

Variables affecting homogeneous acid catalyst recoverability and reuse after esterification of concentrated omega-9 polyunsaturated fatty acids in vegetable oil triglycerides

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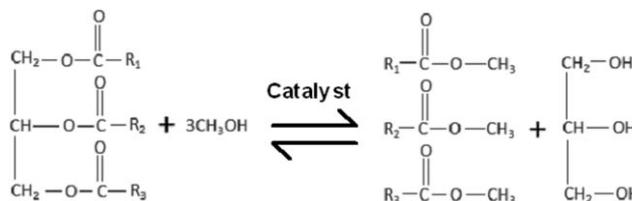
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Global concerns regarding greenhouse gas emissions combined with soaring oil prices have driven the search for renewable diesel fuels derived from either virgin or waste vegetable oils, dubbed “bio-diesels”. A key challenge in the emerging bio-diesel industry is cost-effective pre-treatment of waste vegetable oils to reduce free-fatty acid content prior to transesterification. This article reports, for the first time, recoverability and reusability of hydrochloric and sulfuric acid catalysts for efficient pre-treatment of waste cooking oils for subsequent conversion to bio-diesels. Esterification of omega-9 polyunsaturated fatty acids, particularly 18:2,18:3 linoleic acid with methanol and a homogenous acid catalyst was investigated over a range of fatty acid concentrations. It was determined that greater than 95% by weight of each catalyst was recovered after esterification under all conditions investigated. When recovered methanol was used, containing recovered catalyst and water, it was determined that hydrochloric acid catalyzed esterification exhibits a higher tolerance to water accumulation. After sulfuric acid was recovered and re-used, the observed rate constant decreased more than 50% to a value comparable to that observed for hydrochloric acid at more than three times the water concentration.

Introduction

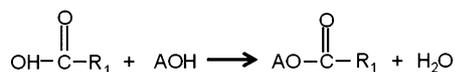
Biomass-derived diesel fuels, termed bio-diesels, can replace petroleum-based diesel fuels with minimum modifications to existing diesel engines, oil heating systems and fuels infrastructure. Biodiesel is non-toxic and biodegradable resulting in less harmful emissions.^{1–8} Biodiesel is currently produced *via* transesterification of triglycerides (TG) with an alcohol, preferably methanol due to its favorable kinetics.^{9,10} The global transesterification mechanism of TG encompasses three sequential reversible reactions wherein triglycerides (TG) react to form diglycerides (DG), monoglycerides (MG) and final product glycerol (G); the overall reaction is presented in Scheme 1 below.

The source of triglycerides for biodiesel production can range from virgin vegetable oils to waste cooking oils, animal fats, and soapstocks.^{9–14} Due to high prices of virgin vegetable oils there is an interest in diversifying feedstock for biodiesel production. Waste cooking oils and animal fats can be used to produce biodiesel; however, they can contain a considerable amount of free fatty acid (FFA).^{9–14} The chemical structure of FFA is simply a hydrocarbon chain (C14–C22, 1–3 double bonds),



Scheme 1 Transesterification.

extending from the carboxylic acid group. In base catalyzed transesterification of vegetable oils, FFA will react with the base catalyst *via* reaction shown in Scheme 2 to form soap. Soap formation can cause considerable loss in yield during biodiesel purification steps by emulsion.^{15–17}



Scheme 2 Soap formation.

Additionally, the acid value or acid content of biodiesel must meet specifications denoted by ASTM method 644–04 in order to be considered ASTM quality. Any considerable amount of FFA will prevent biodiesel from meeting ASTM standards.¹⁸

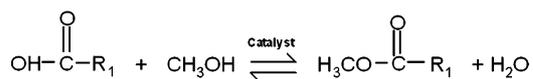
In the interest of producing biodiesel, free fatty acids can be removed from waste cooking oils and animal fats *via* esterification with methanol and catalyst shown in Scheme 3.

Both homogeneous and heterogeneous catalysts have been used for esterification of free fatty acids.^{19–23} Homogeneous acids

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Scheme 3 Esterification.

such as sulfuric acid, hydrochloric acid, nitric acid, and several others can be used to catalyze esterification.^{19,20,24}

When using a homogenous acid catalyst for the esterification of FFA in the presence of triglycerides, the catalyst can be recovered in the methanol layer and re-used. Several variables, however, may affect the recoverability and re-use of the catalyst. For example, if transesterification of triglycerides takes place simultaneously during esterification of FFA, a glycerol layer can form and may result in the loss of the acid catalyst. A study by Goff *et al.*²⁴ reported acid catalyzed transesterification when sulfuric acid was used as a catalyst, however when other acids were used a glycerol layer was not formed; there was no report, however, of how much catalyst was recovered.

In previous reports, the important engineering questions of catalyst recoverability and reusability were not adequately addressed. Most critically, the presence of water, which is a product of esterification, can have an effect on catalyst activity and reaction equilibrium for future use. There have been several studies which note the effect of water on transesterification of vegetable oils;^{24–30} however, there is limited data for effect of water on acid catalyzed esterification of FFA's with methanol in the presence of vegetable oil triglycerides. Liu *et al.*²⁵ investigated the effect of water on sulfuric acid catalyzed esterification of acetic acid. Liu *et al.* report that there is a decrease in initial reaction kinetics with an increase in initial water concentration, and that the loss in strength of catalytic protons is due to water solvation.

The present study compares sulfuric acid and hydrochloric acid as catalysts for the esterification of linoleic acid with methanol in the presence of soybean oil triglycerides. Catalyst recoverability after esterification was investigated at several different initial concentrations of linoleic acid in soybean oil. The effect of water, as a product of esterification, was investigated by re-using the recovered methanol layer for esterification of linoleic acid in the presence of soybean oil. The affect of accumulating water in the methanol layer was further investigated by repeating experiments and changing initial water concentrations.

Experimental

Temperature was held constant at 70 °C for all experiments. Linoleic acid concentrations ranged from 2–15 wt% of the initial soybean oil-fatty acid mixture. Acid catalyst concentration was held constant at 1 wt% of soybean oil triglycerides, and initial methanol concentration was approximately a 6:1 molar ratio with respect to soybean triglycerides. Table 1 provides the six formulations used, where 400 g of soy oil were used in each case.

Reactions were carried out in a 1 L three-neck round bottom flask with a water-cooled reflux condenser to minimize methanol losses. The flask was submerged in a water bath placed on a temperature-controlled magnetic stirring hotplate (Fisher Scientific). The reaction temperature was monitored by thermocouple as well as mercury thermometer, and held within ± 1 °C. Agitation was provided by a magnetic stirrer (1.5 in. \times

Table 1 Initial conditions of six experimental formulations

Experiment #	Acid Catalyst	Vol. of Acid soln. (mL)	Wt. Linoleic Acid (g)
1	H ₂ SO ₄ (97%)	2.25	8.20
2	H ₂ SO ₄ (97%)	2.25	21.0
3	H ₂ SO ₄ (97%)	2.25	70.8
4	HCl (36%)	9.15	8.20
5	HCl (36%)	9.15	21.0
6	HCl (36%)	9.15	70.8

0.75 in. diameter) at 700 RPM. Experiment 5 was repeated at 800 rpm and the initial rate of disappearance of linoleic acid was compared to the same experiment conducted at 700 rpm to verify that the mixing was sufficient to prevent bulk mass transfer limitations.

Virgin soybean oil (400 grams of Whole Harvest's 100% Soy Product) was loaded into the reaction flask and heated to 70 °C. The desired amount of Linoleic acid (Acros Organics, 60%, Tech grade (32% Oleic acid, 8% saturated C:18 fatty acid)) was measured separately and added to the reaction flask. Methanol (111 \pm 0.5 mL of (99.9% HPLC grade, Fischer Scientific)) was measured into a separate 250 mL flask. The amount of added methanol was calculated to correspond exactly to a 6:1 molar ratio of Methanol:TG for the case of pure triolein (MW 885 g/mol). However, since the molecular weight of Soybean TG is typically reported in the range of 860 to 880 g/mol,^{30,31} the actual molar ratio employed in all the experiments below is more accurately 5.95:1. The methanol:Linoleic acid molar ratios were 93.7, 36.6, and 10.86 for FFA levels of 2, 5, and 15 wt%, respectively. Concentrated acid catalyst solution was added to the 250 mL flask using a graduated pipette and mixed with the methanol. Both reagent grade hydrochloric acid (12 Molar- 36%) and sulfuric acid (18 Molar- 97%) were used as catalysts for each experiment. The acid solution volume was adjusted to add acid at 1 wt% of the Soybean TG, or 4 \pm 0.1 g.

Ten (10) mL samples were withdrawn periodically and immediately quenched in an ice bath for 5 minutes. Samples were then centrifuged (Thermo Electron Corp. model HN SII) at 4000 rpm for 2 minutes. After centrifugation the methanol layer was removed from the sample in a 250 mL separatory funnel and discarded. To remove any residual methanol and acid, the oil phase was washed with distilled water in a 250 mL separatory funnel by adding 50 mL of distilled (DI) water, shaking vigorously, and allowing to settle for 5 minutes. After settling the water layer was discarded and the sample was centrifuged again for 2 minutes at 4000 rpm to remove residual water.

The samples were prepared for gas chromatography following ASTM 6584–00 method for analysis of free and total glycerine content in biodiesel.³² The derivatized solution was injected (1 μ l) into a Hewlett-Packard 5890 Series II Gas Chromatograph equipped with Quadrex Aluminum Clad column with 1 meter retention gap and employing a flame ionization detector to determine fatty acid methyl-ester, glycerol and glyceride (tri-, di-, mono-) concentrations. Computer-assisted analysis of resulting chromatograms was performed using Chem-Station software (Hewlett-Packard, now Agilent Technologies). Samples were also prepared for titration following ASTM method D664–00 for acid number of biodiesel samples.¹⁸ After allowing the diluted

sample to mix for one minute, titrant was added drop by drop until the permanent light pink endpoint was reached.

Recoverability experiments

Experiments 1–6 were repeated in order to investigate the recoverability of the unreacted methanol and acid catalyst. Recoverability experiments were conducted as described above but no samples were withdrawn. The reactants were mixed at 70 °C for the period of time required for the concentration of linoleic acid to reach approximately 0.2 wt%, with the time estimated from the results of experiments 1–6. After stopping agitation, the reaction flask was placed in an ice bath where the phases were allowed to separate for 2 hours. The oil phase was decanted using a 1 L separatory funnel. A sample of the oil phase was washed and prepared for titration as previously described.

The recovered methanol layer was decanted into a 100 mL graduated cylinder to measure its volume. The recovered methanol phase was prepared for titration as 10% (by volume) aqueous methanol solutions, where 10 mL of the recovered methanol layer was added to 90 mL of DI water in a 100 mL graduated cylinder. Titrant was made by dissolving 44 grams of potassium hydroxide pellets (87.9%, JT Baker) in 392 mL of DI water to make a 1.74 M KOH solution. Titrant was added drop by drop until the phenolphthalein endpoint was reached.

Reusability experiments

For the initial condition of 5% linoleic acid (experiments 2 and 5), the recovered methanol layer containing the recovered acid catalyst and water, was re-used with a new mixture of 5% linoleic acid in 400 g of soybean oil triglycerides. Due to loss of methanol by consumption, partitioning, and small amounts of evaporation, a small amount of fresh methanol was added to match the volume of methanol initially used, 111 mL. No water was removed from the recovered methanol. Samples were withdrawn periodically and treated as previously described.

To investigate multiple re-use of the methanol and acid where further accumulation of water in the methanol layer is expected, experiments 2 and 5 were also repeated adding different concentrations of DI water to the methanol and acid before the reaction. Samples were drawn periodically and treated as previously described.

Results and discussion

In experiments 1–6, samples were monitored for FFA, bound glycerine (MG, DG, TG) and free glycerine (G). Fig. 1 shows a typical data set, specifically from experiment 2 at the initial condition of 5 wt% initial linoleic acid with sulfuric acid catalyst.

Reproducibility was verified by repeating several of the experiments, and the measured values of the chemical composition remained within 5% of initial measurements in all cases. As shown in Fig. 1, there was significant conversion of FFA to methyl ester. Transesterification of soybean triglycerides did not nearly reach completion; however, there was notable conversion of triglycerides to diglycerides and methyl ester. The majority of transesterification took place after esterification already had reached equilibrium. It was noted that conversion of TG → DG was less than 5% for all of experiments 1–6 before the

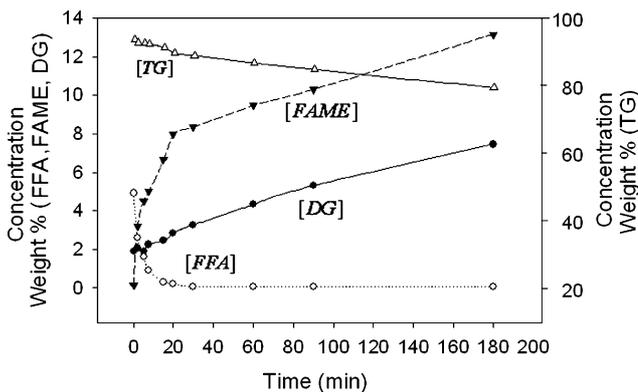


Fig. 1 Representative data collection for experiment 2. Note that since negligible amounts of monoglyceride and glycerol were present, they do not appear in the figure. (○) Linoleic Acid [FFA]; (▲) Methyl ester [FAME]; (●) Diglyceride [DG]; (△) Triglyceride [TG].

concentration of FFA reached 0.2 wt%. Fig. 2(a) shows the concentration of linoleic acid with time, using H₂SO₄ as the catalyst, at different initial concentrations of linoleic acid. Fig. 2(b) displays the equivalent plot using HCl as a catalyst.

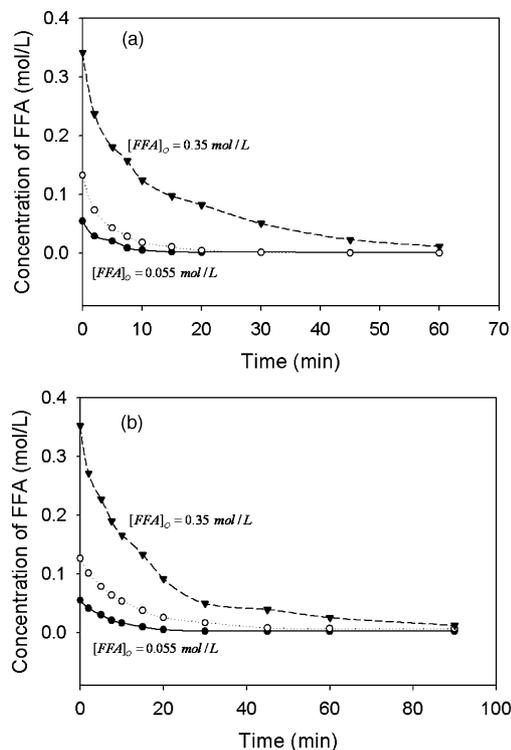


Fig. 2 FFA concentration vs. time at different initial linoleic acid concentrations, (▲) [FFA]₀ = 0.35 mol/L; (○) [FFA]₀ = 0.13 mol/L; (●) [FFA]₀ = 0.055 mol/L. (a) Acid catalyst H₂SO₄. (b) Acid catalyst HCl.

Catalyst recoverability

Recoverability of each acid was determined by repeating experiments 1–6, but withdrawing no samples. Experiments were allowed to run until the concentration of linoleic acid reached 0.2 wt% for experiments 1, 2, 4 and 5, and 0.5 wt% for experiments 3 and 6. After rapidly cooling the final reaction

mixture, it was allowed to separate for two hours, after which each phase was titrated as previously described. After settling, the observed phases were a methanol rich phase containing water and acid catalyst, and an oil rich phase. Slight differences were observed after decanting; a lighter yellow color was observed after esterification of 15 wt% FFA in Soybean Oil with H₂SO₄, and a darker orange after using HCl; also observed by Goff *et al.*²⁴ The dark orange color was not observed when initial FFA concentration was 5 wt% or less.

The concentration of sulfuric acid in the aqueous layer was calculated using an equation provided from a study conducted by Evans *et al.*³³ on the electrolytic dissociation of sulfuric acid in aqueous methanol. The dissociation of sulfuric acid in water (R1–R2) is shown below.



Evans and co-workers reported a strong effect on the dissociation constant of sulfuric acid in 10–20% aqueous methanol. The equation used to calculate the second dissociation constant (K_2), as reported by Evans *et al.*³³ is shown below.

$$\text{p}K_2 = 1.669 + 0.0336m + 0.0126T \text{ (}^\circ\text{C)} \quad (1)$$

In equation (1), m is the volume% of methanol in the aqueous solution and T is the temperature of the solution during titration. It was assumed that the first dissociation for sulfuric acid is in effect infinity and goes to completion. The resulting mol balance for the titration is shown in equation (2) below.

$$n_{\text{OH}^-, \text{ added}} = (2n_{\text{SO}_4^{2-}} + n_{\text{HSO}_4^-})_{\text{in solution}} \quad (2)$$

In equation (2), n represents number of moles. The equilibrium equation for the second dissociation is shown below.

$$K_2 = \frac{[\text{H}_3\text{O}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]} \quad (3)$$

Between equations (2) and (3) there are two unknowns, $[\text{HSO}_4^-]$ and $[\text{SO}_4^{2-}]$ in the sample, which can be solved for using the system of two equations. Table 2 summarizes the results from the recoverability experiments.

In order to examine reusability of each catalyst, experiments 2 and 5 were repeated and the methanol layer was recovered after 2 hours of decanting. Methanol was added to the aqueous

layer in order to make up for methanol consumed by reaction and methanol lost by partitioning in the oil phase and small amounts of evaporation loss. It was assumed that all water produced by esterification ended up in the methanol layer. The methanol/acid/water mixture was then re-used to treat the same amount of linoleic acid as the first run (5 wt% linoleic acid in 400 g Soybean Oil). To investigate further accumulation of water in the methanol layer, experiments 2 and 5 were also repeated adding different concentrations of DI water to the methanol and acid before the reaction. Samples were drawn periodically and treated as previously described.

Fig. 3(a) displays the concentration of linoleic acid with time for esterification catalyzed by H₂SO₄ for the initial run compared to its re-use and experiments with increased initial

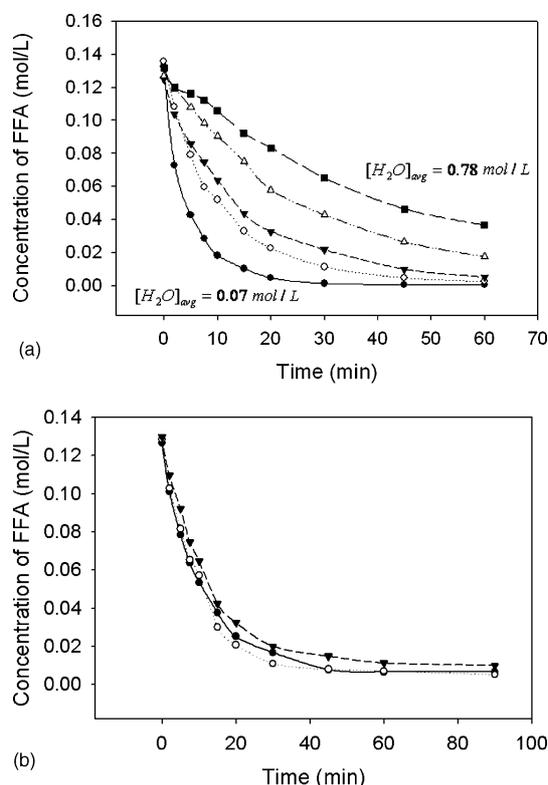


Fig. 3 FFA concentration vs. time with $[\text{FFA}]_0 = 0.13 \text{ mol/L}$ for various water concentrations. (a) Acid catalyst H₂SO₄: (●) Initial run $[\text{H}_2\text{O}]_{\text{avg}} = 0.07 \text{ mol/L}$; (○) Re-use $[\text{H}_2\text{O}]_{\text{avg}} = 0.20 \text{ mol/L}$; (▲) $[\text{H}_2\text{O}]_{\text{avg}} = 0.33 \text{ mol/L}$; (△) $[\text{H}_2\text{O}]_{\text{avg}} = 0.52 \text{ mol/L}$; (■) $[\text{H}_2\text{O}]_{\text{avg}} = 0.78 \text{ mol/L}$. (b): Acid catalyst HCl: (●) Initial run $[\text{H}_2\text{O}]_{\text{avg}} = 0.60 \text{ mol/L}$; (○) Re-use $[\text{H}_2\text{O}]_{\text{avg}} = 0.75 \text{ mol/L}$; (▲) $[\text{H}_2\text{O}]_{\text{avg}} = 0.90 \text{ mol/L}$.

Table 2 Summary of recoverability experiment results

Catalyst	Initial FFA Concentration (mol/L)	Rxn Time (min)	%FFA Final	Catalyst Recovered (g)	Volume of Methanol Layer Recovered (mL)
H ₂ SO ₄ (97%)	0.055	10	0.18	3.92	82
H ₂ SO ₄ (97%) ^a	0.13	20	0.19 ± 0.05	3.86 ± 0.04	74 ± 1
H ₂ SO ₄ (97%)	0.35	60	0.48	3.75	66
HCl (36%)	0.055	20	0.19	3.96	93
HCl (36%) ^a	0.13	60	0.23 ± 0.04	3.97 ± 0.02	84 ± 1
HCl (36%)	0.35	90	0.53	3.86	81

^a Results are an average of 3 repeated experiments.

water concentration; Fig. 3(b) is a similar plot for experiments where HCl was used for the catalyst. Because water is being continuously produced by esterification, water concentrations are denoted as average water concentration throughout the experiment.

The effect of water, accumulated in the methanol phase during esterification, on the re-use of the catalyst and methanol was determined by comparing the observed rate constant between runs. The rate expression employed was a second order, elementary, reversible relationship shown in equation (4).

$$r_{\text{FFA}} = \{r_{\text{FFA}}[\text{A}]\}[\text{FFA}][\text{MeOH}] - \{k_{\text{FFA}}[\text{A}]\}[\text{FAME}][\text{H}_2\text{O}] \quad (4)$$

In equation (4), [A] is the concentration of the acid catalyst; because the catalyst is not consumed during the reaction [A] is a constant and can be combined with the rate constant k_{FFA} . Equation (4) can be written in terms of FFA conversion, where the equation for conversion is given below.

$$x = \frac{[\text{FFA}]_0 - [\text{FFA}]}{[\text{FFA}]_0} \quad (5)$$

Combining equations (4) and (5) the rate expression can be written in terms of FFA conversion. Due to a large molar excess of methanol, the concentration of methanol is assumed to be constant at its initial concentration. Reverse hydrolysis can be neglected, as suggested by Liu *et al.*,²⁵ yielding the rate expression below.

$$\frac{dx}{dt} = \{k_{\text{FFA}}[\text{A}]\}(1-x)(\mathcal{R}-x) \quad (6)$$

In equation (6) \mathcal{R} is the ratio of the initial methanol concentration to the initial FFA concentration, ($[\text{MeOH}]_0/[\text{FFA}]_0$). Integrating equation (6) from $t = 0$ to t and substituting $k_{\text{FFA}}[\text{A}] = k_1$, the following expression can be used to linearize initial FFA concentration data in order to yield a rate constant from the slope.

$$\ln\left(\frac{\mathcal{R}-x}{1-x}\right) - \ln(\mathcal{R}) = k_1[\text{FFA}]_0 t \quad (7)$$

Fig. 4(a) displays the linearization of the initial FFA conversion data when H_2SO_4 was used for a catalyst and the initial concentration of FFA was 5 wt%; individual data sets are at different initial water concentrations. Fig. 4(b) shows the equivalent plot where HCl was used as the catalyst.

Using best fit slopes from Fig. 4(a) and (b), a rate constant was derived, and the effect of average water concentration on the observed rate constant was examined. Fig. 5 shows the affect of water concentration on the observed rate constant for both catalysts. Because HCl was purchased as a 36% aqueous solution, the first data point is at a relatively high water concentration of 0.60 mol/L.

The sensitivity of H_2SO_4 to water displayed in Fig. 5 is in contrast to the lack of sensitivity noted by Kusdiana and Saka.³⁴ The differences in the results illustrated here compared to those previous results is easily explained because Kusdiana and Saka allowed their system 48 hours to react and measured total conversion rather than just conversion of free fatty acid. Perhaps they were observing equilibrium conversions rather than initial free fatty acid reaction rates as illustrated above.

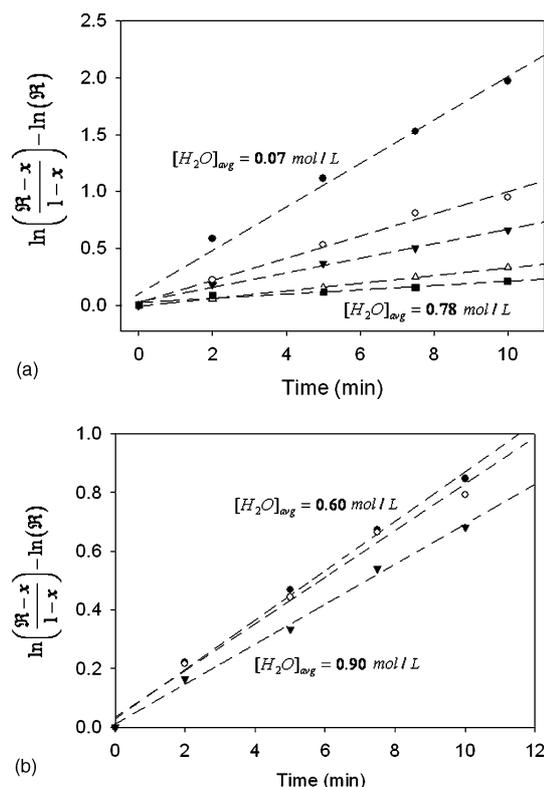


Fig. 4 The initial rate of FFA consumption plotted according to equation (7) with $[\text{FFA}]_0 = 0.13$ mol/L for various water concentrations. (a) Acid catalyst H_2SO_4 : (●) Initial run $[\text{H}_2\text{O}]_{\text{avg}} = 0.07$ mol/L; (○) Re-use $[\text{H}_2\text{O}]_{\text{avg}} = 0.20$ mol/L; (▲) $[\text{H}_2\text{O}]_{\text{avg}} = 0.33$ mol/L; (△) $[\text{H}_2\text{O}]_{\text{avg}} = 0.52$ mol/L; (■) $[\text{H}_2\text{O}]_{\text{avg}} = 0.78$ mol/L. (b) Acid catalyst HCl: (●) Initial run $[\text{H}_2\text{O}]_{\text{avg}} = 0.60$ mol/L; (○) Re-use $[\text{H}_2\text{O}]_{\text{avg}} = 0.75$ mol/L; (▲) $[\text{H}_2\text{O}]_{\text{avg}} = 0.90$ mol/L.

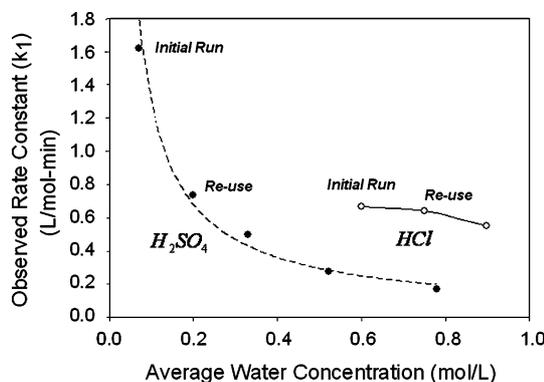


Fig. 5 The esterification rate constant k_1 vs. water concentration at 70 °C: (●) H_2SO_4 (○) HCl.

The experiments above were conducted with HCl and H_2SO_4 levels that range from 11 wt% to 50 wt% with respect to the FFA. Those levels, which correspond to 1 wt% with respect to the soybean triglycerides, are quite high for homogeneous catalysis of FFA. Note, however, that the chemical system of reactions is quite complex as the HCl and H_2SO_4 slowly catalyze the transesterification of the triglycerides as well as more rapidly catalyze the esterification of the free fatty acids.

Several additional experiments were therefore conducted at lower HCl and H_2SO_4 levels. Experiments 2 and 5 (Table 1)

contained 5 wt% FFA relative to triglycerides and 20 wt% acid catalyst relative to the FFA. Additional experiments were conducted with 5 wt% FFA and with acid catalyst levels of 2, 4, and 10 wt% with respect to FFA in order to verify that the results depicted above for FFA are not simply due to an overabundance of acid catalyst. Various amounts of water were added to the reaction mixtures for comparison with the results above.

Just as above, HCl activity was less sensitive to the water than H₂SO₄ activity, but the formulations using low levels of catalyst converted FFA too slowly for industrial needs. For example, the mixture containing 2 wt% H₂SO₄ (wrt FFA) and roughly 0.5 wt% water reduced the FFA from 5 wt% to 1.8 wt% after 90 minutes, whereas at 20 wt% H₂SO₄ (wrt FFA) the FFA was reduced from 5 wt% to 1.8 wt% in less than 5 minutes. The mixture containing 2 wt% HCl and 0.5 wt% water reduced the FFA from 5 wt% to 1.8 wt% in roughly 30 minutes and to 0.3 wt% in 90 minutes, about 1/3 the conversion rate of the case with 20 wt% HCl.

A final comparison between HCl and H₂SO₄ is worth noting in that an experiment was conducted where the number of moles of HCl and H₂SO₄ was matched. At 4 wt% HCl and 10 wt% H₂SO₄, the number of moles is the same due to differences in molecular weight. Using a water content of approximately 2 wt%, the experiment with HCl reduced the FFA content from 5 wt% to roughly 2.2 wt% in 30 minutes, while the experiment with H₂SO₄ reduced the FFA content from 5 wt% to roughly 2.9 wt% in 30 minutes. Thus, we observe that if significant levels of water reside in the mixture, HCl may be more effective than H₂SO₄, and high levels of acid may be used since recovery and recycle are quite straightforward.

Conclusion

Increasing interest has been invested in renewable, environmentally benign alternative fuels due to greenhouse gas emissions and towering oil prices. Biodiesel is renewable, and an immediate replacement for petroleum diesel. A key challenge in economically efficient biodiesel production is the utilization of waste cooking oils and animal fats with high concentrations of free fatty acids. Homogenous acid catalysts have been employed for the esterification of FFA for treatment of waste oils, however in many cases they are not recovered and re-used.

In biodiesel production, it is important to limit waste streams and recover important reactants. After acid catalyzed esterification of free fatty acids in the presence of triglycerides, methanol can be recovered simply by phase separation. The re-use of catalyst can be limited by the formation of a glycerol layer and its tolerance to accumulating water produced by esterification in the methanol layer.

Within the range of conditions investigated in this study it was determined that transesterification is negligible when either sulfuric acid or hydrochloric acid are used to catalyze the esterification of polyunsaturated 18:2,18:3 linoleic acid in the presence of soybean oil triglycerides. Greater than 95% by weight of the catalyst was recovered in the methanol layer under all conditions investigated.

It was found that HCl exhibits a higher tolerance for accumulating water in the methanol layer. After H₂SO₄ was

recovered and re-used, the observed rate constant decreased more than 50% to a value comparable to that observed for HCl at more than three times the water concentration.

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