

APPLICATIONS OF HIGHLY CROSS LINKED
MIXED BED ION EXCHANGE RESINS
IN BIODIESEL PROCESSING

A Thesis

by

YOUSUF JAMAL

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of
MASTER OF SCIENCE

August 2009

Major Subject: Civil Engineering

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Approved by:

Chair of Committee,	Bryan Boulanger
Committee Members,	Robin Autenrieth
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ABSTRACT

Applications of Highly Cross Linked
Mixed Bed Ion Exchange Resins
in Biodiesel Processing. (August 2009)

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Biofuels are a promising solution to society's quest for sustainable energy. In the transportation sector, biodiesel is the leading alternative diesel fuel currently in use today. However, the current global and domestic production of biodiesel is far below the petro-diesel consumption and demand. To increase the availability of biodiesel in the market, new methods of biodiesel production must be developed to take advantage of the plentiful low quality waste derived feed stocks that currently present problems to biodiesel production using conventional methods. This research presents one new approach based upon using heterogeneous highly cross linked mixed bed solid phase catalysts to facilitate the production of biodiesel from feed stocks with high concentrations of free fatty acids (FFA). The performance of the heterogeneous mixed bed catalysts method developed in this research was evaluated and optimized for catalyst concentration and reaction duration while the mixing rate, reaction temperature, initial FFA composition of the feed stock and the alcohol-to-oil molar ratio were kept constant.

The presented method reduces the FFA content of the starting feed stock while limiting the release of water into the reaction. Through experimentation, it was found that FFA removal with the mixed bed resin is due to ion exchange with the quaternary ammonium functional group and not catalysis to form esters. A model describing the heterogeneous processing

method is presented. The outcome of this research is the development of a new processing method that can be used to create biodiesel from poor quality raw feed stock materials.

DEDICATION

I dedicate my work to my parents for showing trust in me and giving me the chance to gain knowledge and a vision for a successful life despite of my disabilities.

“A theory is something nobody believes, except the person who made it. An experiment is something everybody believes, except the person who made it”. - *Albert Einstein*

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Finally, special thanks to my friends, wife and parents for their patience, prayers, and assistance in raising my morale whenever needed.

NOMENCLATURE

AOCS	American Oil Chemists' Society
ASTM	American Society of Testing Materials
DVB	Divinyl Benzene
FFA	Free Fatty Acid
FAME	Fatty Acid Methyl Ester
MB	Mixed Bed
SO ₃ H	Sulfonic Acid Functional Group
N ⁺ R ₃ ·OH	Quaternary Ammonium Functional Group
NO _x	Oxides of Nitrogen (N ₂ O, NO and NO ₂)
R	Alkyl Group
Stdev	Standard Deviation

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1. INTRODUCTION

1.1. Market Background

Biodiesel is a mixture of long chain fatty acid mono alkyl esters (FAMES) derived from triglyceride and fatty acids. As a commercial product, biodiesel is defined as a fuel grade product that meets the quality standards of ASTM 6751 shown in Table 1. Biodiesel is an alternative energy fuel finding popularity in the US and foreign markets because of its perceived lessened environmental impact compared to conventional diesel fuels [1; 2; 3; 4; 5] scalability to small and large markets[2], direct substitution potential into the existing diesel market[6], and renewability [5].

The properties of biodiesel as an attractive transportation fuel include higher cetane number, flash point, 10-12 % by weight oxygen content and lower sulfur, carbon dioxide, and particulate matter emissions compared to petrodiesel fuel [7; 8; 9]. However, biodiesel shows a slight increase in NOx emissions compared to petrodiesel due to incomplete engine combustion [5; 7]. Biodiesel NOx emissions can be reduced, though, by adding cetane enhancers and altering engine ignition times [10]. Because biodiesel is also biodegradable under aerobic and anaerobic conditions (up to 90%+ degradation within 21-28 days [11; 12]), it may pose less environmental risk when spilled. Mixing biodiesel with petroleum diesel is also an attractive option as the use of this ester blend appears to help degrade petroleum diesel in less time than if petrodiesel is spilled alone [11] .

Globally, 90% of biodiesel production is based in the European Union (EU). While the EU leads global biodiesel production, the biodiesel produced in the EU only accounts for 6% of their total transportation requirement [13].

This thesis follows the style of Fuel.

Table 1. Quality standards of ASTM 6751 for biodiesel. Adopted from [14]

Test	ASTM Standard	Limit	Units
Calcium & Magnesium, combined	EN14538	5 max	ppm, (ug/g)
Flash Point (closed cup)	D 93	93 min	^o C
Alcohol Control (must meet one of the following) Methanol Content	EN14110	0.2% max	% Vol.
Flash Point	D 93	130 min	^o C
Water & Sediment	D 2709	0.050 max	% Vol.
Kinematic Viscosity, 40 ^o C	D 445	1.9 - 6.0	mm ² /sec.
Sulfated Ash	D 874	0.02 max	% mass
Sulfur S 15 Grade	D5453	0.0015 max	% mass
S 500 Grade	D5453	0.05 max	% mass
Copper Strip Corrosion	D130	No. 3 max	
Cetane Number	D 613	47 min	
Cloud Point	D2500	Report	^o C
Carbon Residue, 100% sample	D4530	0.05 max	% mass
Acid Number	D 664	0.50 max	mg KOH/g
Free Glycerin	D 6584	0.020 max	% mass
Total Glycerin	D 6584	0.024 max	% mass
Phosphorus Content	D 4951	0.001 max	% mass
Distillation ,T90 AET	D1160	360 max	^o C
Sodium/Potassium, combined	EN 14538	5 max	ppm, (ug/g)
Oxidation Stability	EN 14112	3 min	Hours
Cold soak filtration	Annex to D6751	360 max	Sec.
For use in temperature below -12 ^o C	Annex to D6751	200 max	Sec.

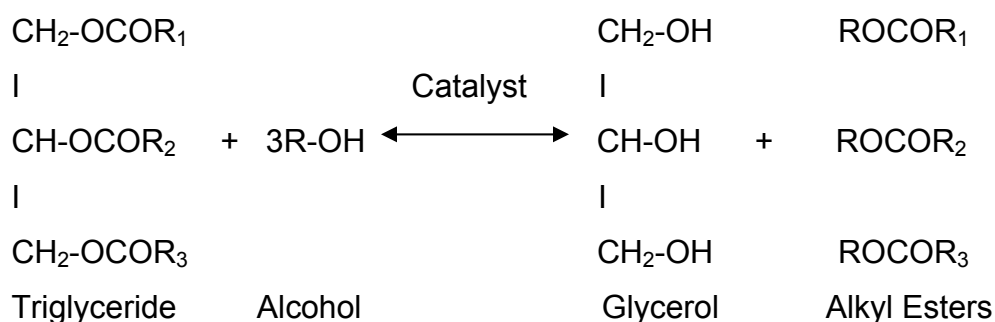
While the use of biodiesel in the US is on the rise, as in Europe, the current rate of US biodiesel supply does not meet existing US diesel demand. The total requirement of transportation diesel fuel in US as of 2007 was 53 billion gallons [15]. Currently, (2007) biodiesel production only generates enough biodiesel to supply 0.67% percent of diesel requirement (358 million gallons). According to the US Energy Information Administration, by 2030 US biodiesel production is expected to rise to 1.2 billion gallons, but that will make up only 1.5 % of projected US diesel demand consumed in 2030 [16]. At the same time, the number of diesel cars in the US is increasing and is expected to reach 11% of the domestic market by 2010 [13]. In order to increase future demand while also increasing the amount of diesel vehicles, the US market is currently attempting to double its biodiesel production.

Today in the US there are 148 biodiesel production facilities. Another 96 facilities are under construction and five production sites are under expansion. This increased capacity is forecasted to boost annual production up to 1.9 billion gallons [17]. The focus of the US biodiesel industry is heavily dependent on soybean oil for biodiesel production [18]. While soybean oil is a high quality feed stock, the raw material is costly to produce and is valued in many other markets. To achieve a globally, more sustainable transportation infrastructure, an investment in biodiesel technology must be realized that moves away from industry's reliance on edible vegetable oils and towards alternatives such as non-edible plant derived oils and/or waste derived feed stocks. This investment must also include an evaluation of new methods for biodiesel production aimed at using low quality feed stock materials to produce high quality biodiesel.

1.2. Biodiesel Production and Feed Stocks

The primary process used to create biodiesel is transesterification. Transesterification reactions produce FAMES through the reaction of

triglyceride-based feed stocks with short chain alcohols in the presence of a catalyst (Figure 1)[7]. The conventional industrial processing of biodiesel relies on transesterification of oil with homogenous (liquid) catalysts in the presence of methanol. Other FAME production methods include thermal cracking, use of microorganisms and in-situ production by lipids solvation [10; 19].



R₁, R₂, R₃ are different alkyl groups

Figure 1. Transesterification reaction. Adopted from [20; 21]

Glycerol is a by-product of transesterification and is used to make pharmaceuticals, soaps, explosives and animal feeds [2]. The conversion of edible vegetable-based oils (triglycerides) to FAMEs through conventional homogeneous transesterification is a well documented, easy to reproduce, and cost effective method for biodiesel production. However, biodiesel can and should also be produced from alternative feed stocks such as rendered animal fats [22], restaurant waste oils [23], grease traps, lipids extracted from wastewater sludge [19; 24], green waste in municipal solid waste, and algae oil [25]. These alternatives are more difficult to process into biodiesel because they

have considerably more impurities, including higher amounts of free fatty acids (FFA) and water.

Use of alternative feed stocks for biodiesel production is of primary interest to biodiesel researchers, because of the challenge associated with their use and production volume scenarios. Even if all edible oils from plant sources produced in the US in 2007 were used for biodiesel production, the estimated amount of biodiesel entering the market would only be 27.14 billion gallons (see estimation calculations in Table 3 in Appendix A) or 51.20 % of petroleum diesel demand in 2007. However, switching all biodiesel production to edible oils is not practical or logical; and even if it were, the resulting production volume is not nearly enough to fulfill petroleum diesel demand [18]. Additionally, use of edible oils for biodiesel production presents problems to the sustainability of biodiesel as an alternative fuel because of the large environmental burdens of chemical agriculture and the use of edible oils as food stuffs. Therefore, use of alternative feed stocks for biodiesel production is required and new methods of production need to be evaluated and initiated.

Many alternative feed stocks are waste streams of significant volume. Oils derived from algae fed the green fraction of municipal solid waste or biosolids, in particular, have the volume of realizable oils that if turned into biodiesel could approach US demand. However, regardless of the alternative feed stock used in the production of biodiesel, significant hurdles prevent attempting to produce biodiesel from high impurity feed stocks using conventional biodiesel methods.

1.3. The Problem with Producing Biodiesel from Low Quality Feed Stocks

The two most significant hurdles associated with producing biodiesel from alternative low quality feed stocks are the feed stock's residual water and high FFA content (greater than 1% by weight). Presence of residual water will

stop transesterification. FFA levels in excess of 1% by weight in the feed will result in saponification in the presence of alkali catalysts. Table 2 shows an estimate of the volume of available low quality feed stocks and their composition. In order to produce biodiesel from these feed stocks, a modified conventional method for biodiesel production has been developed.

Table 2. Quantity and composition of alternative feed stocks.

Alternate Feed	Volume	% Water	FFA level	Potential Biodiesel Yield
Waste water sludge	6.2 million tons (dry solids) annually [19]	Variable 90%-95%	Variable 65% [26]	0.76 billion gallons*
Food scrap fraction of municipal solid waste	12.5% of 251 million ton [27]	Variable 60 to 90% [28]	Variable	3.87 billion gallons*
Rendered Products	4515.6 metric tons [29]	Variable 0.01% to 55.38% [30]	Variable 0.7% to 41.8% [30]	0.61 million gallons*
Algal Oil	32.6 ton per ha [25]	Depend on algae type.	Variable 1.9 to 38%. [31]	659 billion gallons*

*For calculation of yields see Table 4 in Appendix A.

Water produced during esterification within the two step acid-alkali method is removed by gravity separation. This alcohol-water phase is separated from the oil phase and then methanol is recovered for reuse. An equivalent amount of alcohol and catalyst lost due to water is added back into reaction mixture and allowed to react further until the FFA is reduced to below 1% [1].

Once the water and FFA composition of the feed stock and residual water generated during esterification have been removed from the reaction system, the pretreated feed stock consisting entirely of triglycerides can then undergo the second step in the two step conventional method. The pretreated feed stock is then treated with homogenous alkaline catalyst (such as sodium hydroxide or sodium methoxide) in the presence of alcohol to produce high yields of FAMEs through transesterification. As long as the FFA content of the feed stock is less than 1% by weight, transesterification will produce high FAME (biodiesel) yields. Otherwise, soap will form and create a final product that will not separate cleanly, resulting in poor quality biodiesel.

Recently, attention of researchers has focused towards using heterogeneous (solid phase) catalysts instead of homogenous (liquid phase) catalysts for biodiesel production. Heterogeneous catalysts are believed to reduce the amount of pre, intermediate, and post-treatment processing of both edible oils and alternative feed stocks to biodiesel. Because they are not consumed in the reaction as homogeneous catalysts are, there is also the potential for reusing heterogeneous catalysts to decrease the cost of this alternative processing method.

1.4. Use of Heterogeneous Catalysts to Produce Biodiesel

Heterogeneous catalysts have previously been evaluated for esterification and transesterification. The main benefits of moving towards

heterogeneous catalysts to produce biodiesel include non-dissolution of the catalyst in FAMEs, less water and wastewater generation, catalyst recovery, regeneration, and multiple cycle reuse. The most commonly investigated heterogeneous catalysts used for biodiesel production are ion exchange resins. Zeolites and basic metal oxides have also been investigated as potential catalysts. In the future, nanoparticles will also be efficient catalysts and/or catalyst carriers for biodiesel production.

Ion exchange resins with acidic or basic functional groups supported on styrene or polystyrene divinyl benzene (DVB) backbones are the most evaluated resins for biodiesel processing. Their use for liquid phase catalysis involves both heterogeneous and pseudo-homogenous reactions. Pseudo-homogenous reactions are due to the solvated protons within an alcohol-surface phase whereas heterogeneous is due to the availability of the functional group on the resin surface [36].

The structure of the resin directly impacts its function as a catalyst. The structural properties of importance include the degree of cross linking, density of surface functional groups, temperature stability, and surface area. Cross linking is important because it controls the structural stability, as well as internal structure of the resin's pores. Gel type acidic resins have lower acidic site strength than macroporous resins because they have a higher degree of cross linking. Increasing the DVB content, decreases the cross linking, thereby increasing the resin's porosity [37]. More porosity favors more catalysis, because the FFA can also react with sulfonate group internal to the resin. Soaking the resin also helps increase the porosity, with lower cross-linked resins demonstrating higher swelling rates. However, less cross-linked resins are less stable, reducing the amount they can be reused. Therefore, balancing both porosity and structural stability is important. An increase in functional groups increases the available active sites and favors reaction [38]. Finally, strong acid functional groups, such as sulfonic acid, favor esterification, while

strong basic functional groups, such as quaternary ammonium, favor transesterification.

For high FFA feed stocks, the conversion of FFA to FAME using heterogeneous acidic catalysts is lower than in the conventional homogeneous system by about 15 to 25%. Equivalent conversion rates are possible for heterogeneous acid systems if the system is run at higher temperature and pressure. However, most ion exchange resins are not stable under the required operating conditions. Therefore, the most common secondary method to increase conversion of FFA to FAME is by extending the reaction time. When the reaction time is extended up to 8 hours, a conversion of up to 90% is reported depending on the structure and physical properties of the resin [39]. Extending the reaction time limits the commercialization of heterogeneous catalysts for esterification because acidic homogeneous catalysts can produce the same high yield in a fraction of the time.

Basic ion exchange resins have been used to catalyze transesterification, although their use is less reported in the literature. The most commonly reported basic ion exchange resins have a quaternary ammonium function group supported on polystyrene divinyl benzene backbones [40]. Bronsted bases, such as quaternary ammonium, are very stable on polystyrene divinyl benzene supports and can be easily regenerated and reused. Transesterification using Bronsted acids is also demonstrated for heterogeneous acid catalyst systems, however, the reaction kinetics are too slow for commercialization [41].

While acidic and basic ion exchange resins have been demonstrated to facilitate esterification and transesterification, mixed bed resins have not been previously evaluated to our knowledge. Because mixed bed resins have both acidic and basic functional groups on the support, the simultaneous reduction of FFA in feed stock and production of FAMEs is worth exploring.

1.5. Research Objective and Aims

The primary objective of this study was to evaluate the use of mixed bed ion exchange resins in biodiesel processing. In order to meet the objective of the research, the following three aims were established and evaluated:

Aim 1: Evaluate the ability of mixed bed resins to reduce FFA content from a laboratory prepared 5% FFA feed stock.

Aim 2: Determine the mechanism of FFA reduction by comparing FFA removal in the mixed bed resin based system to FFA reduction in an acid resin based system.

Aim 3: Demonstrate a coupled mixed bed – basic resin heterogeneous catalyst system to produce biodiesel from a high FFA feed stock.

2. METHODS

2.1. Materials

Degummed soybean oil, technical grade oleic acid (90%), reagent grade toluene (99.5%), reagent grade isopropyl alcohol (99.5%), 0.1 N potassium hydroxide, reagent grade methanol, mixed bed, acidic and basis resin evaluated in this study (Dowex Monosphere MR-450 UPW and Amberlite MB-150),(Amberlyst 36 wet and Dowex Monosphere M-31) and (Amberlyst A26 OH) were all purchased from Sigma-Aldrich (St Louis, MO). Resin properties are given in Table 5, 6 & 7 in Appendix A. . Phenolphthalein was purchased from Fisher Scientific (Pittsburg, PA).

2.2. Reactor Design

A three neck batch reactor vessel (1000 mL) was used in each experiment (Figure 3). Two of the necks were sealed with rubber stoppers held in place by plastic ring seals. All reactants and a magnetic stir bar were placed/poured into the reactor through the third open neck at different points in the process. Heating and mixing of reaction mixture was done by placing the reactor into a water bath sitting on a combination heating and stirring plate. During the reaction, the third neck was sealed by a rubber stopper with a thermometer inserted through its center. The thermometer was immersed in the reaction fluids in order to monitor the reactor's temperature.

Reactor

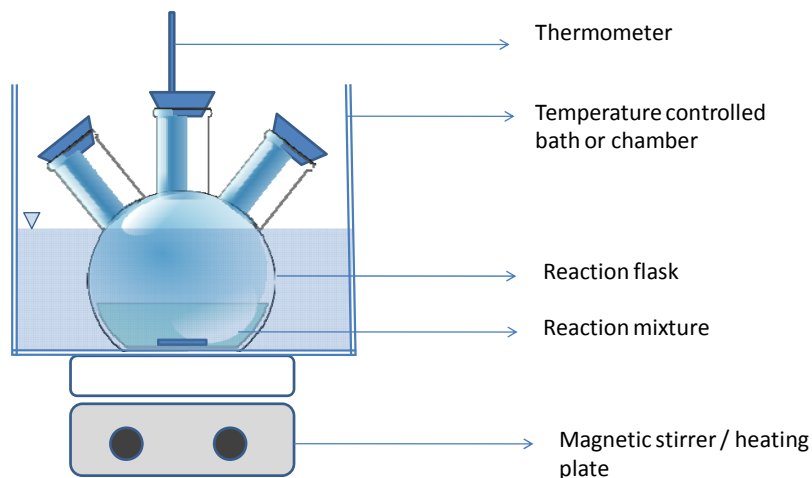


Figure 3. Reactor arrangement.

2.3. Experimental Procedure

All experiments started by soaking the resin in methanol inside of the three neck reactor for 12 hours while stirring at 550 rpm. Three reactors were setup at a time to produce triplicate measurements for each analysis. The amount of methanol used to soak the resin was based upon the 20:1 methanol: FFA molar ratio used in all the experiments. After twelve hours of soaking the resin in methanol, a nominal 5% oleic acid in soybean oil (high FFA feed stock) mixture heated at 50°C in a 1000 mL beaker is poured in to each reactor. The feed stock's exact % oleic acid composition (% FFA) was measured through titration after the mixture was heated within the fume hood at 50°C for 20-30 minutes to remove residual moisture and break any emulsified oil. Once the high FFA feed stock is up to 50°C, the feed stock mixture (200 gms) was

transferred from the beaker in to the methanol catalyst mixture held in the three neck reactors. During the reaction, the mixture was stirred at 550 rpm to keep the resins suspended in oil and the reaction temperature was kept constant between 50-55°C.

For Aims 1 (mixed bed resin) and 2 (acidic resin), the amount of catalyst soaked in methanol was varied to evaluate the effect of catalyst loading on %FFA reduction. The catalyst loadings evaluated were 5%, 10%, 15%, and 20% by weight of the oil mixture. The catalyst loading experiments were evaluated with 12 hours of soaking followed by 24 hours of reaction. Five gram samples (~10 mL) were taken from each reactor to determine the FFA of the reaction mixture at an interval of 2, 4, 8, 12, 16, 20, and 24 hours. At the end of each experimental run, the temperature and mixing rate was reduced to allow the catalyst to settle out of the liquid phase for five minutes. Because three reactors were used to evaluate each catalyst loadings impact on FFA reduction, the FFA content for each reactor is combined to create a triplicate measurement of mean FFA reduction.

The settled reacted mixture was then transferred into 50 mL polyethylene (PE) centrifuge tubes and centrifuged for 15 minutes at 9000 rpm. The supernatant was drained off and stored in new 50 mL PE centrifuge tubes for analysis. When more than one layer was formed in the reaction, each individual layer was separated by decanting the upper layer into a new centrifuge tube. The %FFA in each layer was analyzed through titration and the specific gravity of each observed fraction was determined (see 2.4 for method details for titration and specific gravity analysis). Leftover, non-spent resins collected during centrifugation were stored for later reuse.

Reactions were also carried out with and without methanol with the mixed bed catalyst in fulfillment of Aim 2. For Aim 3, the mixed bed resin producing the best FFA results within two hours was used. The same experimental procedure as Aim 1 was used, followed by the addition of 2% by

weight of oil, strong basic resin (Amberlyst A26 OH), and excess methanol (molar ratio 9:1 methanol to oil) into the reactor. At the end of mixed bed – basic catalyst run, the specific gravity of the top layer measured and the weight of the top layer were recorded. As a quick test to assess biodiesel purity, a small amount of the top FAME layer was pipetted into methanol. A pure FAME that is likely to pass ASTM 6751 dissolves completely in methanol, but an impure FAME layer precipitates out of solution and a dramatic color change is observed.

2.4. Analytical Procedures

The % FFA of the prepared feedstock and reacted samples was determined using the “American Oil Chemists’ Society method for the determination of FFA” AOCS Ca 5a 40 [42]. Briefly, 37.5 g of both toluene and isopropyl alcohol were combined in the bottom of a titration flask. Two ml of phenolphthalein indicator and 2.51 grams of feedstock are added to the titration flask. The mixture was then titrated against 0.1 N potassium hydroxide (KOH) until a light pink color appeared and remained in the solution for 30 seconds. The volume of 0.1 N KOH consumed was noted down and used to calculate the %FFA in the sample using the %FFA of a prepared blank as a benchmark [43]. Equations 1 and 2 show the calculation used to determine first the acid value and then the %FFA in the sample.

Acid Value

$$= \frac{\text{ml of KOH used} * \text{Normality of KOH sol} * \text{molecular weight of KOH}}{\text{Weight of feed stock sample}} \quad (1)$$

$$\% \text{FFA} = \frac{\text{Acid Value}}{2} \quad (2)$$

Eq.(2) for oleic acid based preparations(from [44])

The resulting % FFA in the reacted feed stock was then used to calculate the total removal performance of the FFA from the oil system following equation 3.

$$\% \text{FFA reduced} = \frac{\% \text{FFA, t=0} - \% \text{FFA, t=t}}{\% \text{FFA, t=0}} \quad (3)$$

where: % FFA,t=0 is the FFA of the feed stock before the reaction, and
 % FFA,t=t is the %FFA of the reaction mixture at time = t

The resulting yield of biodiesel (when a FAME layer was present) was obtained according to equation 4.

$$\% \text{ Yield} = \frac{\text{Weight of Biodiesel produced (gms)} * 100}{\text{Weight of feed stock oil (gms)}} \quad (4)$$

The mean and standard deviation of FFA content in samples from the three reactors were used to generate graphs.

2.5. Specific Gravity Measurement

The specific gravity of a sample was determined using a Mettler Toledo Densito 30PX Density Meter purchased from Fisher Scientific. The meter was calibrated against water prior to each measurement.

3. RESULTS AND DISCUSSION

3.1. Results for Aim 1

The effect of the catalyst loading and reaction duration on FFA removal in a laboratory prepared high FFA feed stock was observed for two highly cross- linked mixed bed ion exchange resins under a constant alcohol/oil molar ratio (20:1), temperature (50° C), initial FFA composition (5%), and mixing rate (550 rpm). Experimental data given in Table 8 & 9 in Appendix B. To the best of our knowledge, no work has ever been done with mixed bed resins for FFA reduction in low quality feed oil. This work is supposed to provide a reference point to others and in future more research data will be available for comparison.

The two mixed bed resins evaluated for FFA removal were Dowex Monosphere MR-450 UPW and Amberlite MB-150. The impact of reaction duration and catalyst loading for both mixed bed resins is presented in Figure 4 and 5. Each data point within the figures represents the mean FFA weight % in each of the triplicate reactors (with error bars displayed) as a function of time. Figure 6 displays the percent removal of FFA as a function of catalyst loading for the two mixed bed resins. The highly linear relationship ($R^2 > 0.99$) demonstrates that FFA reduction by both resins is a function of catalyst loading (Figure 6).

Additional evaluation of FFA reduction using mixed bed resins indicates that that the Amberlite MB-150 resin results in faster and greater removal of FFA from the reaction system compared to the Dowex Monosphere resins, even though both resins share the same support and functional groups (sulfonic acid for acidic sites and quaternary ammonium for basic sites). While we were successful in demonstrating that mixed bed resins could be used to remove

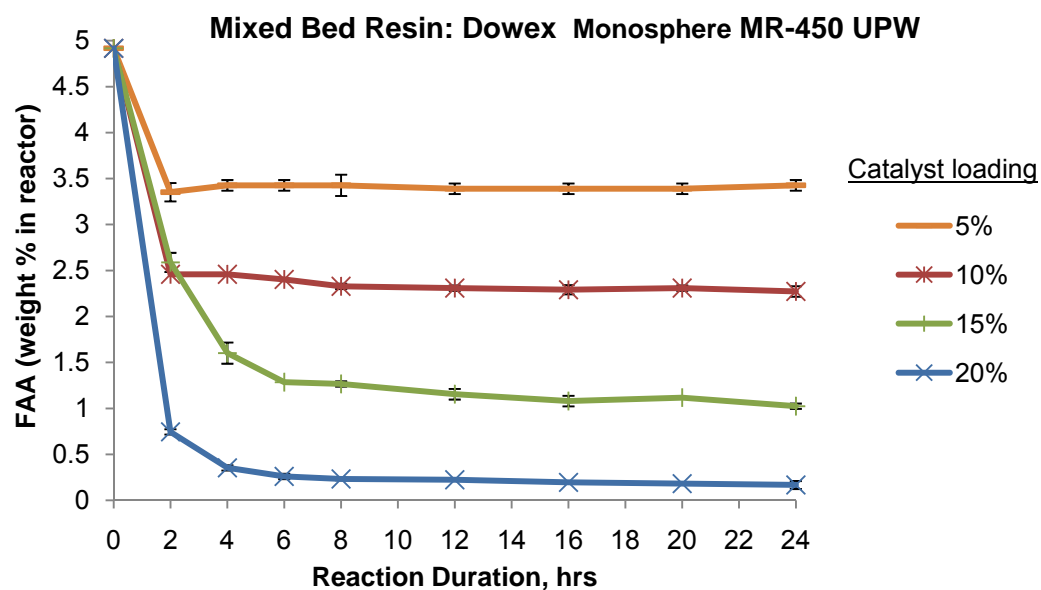


Figure 4. The impact of reaction duration and Dowex Monosphere MR-450 UPW catalyst loading on the reduction of FFA in the reactor.

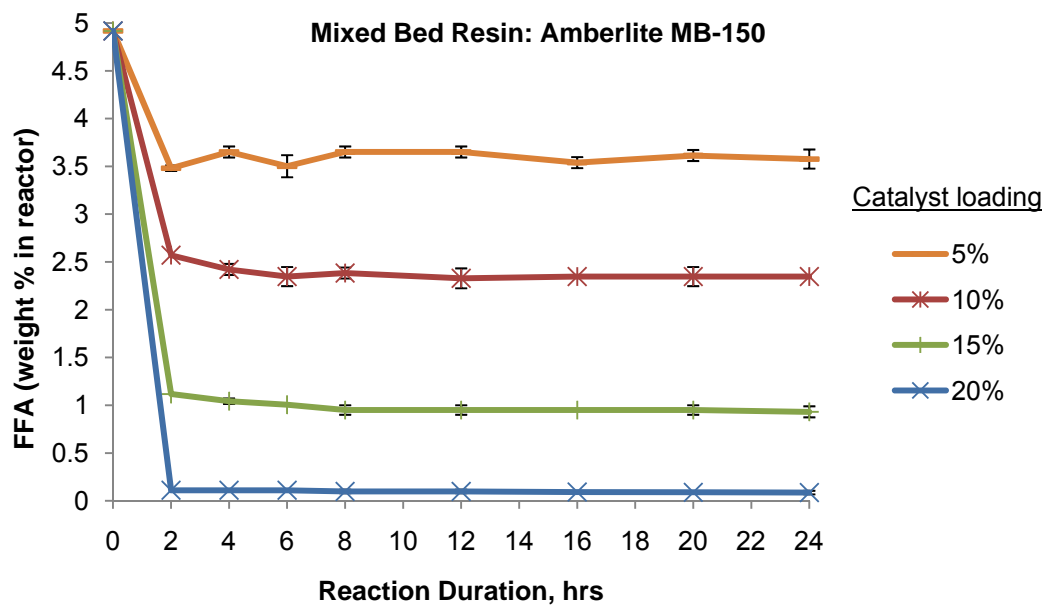


Figure 5. The impact of reaction duration and Amberlite MB-150 catalyst loading on the reduction of FFA in the reactor.

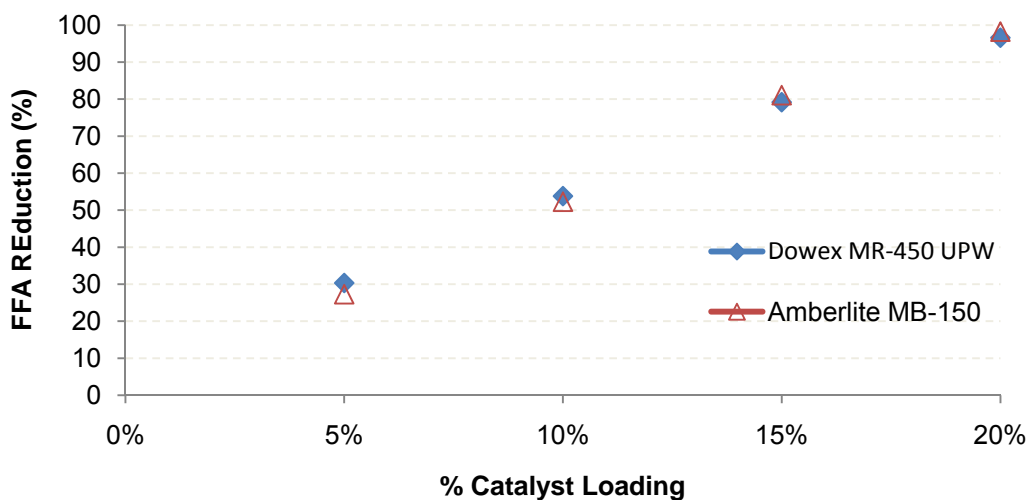


Figure 6. Relationship between catalyst loading and FFA reduction for mixed bed resins.

FFA (> 96% FFA reduction), we did not observe formation of any FAMES in the process. Experimental data given in Table 10 in Appendix B. A lack of FAME production was unanticipated. Based upon previous literature reports [1; 22; 39; 45; 46], we expected FFA in solution to undergo esterification due to the presence of the highly acidic sulfonic acid groups contained in the mixed bed resin. Further comparison of the two resins lead to the initial hypothesis that the quaternary ammonium site, and not the sulfonic acid site, was responsible for the removal of FFA from the system. This observation was hypothesized, because the Amberlite resin has a higher ratio of basic to acidic sites (60:40) compared to the equally proportioned Dowex basic: acidic site ratio (50:50).

3.2. Results for Aim 2

Two acidic resins, Amberlyst 36 (wet) and Dowex Monosphere M-31 were evaluated to determine if the acidic resins alone had any impact of FFA

reduction in the reactor. Experimental data given in Table 11 & 12 in Appendix B. These two acid resins were selected because they had the same support and functional group (sulfonic acid) as the mixed bed resins. Figure 7, 8, and 9 present the results of the acidic resin performance evaluation for removing FFA from the reactor systems. For both of the acidic resin based systems, FFA was not reduced or removed within the system. These experiments prove that the basic site, not the acidic site, is responsible for removing FFA from the system when mixed bed resins are used.

While a second phase was observed in the heterogeneous acid catalyst system after 24 hours, the specific gravity of the second phase was that of the soybean oil. This phase was likely a di- or mono glycerol phase and could not have come from esterification of FFA, because the FFA concentration decreased negligibly (less than 5% with both resins). To gain a deeper understanding of our acidic catalyst results, we went back to the earlier literature that appeared to give contradictory results to our conclusions. After rereading the earlier literature reports [39; 46], we feel confident that our results, while different, are correct. In these earlier reports the temperature was elevated to higher than 100° C. Because the maximum operating temperature of most resins is less than 60° C, the previous reports likely destroyed the resin structure resulting in the release of sulfonic acid functional groups into solution. The earlier reports also never directly tracked FFA. Instead they evaluated the conversion of the triglyceride molecule. Therefore, our results did not contradict previous reports and FFA removal in the mixed bed systems is due to the basic quaternary ammonium functional group.

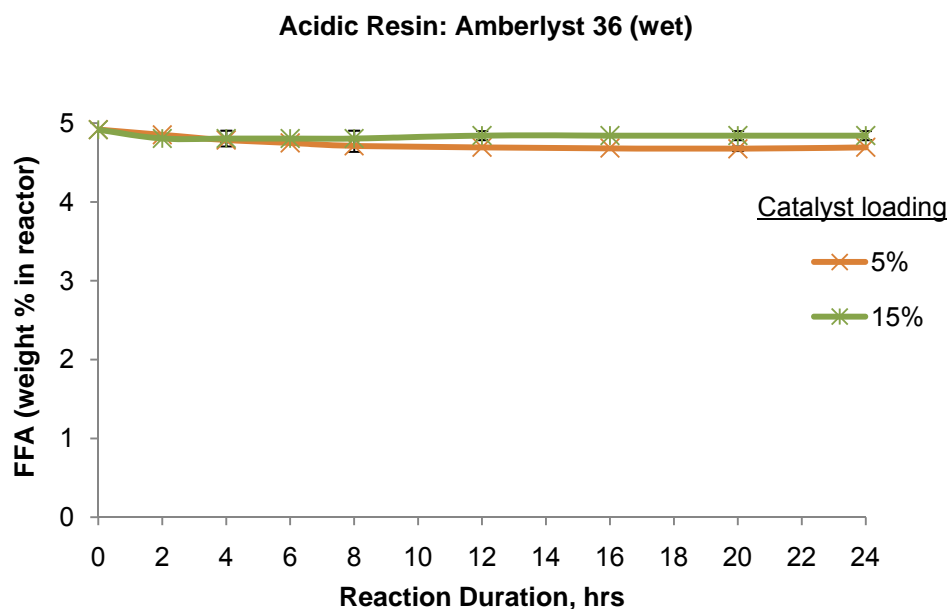


Figure 7. The impact of reaction duration and Amberlyst 36 (wet) catalyst loading on the reduction of FFA in the reactor.

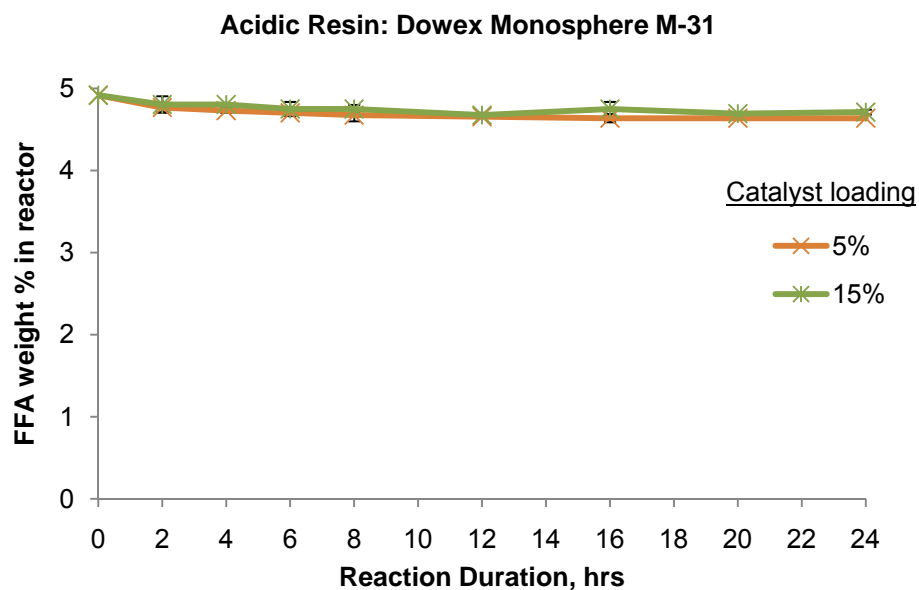


Figure 8. The impact of reaction duration and Dowex Monosphere M-31 catalyst loading on the reduction of FFA in the reactor.

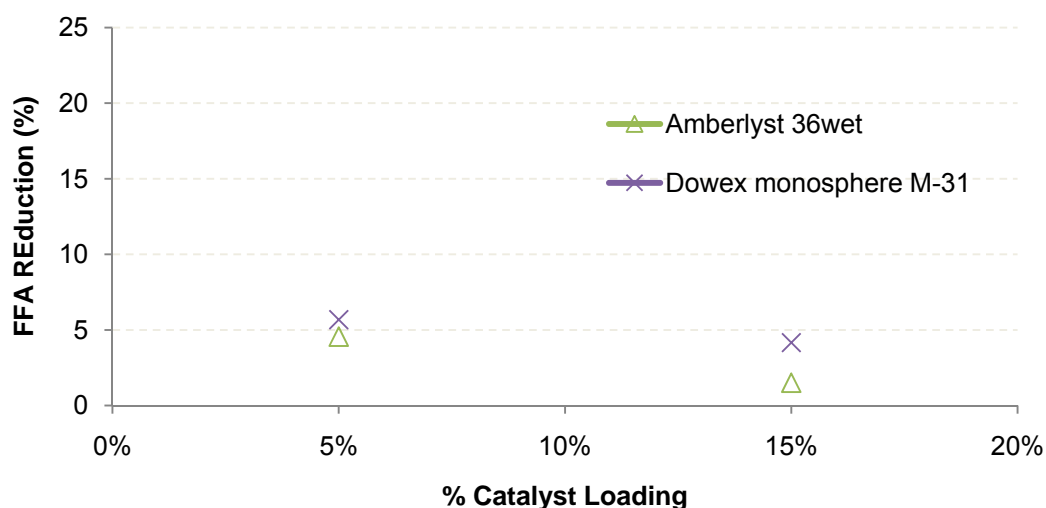
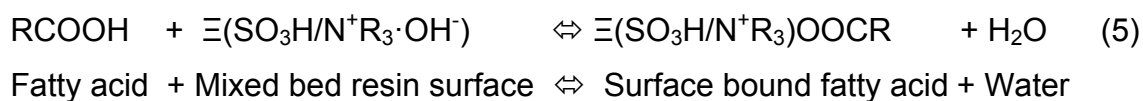


Figure 9. Relationship between catalyst loading and FFA reduction for acidic resins.

One additional set of experiment was run in triplicate to confirm FFA removal in the system was due to ion exchange on the quaternary ammonium functional group and not catalysis. Because esters will not form without the presence of an alcohol (methanol in our experiments), the mixed bed resin system was run without methanol. Table 13 in Appendix B shows the results of the experimental system with and without methanol added.

The results of this experiment clearly indicate methanol is not involved in the reaction; therefore, FFA removal is a function of ionic exchange and not catalysis. The ion exchange is occurring on the quaternary ammonium site, because there was no FFA removal in the system containing acid catalyst with the same support as demonstrated in the previous set of experiments. The following reaction mechanism is, therefore, suggested



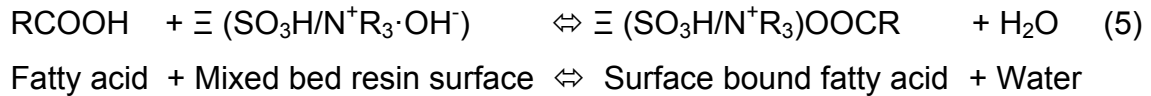
In order for this reaction to occur, the fatty acid must first be deprotonated. We hypothesize this happens in the microenvironment just above the highly basic quaternary ammonium functional group. The equilibrium dissociation constant of oleic acid in a lipid medium, K_{app} , was estimated to be 7.0 [47]. Because the microenvironment surrounding the site should be pH 9.0 or higher, the fatty acid should deprotonate within the microenvironment near the site and favor attachment.

3.3. Results for Aim 3

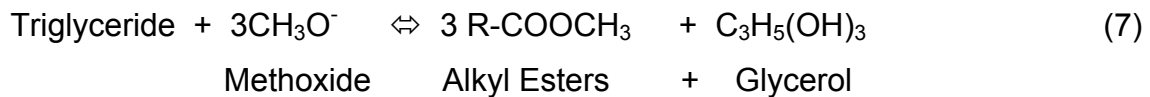
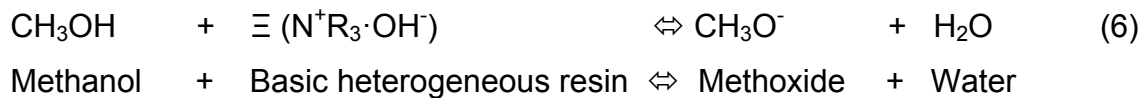
A final series of experiments was run to demonstrate that heterogeneous ion exchange resins can be used to create biodiesel from high FFA feed stocks. A 15% catalyst loading of Amberlyte MR-150 was added to the same laboratory prepared 5% FFA soybean oil feed stock used in Aims 1 and 2. After 4 hours of run time, the FFA level of the oil was reduced below 1.0% of the total sample weight. A heterogeneous basic resin, Amberlyte A26 OH, was then added at 2% catalyst loading by weight. The Amberlyte A26 OH was added without presoaking in methanol as presoaking is not reported to increase transesterification conversion rates by this resin [40]. The transesterification was then carried out for 4 hrs by adding methanol (9:1). The resulting products were separated by centrifuge and the ester yield and specific gravity were calculated as per equation 4. The mean specific gravity of the resulting esters was 0.86 and the average yield was 40.9%. Additional optimization and refinement of our newly proposed and completely heterogeneous process will result in higher ester yields as demonstrated by other researchers. Liu and Lotero [40], for instance, reported a 90% biodiesel yield from pure soybean oil when using Amberlyte A26 OH at 2% catalyst loading in 240 min. The following reaction mechanism gives a complete picture of our novel heterogeneous biodiesel processing method solely based upon heterogeneous catalysts. This

new approach to biodiesel processing will be called “lock processing” as FFA residuals are first locked on the surface of the mixed bed using ion exchange and then excess methanol is added to facilitate transesterification according to:

1. Ion exchange of FFA onto quaternary ammonium site on resin



2. Transesterification of soybean oil (triglyceride, TG) through methoxide as reported by [2]



4. SUMMARY

4.1. Conclusions

Experiments for FFA reduction in a laboratory prepared high FFA feed stock were conducted using highly cross linked acidic and mixed bed resins. AOCS method Ca 5a 40 was used for analysis, based on our results, the following conclusions can be reported:

- Quaternary ammonium functional group acts as ion exchange site for FFA.
- Increasing the quaternary ammonium functional site density in mixed bed resins helps increase the speed and amount of observed FFA removal from the bulk feed stock.
- Heterogeneous resin systems can be used to process low quality feed stocks to biodiesel.

4.2. Future Work

The main focus of my future work will be to develop a one step biodiesel process with mixed bed ion exchange resins using different short chain alcohols. Currently biodiesel is produced from high quality feed stock plant oils containing mainly triglycerides. For a low quality feed stock system having FFA >1% use of single basic catalyst causes separation problems of glycerol from esters. A two step method is, therefore, required to reduce % FFA < 1 % before following the basic catalyst reaction for triglycerides. In the true one step biodiesel processing method I will be developing, the use of a single mixed bed resin system with alcohol will generate biodiesel even from poor quality high FFA feed stocks.

Another focus will be to optimize our developed two-step heterogeneous catalyst reaction process for various low quality feed stocks. A matrix will be developed for the industry to determine the catalyst loading needed in a reactor to remove FFA to below 1%. Factors involved in the matrix will include catalyst loading, %FFA of the initial feed stock, the resulting biodiesel yield and quality.

Finally, I'd like to begin research of working with algae to hyper-accumulate oil in their cell walls when fed societal waste materials. The oil can then be extracted from the algae and turned into biodiesel through our developed methods. I plan to study and grow various strains of algae on industrial and domestic wastewater.

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APPENDIX A

RAW DATA & CALCULATIONS

Table 3. US Production of various edible oils of plant origin
(million pounds / year) from 2000-2007. [48]

Year	Corn Oil	Cotton	Peanut	Canola	Saf flower	Soy bean	Sun flower	Total Edible Oil
2000	2,403	847	179	641	102	18,420	873	23,465
2001	2,461	876	231	582	85	18,898	673	23,806
2002	2,453	725	286	496	92	18,430	345	22,827
2003	2,396	874	173	601	106	17,080	595	21,825
2004	2,396	957	126	798	71	19,360	265	23,972
2005	2,483	951	181	839	75	20,387	544	25,461
2006	2,590	849	166	875	80	20,487	625	25,673
2007	2,560	860	172	877	68	21,195	659	26,391

For conversion of 26,391 million pounds of plant oil to possible biodiesel, A 90% transesterification to biodiesel is assumed. Specific gravity (0.875) of methyl esters is considered for conversion in to gallons this will give biodiesel production yield 27.14 billion gallons.

$$\text{Conversion} = (26391 * 10^6 * 0.9) / 0.875 = 27.14 \text{ billion gallons.}$$

Table 4. Projected biodiesel from various alternative feed stocks.

Alternate Feed Stock	Available stock	Available oil	Biodiesel produced
Waste water sludge (dry solids) [19]	6.2 million tons (dry solids) annually = $6.2 \times 10^6 \times 6\%^a$ = 0.37 million tons of extracted lipids	$0.37 \times 10^6 \times 2000 =$ 0.74 billion pound of oil	$0.54 \times 10^9 \times 90\%^b /$ $0.875^c = 0.76$ billion gallons
Food scrap fraction of municipal solid waste [27]	251 million ton * $12.5\%^d =$ 31 million ton of food scrap	$31 \times 10^6 \times 6\%^a = 1.8$ million ton of extracted lipids * $2000 = 3.76$ billion pounds of oil	$3.76 \times 10^9 \times 90\%^b /$ $0.875^c = 3.87$ billion gallons
Rendered Products [29]	4515.6 metric tons * $6\%^a = 270$ metric ton of extracted lipids	$270 \text{ Mton} \times 2200 =$ 0.59 million pounds of oil	$0.59 \times 10^6 \times 90\%^b$ $/0.875^c = 0.61$ million gallons.
Algal Oil [25]	$9,826,630 \text{ sq km}^e *$ $100 \text{ ha} = 0.98$ billion hector * $1\%^f$ of area = 9.8 million hector	$32.6 \text{ tonne per ha}^g$ 0.32 billion ton of oil * $2000 = 640.69$ billion pounds of oil	640.69×10^9 $* 90\%^b / 0.875^c =$ 659 billion gallons

1 ton = 2000 lbs, 1 Mton = 2200 lbs, 1 sq km = 100 hectors

- a. Considering 6% extraction of lipids.
- b. Considering 90% conversion of oil to biodiesel.
- c. Specific gravity of methyl esters.
- d. Fraction of food in municipal solid waste.
- e. Total land area of USA.
- f. Considering 1% of total area of USA.
- g. Algal oil produced by algae per hector [25].

Table 5. Properties of Dowex Monosphere Resins.

Resin	Dowex Monosphere MR-450 UPW* Mixed Bed	Dowex Monosphere M-31* Acidic
Type	Gel	Macroreticular
Matrix	Styrene-Divinyl benzene	Styrene-Divinyl benzene
Functional group	Sulfonic Acid & Quaternary Ammonium groups	Sulfonic Acid
Form	OH^- & H^+	H^+
Water Retention Capacity	46-53% ---- H^+ form 55-65% ---- OH^- form	50-54% by weight
Exchange capacity	1.9---- H^+ form (eq/L) 1.0---- OH^- form (eq/L)	Wet volume acid capacity = 1.85 meq/mL min. Dry volume acid capacity = 5.0 meq/mg min.
Mean particle size	$360 \pm 50(\mu\text{m})$ ---- H^+ form $590 \pm 50(\mu\text{m})$ ---- OH^- form	> 90% 400-650 microns
Pore volume	-	33%

*Manufacturer (Dow Chemical Company).

Table 6. Properties of Amberlyst Resins.

Resin	Amberlyst 36 (wet)* Acidic	Amberlyst A26 OH* Basic
Type	Macroreticular	Macroreticular
Matrix	Styrene-Divinyl Benzene	Styrene-Divinyl Benzene
Functional group	Sulfonic Acid	Quaternary Ammonium groups
Form		OH
Moisture Holding Capacity	51 to 57%	66 to 75 %
Concentration of active sites	≥ 1.95 eq/L	> 0.80 eq/L
Particle size Harmonic mean	600-850 μm	0.560 - 0.700 μm
Surface area	33 m^2/g	30 m^2/g
Average pore diameter	240 Å	400Å

* Manufacturer (Rohm & Hass Company).

Table 7. Properties of Amberlite Resin.

Resin	Amberlite MB-150* Mixed Bed
Type	Gel
Matrix	Styrene-Divinyl benzene
Functional group	Sulfonic Acid & Quaternary Ammonium groups
Ionic form	Hydrogen/Hydroxide
Ionic capacity	0.55 meq/mL
Volumetric composition	40% cation/60% anion
Particle size	0.55 mm approximate 16 to 50 mesh size
Operating Ph	0-14
Operating Temperature	140 ⁰ F

* Manufacturer (Rohm & Hass Company).

APPENDIX B

LABORATORY EXPERIMENTAL DATA

Table 8. Experimental data for Dowex Monosphere MR-450 UPW.

Reaction Duration	Catalyst Loading							
	5%		10%		15%		20%	
	Mean %FFA	Stdev	Mean %FFA	Stdev	Mean %FFA	Stdev	Mean %FFA	Stdev
0	4.9179		4.917	0	4.917	0	4.917	0
2	3.3525	0.1	2.4585		2.5889	0.1041	0.745	0.0289
4	3.4270	0.0577	2.4585		1.6017	0.1155	0.3538	0.0289
6	3.4270	0.0577	2.4026		1.2851		0.2607	0.0289
8	3.4270	0.1155	2.3281	0.0289	1.2665	0.0289	0.2328	0.0144
12	3.3898	0.0577	2.3095	0.0289	1.1547	0.0577	0.2235	
16	3.3898	0.0577	2.2909	0.05	1.0802	0.0577	0.1955	
20	3.3898	0.0577	2.3095	0.0289	1.1175		0.1815	
24	3.427	0.0577	2.2723	0.0577	1.0244	0.0289	0.1676	0.0433

Table 9. Experimental data for Amberlite MB-150.

Reaction Duration	Catalyst Loading							
	5%		10%		15%		20%	
	Mean %FFA	Stdev.	Mean %FFA	Stdev.	Mean %FFA	Stdev.	Mean %FFA	Stdev.
0	4.917		4.917		4.917		4.917	
2	3.48	0.0289	2.5703		1.1175		0.1106	
4	3.6505	0.0577	2.4213	0.0577	1.043	0.0289	0.1106	
6	3.5015	0.1155	2.3468	0.1	1.0057		0.1106	
8	3.6505	0.0577	2.384	0.0577	0.9499	0.05	0.0983	0.0191
12	3.6505	0.0577	2.3281	0.1041	0.9499	0.05	0.0983	0.0191
16	3.5388	0.0577	2.3468		0.9499		0.0922	
20	3.6133	0.0577	2.3468	0.1	0.9499	0.05	0.0892	
24	3.576	0.1	2.3468		0.9312	0.0577	0.0861	0.0191

Table 10. FFA reduction with resin loadings in 24 hrs.

Catalyst Loading	5%	10%	15%	20%
<u>%FFA reduction with resin</u>				
Dowex monosphere MR-450 UPW	30.31	53.78	79.16	96.59
Amberlite MB-150	27.27	52.27	81.06	98.25
Amberlyst 36 wet	4.56		1.51	
Dowex monosphere M-31	5.68		4.16	

Table 11. Experimental data for Amberlyst 36 (wet).

Reaction Duration	Catalyst Loading			
	5%		15%	
	Mean %FFA	Stdev.	Mean %FFA	Stdev.
0	4.9179		4.917	
2	4.8523		4.8053	
4	4.7867	0.0289	4.8053	0.1
6	4.7494		4.8053	
8	4.7122	0.0764	4.8053	0.1
12	4.6936		4.8426	0.0577
16	4.6843		4.8426	
20	4.675	0.0289	4.8426	0.0577
24	4.6936		4.8426	0.0577

Table 12. Experimental data for Dowex Monosphere M-31.

Reaction Duration	Catalyst Loading			
	5%		15%	
	Mean %FFA	Stdev.	Mean %FFA	Stdev.
0	4.917		4.917	
2	4.7681	0.0577	4.8053	0.1
4	4.7308	0.0289	4.8053	
6	4.7029		4.7495	0.086
8	4.675	0.0764	4.7495	0.05
12	4.6563		4.675	0.0289
16	4.6377	0.05	4.7495	0.0866
20	4.6377		4.6936	0
24	4.6377		4.7122	0.0289

Table 13. Effect of methanol on FFA reduction by mixed bed resins.

Time (hrs)	FFA (% weight of sample) with methanol		FFA (% weight of sample) without methanol	
	Mean	Stdev.	Mean	Stdev.
0 hr	4.917	0	4.917	0
2 hr	0.745	0.0289	0.7636	0.0289
4 hr	0.316	0.0289	0.3073	0.0433

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