
Soybean oil/ethanol	240	4	<5
Soybean oil/ethanol	240	18	<5
Soybean oil/ethylene glycol	200	4	<1
Soybean oil/ethylene glycol	240	4	<1
Soybean oil/ethylene glycol	200	18	12
Soybean oil/ethylene glycol	240	18	60
Equal masses			
Soybean oil/glycerin	200	18	>95
Soybean oil/glycerin	240	18	>95
Soybean oil/glycerin	260	18	>95
Soybean oil/diethylene glycol	200	18	>95
Soybean oil/diethylene glycol	240	18	>95
Soybean oil/diethylene glycol	260	18	>95
Mole ratio 1.8:1			
Soybean oil/diethylene glycol	200	18	35
Soybean oil/diethylene glycol	240	18	>95
Soybean oil/diethylene glycol	260	18	>95
Equal masses in methyl ester of soybean oil (1 g oil, 1 g ethanol, 2 g methyl ester)			
Soybean oil/ethanol	200	18	<1
Soybean oil/ethanol	240	18	78
Soybean oil/ethanol	260	18	>95
Soybean oil	300	Polymerization occurred, plugging the reactor	

Given the success of the flow-reactor systems, which are much simpler and cheaper for industrial processing of fats and oils, our attention turned to developing this system for our primary application of producing cetane improvers while minimizing production costs. For this application, we are looking at a system where 2 mol of DEG are reacted with 1 mol of the triglyceride. Ideally, the product will consist of mainly the monoglycol product and monoglycerides—each possessing free hydroxyl group(s) suitable for nitration. The acetate ester derivative of the product from this 2:1 molar reaction was analyzed by GC/MS to determine the product distribution. The majority (51.2%) of the product was the desired monodiethylene glycol fatty acid ester. Diesters of DEG were present next in abundance at 27.9% of the total; 9.9 and 9.8% of the total were found to be the diglyceride and monoglyceride products, respectively. Free glycerin was found to contribute only 0.7% of the total, while residual DEG contributed only 0.5%. The high amount of monoglycol product with low amounts of free glycerin and DEG suggests that this line of products may be ideal for development into a vital line of cetane improvers.

Alcoholysis with ethanol was investigated because of the importance of methyl and ethyl ester reactions toward the production of biodiesel. Packed-bed-reactor technology could

reduce conversion costs. As summarized in Table 2, equal-mass mixtures of ethanol and soybean oil did not react. To determine if this could be attributed to mixing problems between the ethanol phase and soybean phase, a methyl ester of soybean oil was used as a solvent to homogenize the mixture. With this solvent, high conversions were achieved. In practice, half of the alcoholysis product could be recycled during reactions to provide a similar reaction environment.

One final issue for consideration was the impact that free fatty acids, which may be present in unprocessed fats/oils, would have on the calcium carbonate catalyst. Thus, soybean oil was spiked with about 5 wt% fatty acids (prepared by hydrolysis of the same soybean oil). This mixture was reacted with DEG (1.8 mol DEG/1 mol oil) under the same conditions as those used in the other batch-reaction studies. Spectra (IR and <sup>1</sup>H NMR) of the products of these reactions showed complete conversion of the starting oil to the desired glycol product. No evidence for residual free fatty acids or the corresponding calcium salt was seen in any of the spectra obtained. The product mixture was also titrated against KOH, and significant reductions in the amount of free fatty acids were observed. Therefore, the presence of free fatty acids in an oil/fat (such as that found in crude oils) does not poison the catalytic activity of calcium carbonate. In fact, our titration results

strongly indicate that the free fatty acids were esterified over the calcium carbonate catalysts with a final free fatty acid concentration of less than 10% of the initial concentration.

*Mechanistic and environmental aspects of calcium carbonate.* Between the robust catalytic activity and the low cost of calcium carbonate, this is a promising reaction for industrial scale-up. At this point, the identity of the active site is not known. It is possible that calcium carbonate may function as a simple Brønsted base catalyst. The double-bond migration, observed in the  $\text{Na}_2\text{CO}_3$ - and  $\text{K}_2\text{CO}_3$ -catalyzed reactions, indicates that at these reaction temperatures the carbonate anion is an extremely strong base. Another possibility is that trace amounts of calcium oxide may form on the surface of the calcium carbonate particulates leading to the desired reaction. Furthermore, the calcium ion may participate in the reaction kinetics through Lewis acid complexation to the carbonyl group of the triglyceride. Further studies are needed to distinguish between these mechanisms. From a practical perspective, the exact mechanism is unimportant. The calcium carbonate catalyst is cheaper and is considerably more robust than calcium oxide particles.

Calcium is common in the environment and is available at very low costs compared to commonly used catalytic metals such as platinum. Trace amounts of calcium carbonate that are released to the environment generally have a very low environmental impact since calcium is already prevalent. Any residual acid catalysts that may be present from an earlier processing step can be neutralized directly in the packed-bed reactor. Spent catalyst can be easily destroyed in cement kilns.

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