J Am Oil Chem Soc (2009) 86:83–91
DOI 10.1007/s11746-008-1318-7

ORIGINAL PAPER

A Novel Method for the Production of Biodiesel from the Whole Stillage-Extracted Corn Oil

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Received: 5 September 2008 / Revised: 21 October 2008 / Accepted: 28 October 2008 / Published online: 26 November 2008

Abstract The extraction of corn oil from whole stillage and condensed distillers' solubles (CDS) with hexane and its conversion to biodiesel were investigated. The analysis of the extracted oil showed 6–8 wt.% free fatty acid (FFA) in this oil. Acid, base, acid–base, and acid–base catalyzed transesterifications with intermediate neutralization with anion exchange resin were investigated. Experiments were performed with model corn oil substrates which contained 1.0–6.0 wt.% FFA. The effect of catalyst at 0.50–1.25 wt.% was studied at a 1:8 oil/methanol molar ratio. At 6.0 wt.% FFA concentration, the acid-catalyzed scheme was slow and resulted in less than 20% yield after 4 h, while the base-catalyzed was mostly consumed by the FFA and very little conversion was achieved. The acid–base catalyzed scheme succeeded in reducing the FFA content of the oil through the acid-catalyzed stage, and yields in excess of 85% were achieved after the second stage of the reaction with a base catalyst. However, formation of water and soap prevented the separation of product phases. An alternative acid–base catalyzed scheme was examined which made use of a strong anion exchange resin to neutralize the substrate after the initial acid-catalyzed stage. This scheme resulted in the effective removal of the acid catalyst as well as the residual FFA prior to the base-catalyzed stage. The subsequent base-catalyzed stage resulted in yields in excess of 98% for a 7.0 wt.% FFA corn oil and for the corn oil extracted from CDS.

Keywords Biodiesel · Free fatty acid · Transesterification · Whole stillage · Distillers' grains · Fatty acid methyl esters (FAME) · Anion exchange resin

Introduction

There has been a considerable increase in the production of biodiesel in recent years. This interest has resulted in a record production of 450 million gallons biodiesel in the US in 2007 [1]. Most of the current production of biodiesel utilizes high quality soybean oil. Other sources of triglycerides (TG) such as waste cooking oil and yellow grease have also been investigated as raw material for biodiesel production. These alternative sources have been successfully converted to biodiesel with a promise of a cost-effective fuel [2]. Nevertheless, processing challenges remain to be unraveled. Another low-cost source of TG may be found in distillers' grains, the byproduct of dry grind ethanol production. The annual production of distillers' grains was 14.6 million metric tons in the year 2007 [3]. Distillers' grains contain about 8–10 wt.% oil (db) and are predominately used as an animal feed supplement. The oil content of distillers' grains is beyond what is needed in the feed and if extracted is a good source of TG for biodiesel production.

Transesterification of vegetable oils is the most effective process for the transformation of the triglyceride molecules into smaller, straight-chain molecules of fatty acid methyl or ethyl esters. In this transformation, the viscosity of vegetable oils is reduced from 10 to 15 times to about twice that of No. 2 diesel fuel. Other fuel specifications such as cetane number, energy content, and density of fatty acid esters are also similar to those of petroleum-based diesel fuel [4]. Moreover, biodiesel is essentially sulfur free

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and the engines fueled by biodiesel emit significantly fewer particulates, hydrocarbons, and less carbon monoxide than those operating on conventional diesel fuel engines. However, NO_x levels are slightly higher than those of diesel engines operating on conventional diesel fuels [5, 6]. The conventional biodiesel technology involves the use of an inorganic base or an acid catalyst at or near the boiling temperatures of the TG/alcohol mixture.

The transesterification of TG using acid catalysts has been signified by slow rate of reaction. High molar ratios of alcohol to oil and long reaction times are required for the acid-catalyzed transesterification of TG to reach high conversions. Freedman et al. [7] explored H_2SO_4 catalyzed transesterification of soybean oil with methanol, ethanol and 1-butanol. After 18 h of incubation, the conversion of TG to esters was unsatisfactory at 1:6 and 1:20 molar ratios, while at a molar ratio of 1:30, high conversions were obtained after 69 h for all three alcohols. Liu et al. [8] studied the effect of water on H_2SO_4 -catalyzed esterification of acetic acid and reported a significant decrease in the initial reaction kinetics due to catalyst impairment as water was produced from the condensation of acetic acid and methanol. Goff et al. [9] studied the acid-catalyzed transesterification of soybean oil using 0.1–1.0 wt.% of sulfuric, hydrochloric, formic, acetic, and nitric acids. Sulfuric acid was reported to be the only effective acid where >99 wt.% conversions of TG was observed at 0.5 wt.% acid loading, 1:9 molar ratio of TG to alcohol, 100 °C, and 8 h. Canakci and Van Gerpen [10] studied the effect of the oil/alcohol molar ratio and free fatty acid (FFA) on the transesterification of soybean oil with H_2SO_4. They reported a strong inhibition of catalytic activity when the water concentration was increased to above 0.5 wt.%. Formation of water at or above this level was attributed to the presence of FFA at > 5.0 wt.% in the initial soybean oil.

Most of the current production of biodiesel utilizes an alkaline catalyst which is mainly due to the fast rate of reaction and near complete conversion of reactants to biodiesel. Noureddini and Zhu [11] studied the kinetics of base-catalyzed transesterification of soybean oil. A reaction mechanism consisting of a short initial mass transfer controlled region followed by a kinetically controlled region was proposed. The activation energies suggested the domination of Arrhenius kinetics for the forward reactions. Muniyappa et al. [12] studied the effect of variables on base-catalyzed transesterification of soybean oil with methanol. They reported that an increase in the amount of catalyst (0.05–0.50 wt.%) and reaction time (10–75 min) had little effect on the yield of fatty acid methyl esters (FAME), while increases in the rate of mixing resulted in increases in the FAME yields. In the base-catalyzed transesterification of TG, the need for a low concentration of FFA in the starting material has been stressed by researchers [7, 10]. Freedman et al. [7] placed an upper limit of 1% FFA for the base-catalyzed transesterification of TG. At FFA levels beyond 1%, the formation of soap prevented the separation of ester and glycerol products. Triglyceride sources containing more than 1% FFA are considered high FFA oils for base-catalyzed transesterification purposes.

The conversion of high FFA oils to biodiesel has been investigated primarily through the use of waste cooking oils and model substrates made by the addition of FFA to a vegetable oil. Zheng et al. [13] studied the acid-catalyzed transesterification of waste frying oil containing 6.0 wt.% FFA at 1:74 to 1:245 molar ratios of TG to alcohol and reported conversion in excess of 99% after 4 h incubation when subjected to 169–190 kPa of pressure. Canakci and Van Gerpen [2, 14] studied a two-stage acid–base catalyzed transesterification scheme using 20–40 wt.% model substrates and yellow and brown grease feed stocks. The process involved an initial conversion of FFA to FAME using an acid catalyst where the FFA concentration was reduced to below 1.0 wt.%. The water formed was separated from the organic layer by settling, and the transesterification reaction was then completed by a base catalyst. Issariyakul and co-workers [15] examined the transesterification of waste fryer grease containing 5.0–6.0 wt.% FFA with a mixture of methanol and ethanol in a one-stage base and a two-stage acid–base system. The two-step system resulted in a conversion in excess of 90% compared to about 50% conversion in a single stage system. In this method, after the completion of the first stage of the reaction, silica gel was added to remove water from the reaction media prior to the second stage of the reaction.

Ghadge and Raheman [16] studied a two-step transesterification of mahua oil which contained 19.0 wt.% FFA. The initial step was an acid-catalyzed esterification of FFA to FAME with 1% H_2SO_4 which was followed by the separation of the organic phase by settling and the transesterification of the organic phase with 0.70 wt.% potassium hydroxide. The fuel properties of the biodiesel product were in accord with the biodiesel standards. Wang and co-workers [17] studied a traditional acid and a two-step acid/alkali catalyzed transesterification of waste cooking oil and reported 97.22% conversion of FFA to FAME with ferric sulfate as acid catalyst and potassium hydroxide as the transesterification catalyst at an oil to alcohol molar ratio of 1:10 and a reaction time of 4 h. With the traditional sulfuric acid-catalyzed process the conversion was 90% for the FFA at the oil to alcohol mole ratio of 1:20 and a reaction time of 10 h. Hancsok et al. [18] studied a two-stage acid/alkali transesterification of oil containing up to 32.0 wt.% FFA. The first step was an acid-catalyzed esterification of the FFA with H_2SO_4 for 4 h followed by a second-stage transesterification with sodium methylate for 2 h. They reported a FAME yield of more than 96.5% for the samples with less than 20.0 wt.% FFA content and a 60% yield for the sample with 32.0 wt.% FFA content. In both stages of the reaction, tetrahydrofuran and dioxane were used as co-solvents.

The objective of this study was to develop a process for the conversion of distillers' grains oil to biodiesel. A one-stage base, a one-stage acid, and a two-stage acid–base-catalyzed systems were examined. A two-stage acid–base scheme was then developed which utilized an intermediate removal of water and acid from the reaction media by a strong anionic (OH^- or Cl^- form) exchange resin prior to the base-catalyzed transesterification step. The procedure for the extraction of oil from distillers' grains was also optimized. Samples used in the optimization experiments were model compounds made from pure corn oil and a technical grade linoleic acid (60%) with the balance consisting of oleic, linolenic, palmitic, and stearic acids. Actual corn oil extracted from condensed distillers' solubles (CDS) was used to validate the results for the model substrates. Please note that the corn oil extracted from CDS is expected to have a composition similar to that of the oil in the whole stillage (WS) and dried distillers' grains with solubles (DDGS). This is due to the dry grind processing scheme where after the separation of ethanol from the beer stream, the formed WS stream is filtered to form the wet distillers' grains (WDG) cake and the CDS streams which are combined and dried to form DDGS. The samples used in this study were taken from Abengoa Bioenergy, a dry grind corn ethanol facility in York, NE, as shown in the process flow diagram of Fig. 1.

Experimental Procedures

Materials

Samples of the dried distillers' grains (DDG), WS and CDS were collected at the Abengoa Bioenergy (Dry-milling ethanol facility, York, NE) on three independent dates. CDS and WS samples were collected in 20-L containers and then separated into 1-L containers. At the time of sampling, the DDG samples did not contain the CDS. The collected biomass samples were stored at 4 °C prior to use. The DDG and CDS samples were used in the original form with no further processing. For the WS samples, the particle size of this solid mater was reduced by mixing in a blender (Warning Laboratory, Torrington, CT) for 2 min prior to use. WS so prepared was then used without further drying.

Hexane was purchased from EM science (Gibbstown, NJ). All the calibration standards, bis-(trimethylsilyl) trifluoroacetamide (BSTFA), pyridine, linoleic acid (60% technical grade), H_2SO_4 (95–98%), potassium hydroxide pellets (88%), barium hydroxide (95%), toluene (anhydrous), potassium hydrogen phthalate and methanol (ACS reagent) were purchased from Sigma Aldrich Chemical Co. (St. Louis, MO). NaOH pellets (98.8%) were purchased from VWR (Chicago, IL). Anion exchange resins Dowex SBR LCNG hydroxide form and Dowex 21 K XLT resins were purchased from Sigma Aldrich Chemical Co. (St. Louis, MO). Corn oil was edible grade oil purchased from a supermarket.

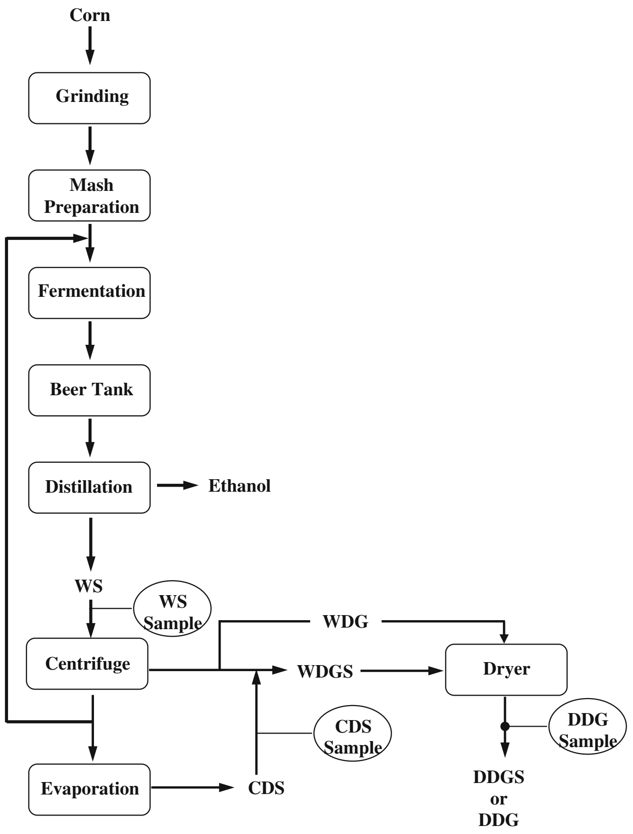

Fig. 1 Dry grind process flow diagram and collected sample streams. *CDS* condensed distillers solubles, *DDG* dried distillers' grains, *DDDG* dried distillers' grains with solubles, *WS* whole stillage, *WDG* wet distillers' grains with solubles, *WDGS* wet distillers' grains with solubles

Oil Extraction

The extraction procedure consisted of an initial mixing of 20 g of the samples with a prespecified amount of hexane in an Erlenmeyer flask at 600–800 rpm with a magnetic stirrer. After a prespecified period of mixing, a bench-top centrifuge (Multi Ventilated 8464, Thermo Electron Corporation, Milford, MA) was used to separate the organic phase which consisted mainly of hexane and the extracted oil, from the rest of the substrate. Centrifugation was at

11,000 *g* for 10 min. Hexane was separated from the extracted oil by a vacuum rotovap (Brinkmann Instruments Inc., NY). The extracted oil was analyzed with a gas chromatograph. Acid values of the extracted oil and the model substrates were determined using Methods of the American Society for Testing and Materials (ASTM) official method D-974 [19].

Transesterification Reactions

The transesterification reactions with acid or base catalyst were carried out in a three necked 500 mL round bottomed flask. The stoichiometric molar ratio of TG to the oil in the transesterification reaction is 1:3. A 1:8 molar ratio of oil to methanol, which is a typical ratio for the transesterification of vegetable oils, was used in all experiments. The reaction flask was initially charged with 40.0 g of oil and prespecified amounts of FFA (1.0–6.0 wt.% at 1.0% intervals, based on the amount of oil), 11.62 g of methanol and a prespecified amount of catalyst (0.25–1.25 wt.% at 0.25% intervals, based on the amount of oil). The catalyst was either NaOH or H_2SO_4. The reaction mixture was heated and stirred over a heater/stirrer device (Glass-Col, Terre Haute, IN), while under a total reflux condenser and at atmospheric pressure. Under atmospheric total reflux conditions, the temperature of the reaction was 68–69 °C. For the single catalyst schemes, the transesterification reaction was carried out for 90 min and 4 h for the base and the acid-catalyzed reactions, respectively. At the conclusion of the procedure, the reaction mixture was allowed to separate by gravity into an upper layer of FAME and a lower layer of glycerol which contained most of the unreacted methanol.

Acid–Base Catalyzed Transesterification with Base Neutralization

The acid-catalyzed transesterification was carried out first. The same amount of oil and methanol as for a single catalyst system was used. Variations in the FFA concentration in the 1.0–6.0 wt.% range with 0.5 wt.% H_2SO_4 were carried out for 30 min. The reaction mixture was allowed to settle down in a separatory funnel and the bottom aqueous layer was discarded. The base-catalyzed transesterification was carried out on the top organic layer for 1 h with a nominal 0.25 and 1.0 wt.% NaOH concentration. The nominal amount of the NaOH was the total amount of NaOH added to the system minus the amount needed to neutralize the residual H_2SO_4 in the reaction mixture. The acid–base procedure was also performed on the oil extracted from CDS. The reaction mixture was then allowed to separate by gravity settling as with a single step catalyzed procedure.

Acid–Base Catalyzed Transesterification with Ion Exchange Neutralization

The procedure followed the steps presented in the previous section for the acid–base-catalyzed transesterification except for the H_2SO_4 neutralization step. A strong anion exchange resin was used to remove the residual H_2SO_4 prior to the base catalyzed transesterification. Consequently, the entire acid catalyzed reaction mixture was passed through an ion exchange column. The column was 1/2” in diameter and 12” long and had a glass frit installed in the lower section to support the ion exchange material (10 g). The resins were hydrated with deionized water prior to use. After passing through the column, the reaction mixture was allowed to separate by gravity settling in a separatory funnel resulting in two layers of which the bottom aqueous layer was discarded. The upper organic layer was transesterified with 0.50 wt.% NaOH for 1 h. The reaction mixture was then allowed to separate by gravity settling as with a single step catalyzed procedure.

Regeneration and reuse of the spent resins were examined. The resins were regenerated when the break point was reached. The break point was at a point where more than 5% of the hydrogen ions (H_2SO_4 catalyst) remained in the substrate after the substrate was passed through the resin column. The spent resins were washed with hexane and deionized water prior to the regeneration. A 1-M NaOH solution was used for the regeneration of Dowex SBR LCNG OH^- resin and a 1-M NaCl solution was used for the regeneration of Dowex 21 K XLT Cl^- resin. The regeneration solution was passed directly through the ion exchange column. The resins were washed with deionized water prior to use.

Sampling and Analysis

Samples were drawn at pre-specified time intervals. In the acid-catalyzed reactions, samples were taken at 15, 30, 60, 120, 180 and 240 min. In the base-catalyzed reaction, samples were taken at 15, 30, 60 and 90 min. Samples were 0.8–1.2 mL in volume and were collected in 10-mL test tubes filled with 2 mL of distilled water. The test tubes were kept in an ice bath at 4 °C prior to use. Samples were quenched in the test tubes by placing them in the ice bath immediately after removal from the reactor. The test tubes were then shaken to stop the reaction. Upon mixing with water, glycerol and catalyst were transferred to the water phase, while, the FAME and the unreacted glycerides formed the organic layer. The layers were then centrifuged at 1,500 g for about 15 min to ensure a thorough separation. All experiments were repeated twice. The presented result reflect the mean values and the standard deviations.

Samples were derivatized with BSTFA prior to gas chromatography (GC) analysis. During the derivatization, the silylating agent reacts with the carboxyl groups of FFA and results in trimethylsilylated fatty acids which are readily separated and quantified. The derivatized samples were analyzed by GC to determine the concentration of FAME, FFA, monoglycerides (MG), diglycerides (DG), and TG. A Hewlett-Packard (Wilmington, DE) 6890 Series GC system was used for the chromatography work and a HP Chemstation software was used for the data analysis. The GC was equipped with a HP-5 column. Sample volumes were 2 μL; the carrier gas was helium; and the GC was operated in constant flow mode with an initial flow rate of 12 ml/min and nominal pressure of 34 psi. A split injector was used with a split ratio of 15:1 at a temperature of 325 °C. The flame ionization detector (FID) was operated at 350 °C and used a helium makeup flow to maintain a constant detector flow of 25 mL/min. The oven was initially held at 80 °C and was then elevated to 180 °C at 15 °C/min, to 250 °C at 5 °C/min, and finally to 325 °C at 8 °C/min. The oven was held at this temperature for 22.95 min before returning to 80 °C. Total run time for this method was 60 min. Calibrations were carried out using mixtures of FAME, FFA, glycerol, mono-, di-, and triglycerides. The standards were derivatized in the same fashion as the reaction samples.

Results and Discussions

Oil Extraction and Compositional Analysis

Extraction of oil with an organic solvent is perhaps the most efficient method for the recovery of oil from an aqueous oil-bearing material. This method is particularly useful for a material low in oil content such as WS which contains about 1–2% oil (9–11% on db). Hexane-type naphtha is the most widely used solvent and the one generally preferred by the oil refining industry [20]. Experiments were performed to optimize the conditions for the extraction of oil from the WS and CDS samples with hexane. The effects of solvent (0.033–0.33 g-solvent/g-substrate db), and time (10–120 min) were explored. The effect of variations in the mass of solvent on the amount of the extracted oil at a fixed extraction period of 30 min is presented in Fig. 2. Examination of this figure reveals an increasing trend in the amount of the extracted oil as the mass ratio of the solvent to substrate was increased from 0.03 to 0.20. Further increases in this ratio from 0.20 to 0.30 did not result in a significant increase in the amount of extracted oil. The percentage of the extracted oil at the solvent/substrate mass ratio of 0.20 was 9.8 ± 0.6 and 12.0 ± 0.8 wt.% on db for CDS and WS, respectively.

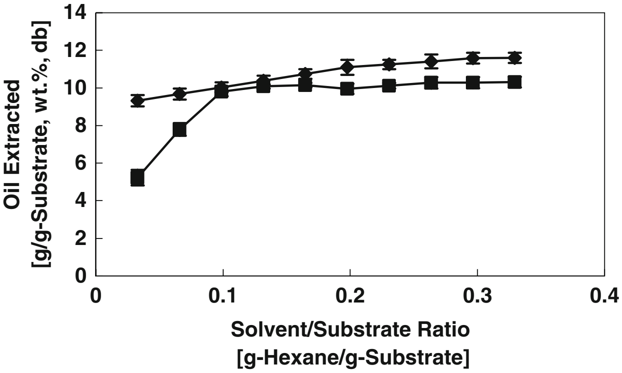

Fig. 2 Effect of solvent/substrate ratio on the extraction of oil from CDS subjected to 30 min mixing; (*filled diamonds*) CDS, (*filled squares*) WS

The time courses of the extraction of oil from WS and CDS with hexane was studied. A factor of interest in the extraction of oil-seeds by hexane is the thickness of the flakes. This was not a factor in this study as corn is milled before processing and the distillers' grain samples used for the extraction were ground further and consisted mostly of fine particles. Experiments were performed with a solvent/substrate mass ratio of 0.20 which was presented earlier as the optimum ratio. Examination of the results showed an increase in the amount of the extracted oil as extraction time was increased. This relationship ultimately leveled off in time. For the WS samples, 9.8 wt.% oil (db) was extracted after 30 min which increased to 10.5 wt.% after 240 min. For the CDS samples, the amount of the extracted oil was 12.7 wt.% (db) after 50 min which increased to 13.3 wt.% after 240 min. The extracted oil from WS, CDS and DDG were analyzed with a GC. The compositional analysis of the extracted oil is presented in Table 1. As expected, the concentration and composition of oil in the WS, CDS and DDG samples were similar and within the standard deviations of the data for these samples.

Table 1 Composition of oil samples

Substrate	Composition (wt.%)				
	FFA		MG	DG	TG
	Saturated[a]	Unsaturated[b]			
DDG	1.8 ± 0.2	5.6 ± 0.4	0.7 ± 0.2	0.6 ± 0.2	91.1 ± 0.3
WS	1.7 ± 0.1	5.9 ± 0.3	0.6 ± 0.1	0.6 ± 0.3	91.3 ± 0.2
CDS	1.5 ± 0.3	5.9 ± 0.4	0.5 ± 0.2	0.4 ± 0.4	91.1 ± 0.5
Linoleic acid	2.3 ± 0.2	97.8 ± 0.4	0	0	0
Corn oil	0.1 ± 0.1	0.8 ± 0.2	0	0	98.8 ± 0.1

WS whole stillage, *DDG* dried distillers' grain, *CDS* condensed distillers solubles, *MG* monoglyceride, *DG* diglyceride, *TG* triglyceride

[a] Includes palmitic and stearic acids

[b] Includes linoleic, linolenic and oleic acids

Acid-Catalyzed Transesterification

The transesterification of TG using acid catalysts is known for its slow reaction rate [7]. However, for high FFA oils the esterification of FFA with an acid catalyst to FAME has proven to be an effective way to reduce the FFA content of such oils and makes them a suitable substrate for base-catalyzed transesterification [2]. Experiments were performed to study the time courses of the transesterification of corn oil containing 1.0–6.0 wt.% FFA (at 1% intervals) and at 0.50–1.25 wt.% (at 0.25% intervals) H_2SO_4 concentration. The formation of FAME was monitored. Meanwhile, the depletion of FFA was monitored by measuring the acid value of the substrate as this is critical in the base-catalyzed transesterification of TG. Examination of the results for the acid values of the substrates before and after 30 min of acid-catalyzed reaction showed that the FFA acid concentration was reduced to less than 0.25 wt.% (0.5 mg KOH/g) in all cases (Table 2). However, the overall transesterification yields after 4 h of reaction confirmed a slow reaction rate and a poor FAME yield for the acid-catalyzed reactions. In general, increases in the concentration of FFA had a negative effect and resulted in a lower rate and yields for the reaction, while increase in the catalyst concentration had the opposite effect. For example, at 1.0 wt.% H_2SO_4 concentration, an increase in the amount of FFA from 1.0 to 6.0 wt.% reduced the 4 h FAME yield from 40 to 22 wt.%. Similarly, increases in the FFA content from 1.0 to 6.0 wt.% at 0.50, 0.75 and 1.25 wt.% H_2SO_4 concentrations decreased the FAME yields from 16 to 13%, 27 to 17% and 53 to 26% wt.%, respectively. The decrease in ester yields as a result of increases in FFA concentration was in accordance with other studies [10]. The reduction in ester yields is attributed to the formation of water as a result of esterification, which strongly inhibits the catalytic activity of H_2SO_4 [8].

Base-Catalyzed Transesterification

Unlike acid catalysts, the base-catalyzed transesterification of TG is exemplified by fast rate of the reaction [21]. The presence of FFA, however, has shown to have detrimental effect on the rate and downstream separation of the reaction products [7]. Experiments were performed to study the time courses of the transesterification of corn oil with 1.0–6.0 wt.% FFA (at 1% intervals) content and at 0.50–1.25 wt.% (at 0.25% intervals) NaOH concentrations. A representative set of results at 0.75 wt.% catalyst concentration is summarized in Fig. 3. The trend lines for the time course of the transesterification reaction in this figure show a well defined correlation between the concentration of FFA in the substrate and the FAME yields. Increases in the substrate's FFA concentration from 1.0 to 6.0 wt.% resulted in the reduction of the FAME yields from 97 to 8 wt.%. This is mainly attributed to the consumption of NaOH by the FFA, formation of soap and consequently, its lack of availability to catalyze the reaction. This behavior correlates well with the stoichiometric ratios between the moles of the available NaOH and the FFA. For example, at 3.0 and 4.0 wt.% FFA concentrations, the utilization of the NaOH by the FFA is expected to be about 70 and 90%, respectively, and practically all the catalyst is expected to be utilized by the FFA at 5 wt.% + FFA concentrations. Similar trends were observed at catalyst concentrations of 0.5, 1.0, and 1.25 wt.%. This behavior was consistent with the literature findings [7]. The treatment of high FFA oils with NaOH and the formation of soap are also problematic in the downstream processing of the products, as the formed soap tends to prohibit the separation of FAME and glycerol phases and also decreases the catalytic activity [7, 22]. Experimental results confirmed this occurrence as the concentration of FFA was increased beyond 1.0 wt.%.

Table 2 Acid values for the samples after the completion of the acid-catalyzed esterification with 0.5% sulfuric acid and after passing through DOWEX LCNG OH^- resin

Wt.% FFA or sample name	Before esterification (mg of KOH/g)	After acid-catalyzed esterification (mg of KOH/g)	After acid-catalyzed esterification and ion exchange neutralization (mg of KOH/g)
1	2.3 ± 0.4	0.2	0
2	3.8 ± 0.3	0.2	0
3	6.1 ± 0.5	0.3	0
4	8.4 ± 0.1	0.4	Traces
5	9.9 ± 0.3	0.5	Traces
6	12.2 ± 0.2	0.5	Traces
7	15.2 ± 0.4	0.4	Traces
8	19.0 ± 0.5	0.5	Traces
DDG	17.4 ± 0.4	0.4	Traces
WS	18.8 ± 0.5	0.4	Traces
CDS	19.1 ± 0.6	0.5	Traces

WS whole stillage, *DDG* dried distillers' grains, *CDS* condensed distillers solubles

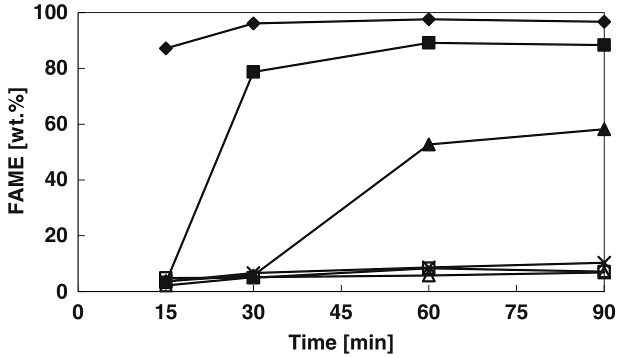

Fig. 3 Effect of FFA and reaction time on the formation of FAME with 0.75 wt.% NaOH and 1:8 oil to alcohol molar ratio; (*filled diamonds*) 1% FFA, (*filled squares*) 2% FFA, (*filled triangles*) 3% FFA, (*multiplication symbols*) 4% FFA, (*open triangles*) 5% FFA, (*open squares*) 6% FFA

Acid–Base Catalyzed Transesterification with Base Neutralization

Experimental results presented earlier for the acid- and base-catalyzed transesterification of a corn oil with up to 6.0 wt.% FFA suggest that a two step acid–base scheme as a realistic approach for achieving high conversion of the substrate into FAME at a relatively fast reaction rate. In this scheme, the high FFA substrate is first subjected to an acid-catalyzed reaction where the level of FFA in the substrate is reduced to less than 0.25 wt.% (0.5 mg KOH/g) and is suitable for the base-catalyzed reaction (Table 2). The procedures described earlier in the methods section were followed. Corn oil with 1.0– 6.0 wt.% FFA and actual corn oil extracted from CDS were examined. The concentration of the H_2SO_4 was 0.5 wt.% and the NaOH was at 0.25 and 1.0 wt.%. Results for the substrates' acid values summarized in Table 2 show that the acid-catalyzed step was effective in the esterification of the FFA when the FFA concentration was lowered to less than 0.25 wt.% in all cases. The overall results presented in Figs. 4 and 5 suggest that an increase in the concentration of FFA in the substrate resulted in a decrease in the yield of FAME. This trend was more distinct at 0.25 wt.% NaOH compared to at 1.0 wt.% NaOH level. The formation of FAME was decreased from 90 to 25 wt.% at 0.25 wt.% NaOH compared to a decrease from 95 to 80 wt.% at 1.0 wt.% NaOH concentration (Figs. 4, 5). The lower yield of FAME at the lower NaOH concentration was expected as a fraction of NaOH is consumed by the residual FFA in the substrate (Table 2) which makes the availability of the catalyst for the transesterification reaction more limited. The reaction results for the actual oil extracted from the CDS were similar to the model oil samples at 7.0 wt.% FFA concentration (Figs. 4, 5).

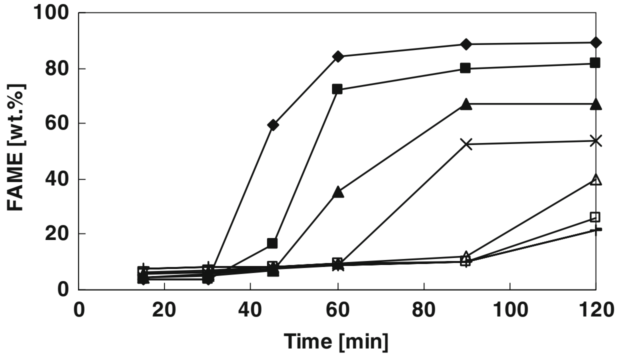

Fig. 4 Effect of FFA on the formation of FAME with 0.5 wt.% H_2SO_4 for 30 min followed by 0.25 wt.% nominal NaOH for 90 min; (*filled diamonds*) 1% FFA, (*filled squares*) 2% FFA, (*filled triangles*) 3% FFA, (*multiplication symbols*) 4% FFA, (*open triangles*) 5% FFA, (*open squares*) 6% FFA, (*plus symbols*) 7% FFA, (*minus symbols*) oil extracted from CDS

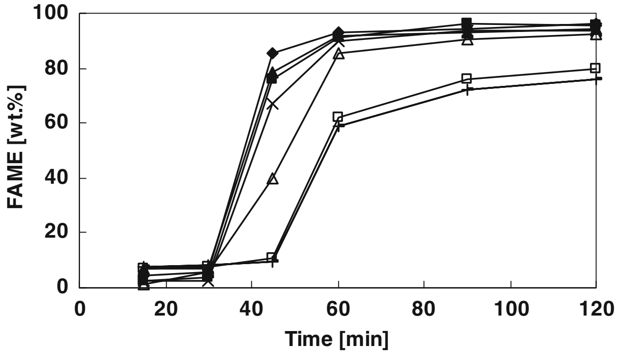

Fig. 5 Effect of FFA on the formation of FAME with 0.5 wt.% H_2SO_4 for 30 min followed by 1.0 wt.% nominal NaOH for 90 min; (*filled diamonds*) 1% FFA, (*filled squares*) 2% FFA, (*filled triangles*) 3% FFA, (*multiplication symbols*) 4% FFA, (*open triangles*) 5% FFA, (*open squares*) 6% FFA, (*plus symbols*) 7% FFA, (*minus symbols*) oil extracted from CDS

In all cases studied, the acid–base catalyzed scheme resulted in little or no separation of FAME and the glycerol products. The inability of the product phases to separate is believed to be caused by the presence of emulsifying compound(s) and water [7, 22]. While efforts were made by means of gravity settling to separate the formed water due to the esterification of FFA, no appreciable amount of water was separated in this manner. The formation of emulsifying compounds may be the result of: (1) the formation of soap due to the presence of the residual FFA in the substrate after the completion of the acid catalyzed reaction and the neutralization of the substrate (Table 2), and (2) the presence of MG and DG which are the intermediated during the stepwise transesterification of TG and are present particularly during the earlier stages of the reaction. The formation of soap and possibly MG and DG along with the presence of water is believed to have caused difficulties in the separation of the transesterification products.

Acid–Base Catalyzed Transesterification with Ion Exchange Neutralization

An alternative acid–base catalyzed scheme was examined which made use of strong anion exchange resins to neutralize the substrate after the initial acid-catalyzed stage. This scheme is believed to be effective in removing the acid catalyst as well as the residual FFA and will eliminate potential formation of soap and aid in the separation of the transesterification products. Experiments were performed to study the time course of the transesterification of corn oil with 5.0, 6.0 and 7.0 wt.% FFA and actual corn oil extracted from CDS at 0.5 wt.% H_2SO_4 for 30 min. This was followed by passing the reaction mixture through an ion exchange column. Two strong anion exchange resins (Dowex SBR LCNG OH^- and Dowex 21 K XLT Cl^-) were investigated. As the results for the substrates' acid values indicate (Table 2), Dowex SBR LCNG OH^- resin effectively removed the H_2SO_4 catalyst as well as the residual FFA. For the samples with less than 3.0 wt.% FFA, the acid values were zero after they were passed through the resins. All other samples showed only traces of FFA (<0.03 mg KOH/g). Similar results were obtained with Dowex 21 K XLT Cl^- resin. The base-catalyzed transesterification was then carried with a practically FFA-free substrate at 0.50 wt.% NaOH for 1 h. The transesterification results for the 7.0 wt.% FFA corn oil and the corn oil extracted from CDS, which were neutralized with Dowex SBR LCNC OH^-, are presented in Fig. 6. As is shown in this figure, yields of FAME in excess of 98 wt.% were achieved with both substrates. Similar results were obtained at lower FFA concentrations with Dowex SBR LCNC OH^-, and also with the Dowex 21 K XLT Cl^- resins.

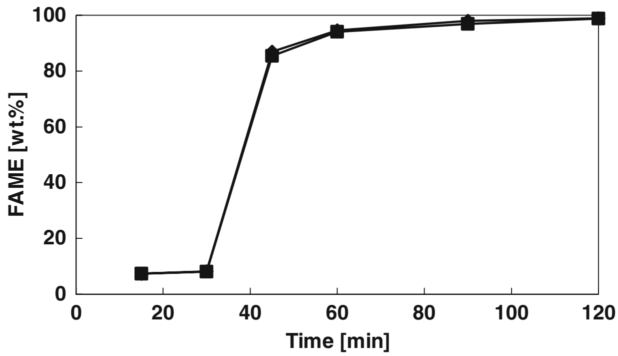

Fig. 6 Formation of FAME with 0.5 wt.% H_2SO_4 for 30 min, removal of acid with Dowex SBR LCNG OH^- resin followed by 0.50 wt.% NaOH for 60 min; (*filled diamonds*) 7% FFA, (*filled squares*) oil extracted from CDS

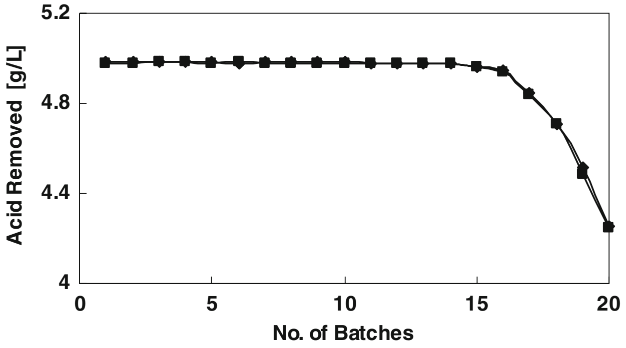

Fig. 7 Breakthrough curve for Dowex SBR LCNC OH^- anion exchange resin; (*filled diamonds*) Dowex SBR LCNG resin, (*filled squares*) Dowex SBR LCNG resin regenerated with NaOH

Experiments were performed to measure the ionic capacity of the resins used for the neutralization of the acid-catalyzed reactions and the potential for the regeneration of the spent resin. The capacity of the resin was measured by constructing a breakthrough curve for the column of resin which was described earlier in the procedures. The column was subjected to consecutive batches of acid-catalyzed substrates (40 g each). The resulting breakthrough curve for Dowex SBR LCNC OH^- is presented in Fig. 7. As this figure shows, resins' exchange capacity remained constant for 14 batches, where, slightly over 0.20 g equivalent of H_2SO_4 was removed from each batch (5.0 g H_2SO_4/L). Based on the fact that 0.20 g of H_2SO_4 was used in each batch (0.50 wt.%), the excess amount over this figure is attributed to the removal of the residual FFA by the resin. This amount correlated well with the expected remnants of FFA as measured by the acid value numbers after the acid-catalyzed reactions. Further uses beyond 14 batches resulted in incomplete removal of the hydrogen ions and about 10% loss of activity was recorded after 20 batches. At this point, the resins were considered spent and were regenerated with their respective cationic solutions as described earlier in the procedures section. As Fig. 7 shows, the regenerated resin performance matched the performance of the fresh resin.

Acknowledgments The authors express their gratitude to the Nebraska Center for Energy Science Research for their support of this work.

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