UBC Social Ecological Economic Development Studies (SEEDS) Student Report

Investigation of Solid Acid Catalyst Functionalization for the Production of Biodiesel

Elliot James Nash

University of British Columbia

CHBE 493/494

4 April 2013

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Investigation of Solid Acid Catalyst Functionalization for the Production of Biodiesel

By

Elliot James Nash

Thesis
CHBE 493/494
4 April 2013

The Faculty of Applied Science

(Chemical and Biological Engineering)

The University of British Columbia (Vancouver)

Abstract

The adoption of biodiesel as an alternative fuel is gaining momentum despite its large production cost and the competition with agricultural crops for land. To resolve both of these drawbacks, waste vegetable oils can be used as a feedstock for biodiesel production. However, waste vegetable oils generate by-products that create the need for more complicated synthesis procedures to deal with. Solid acid catalysts have demonstrated the ability to simplify this procedure into one reaction and separation procedure. However, the most efficient way to develop a solid acid catalyst has yet to be determined. The primary objectives of this thesis are to: continue the development of a solid acid catalyst for use in the UBC biodiesel project: investigate the effect of different functionalization methods on the development of the acid density of the catalyst; and analyze the effect of functionalization steps on the esterification activity of the catalyst. The acid catalysts were produced by increasing the surface area and porosity of biochar through chemical activation with potassium hydroxide. Then the catalyst was functionalized by contacting the biochar with fuming sulfuric acid, either by direct contact (BC-A-LS), vapour phase contact (BC-A-VS), or ozonating the biochar (BC-A-O). These procedures increase the acid density of the biochar to between 0.22-0.7 mmoll/g. The functionalized biochars were tested for their ability to esterify free fatty acids (oleic acid) with methanol. Esterification of the fatty acids was conducted over 10 hours with a 10:1 methanol to oleic acid ratio. BC-A (activated but non-functionalized biochar), BC-A-O, BC-A-LS, and BC-A-VS had oleic acid conversion of 7.3%, 24.3%, 28.3% and 42.9%, respectively. A positive relationship between acid density and catalytic activity was demonstrated by the collected data, but further conclusions from the data have been limited by the errors associated with the conversions.

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Nomenclature

BC – Biochar

BC-A – Sample of biochar that is chemically activated

BC-A-LS - Sample of biochar activated and functionalized with liquid sulfonation

BC-A-O - Sample of biochar activated and functionalized with ozone

BC-A-VS – Sample of biochar activated and functionalized with vapour sulfonation

CO_2 – Carbon dioxide

FFA – Free fatty acid

GC – Gas chromatography

HCL – Hydrochloric acid

KOH – Potassium hydroxide

MS – Mass spectrometry

NaOH – Sodium hydroxide

WVO – Waste vegetable oil

Acknowledgments

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SECTION 1 Introduction

1.1 Background

Biodiesel, a long chain of fatty acid mono-alkyl esters, is a renewable fuel derived from the catalyzed or uncatalyzed reaction between vegetable oil or lipids and an alcohol. Esterification and transesterification are the most common reaction pathways for its production. Esterification of free fatty acids (FFA), shown in Figure 1-1, with an alcohol produces water and biodiesel.

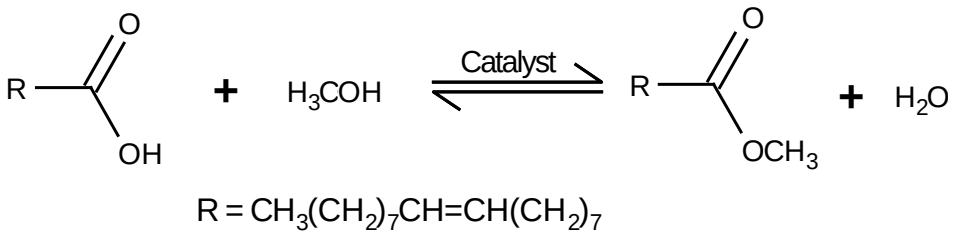


Figure 1–1 Esterification reaction

Transesterification, shown in Figure 1-2, is the reaction between vegetable oils (triglycerides) and alcohol to produce methyl esters (biodiesel) and glycerin.

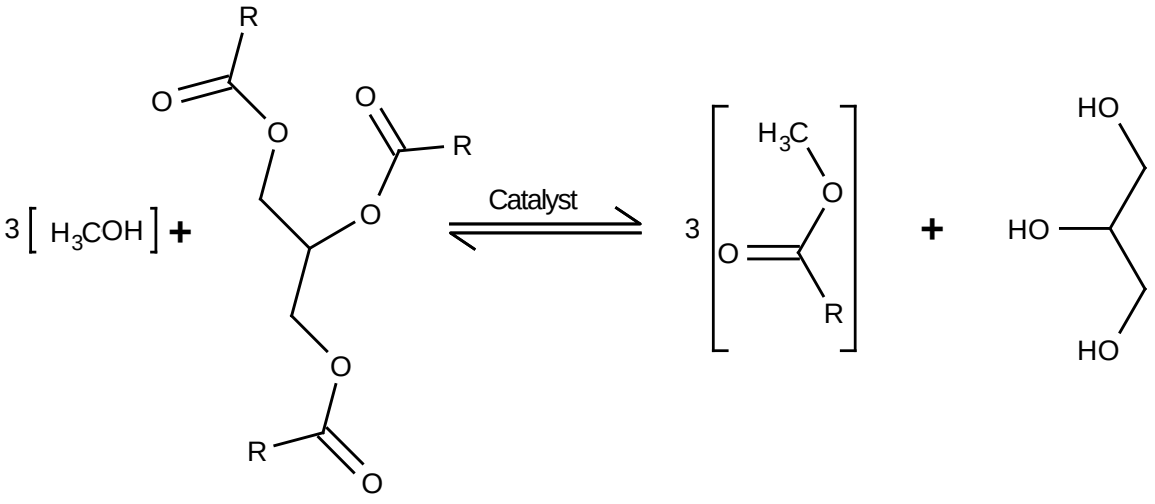


Figure 1–1 Transesterification reaction

Biodiesel was produced by transesterification as early as 1853 by scientists E. Duffy and J. Patrick, many years before the development of the diesel engine. Rudolf Diesel, the inventor of the diesel engine, ran an early model of his engine using peanut oil at the Paris Exhibition in 1900 (Canakci and Sanli 2008). Although biodiesel was phased out in favour of fossil fuels, it continued to be used in a number of countries throughout the

first half of the 20th Century. The oil crisis in 1970 renewed interest and research in biodiesel (Sorrell et al. 2010).

Biodiesel has been studied increasingly due to diminishing fossil fuel reserves, the increased cost of energy, and its inherent environmentally friendly characteristics. Biodiesel is produced from renewable and natural feedstocks, creates 40-80% less carbon dioxide (CO_2) emissions on a life cycle analysis than conventional diesel, and is less toxic than conventional fossil fuels (Tyson 2001). However, these advantages are offset by biodiesel's high production cost and effects on food supply. The three most significant factors affecting the cost of biodiesel production are associated with the catalyst, by-product treatment, and feedstock (West et al. 2008). The conventional homogeneous base catalysts used for large-scale biodiesel production are expensive and difficult to recover and reuse. Expensive operations, such as distillation or water washing, are required to remove by-products, such as glycerol soap or water, in order for the final product to meet stringent quality requirements. The purchase of vegetable oil feedstocks accounts for 64 - 80% of the total cost of biodiesel production (Januan 2012). In addition, the purchase of vegetable oil feedstock for biodiesel production may lead to an increase in food prices in vulnerable markets, thereby creating a scarcity of food (Escobar et al. 2009).

These feedstock challenges can be addressed by the use of an alternative inexpensive feedstock, waste vegetable oils (WVO). WVO is a broad term that encompasses waste oils and rendered fats. Using this waste for fuel production avoids competition with edible feedstocks. However, there are problems associated with the use of waste oils. WVO contains unfavourable components such as excess water and a high concentration of free fatty acid (FFA), 15-33 wt.% (Suwannakarn 2008). In comparison, standard feedstock FFA composition is roughly 0.5 wt.% (Suwannakarn 2008). FFA interferes with transesterification and produces a soapy by-product that can deactivate catalysts and must be separated from biodiesel before it can be sold (Lotero et al. 2005). Therefore, biodiesel production from WVO must be done in a two-step process that involves first the esterification of FFAs, and then transesterification of the remaining triglycerides. This process is expensive and inefficient because each reaction involves a different catalyst and must be followed by expensive washing and neutralization operations. This process could be simplified by conducting both reactions with one heterogeneous catalyst.

Biodiesel production using a heterogeneous catalyst has fewer unit operations, simpler separation steps and does not require neutralization steps. Solid catalysts can catalyze esterification and transesterification simultaneously. Additionally, biodiesel production using a heterogeneous catalyst is the most economically viable process of four large-scale biodiesel production processes with WVOs as the feedstock studied by West et al. (2008).

Solid catalysts are classified by the active sites upon them. Generally, there are three types of solid catalyst: acidic, basic, or enzymatic. Enzyme catalysts use lipase to catalyze the transesterification reaction. While enzyme catalysts have high catalytic activity and are theoretically renewable, their high costs and the leaching of enzymes limits the use of enzyme catalysts for biodiesel production (Enweremadu and Mbarawa 2009). Enzyme catalysts also deactivate in the presence of glycerol so alcohol and triglycerides content must be controlled through separation (Du et al. 2008). Solid base catalysts require shorter reaction times and lower reaction temperatures compared to solid acid catalysts (Hara 2009). However, solid base catalysts are also not ideal for processing WVO as they deactivate in the presence of water, a by-product of esterification (Lotero et al. 2005). Solid acid catalysts are insensitive to FFA content, can simultaneously conduct esterification and transesterification, reduce purification steps, and are easily separated from the biodiesel (Suwannakarn 2008) making them the best option for processing WVOs.

1.2 CHBE Sustainability Club

Biodiesel production at the University of British Columbia began in 2002, but it has not consistently produced biodiesel due to financial constraints, and the move of the biodiesel facility. The Chemical and Biological Engineering Sustainability Club initiated biodiesel production in 2011. The goal of the club is to produce biodiesel on a pilot scale for use by the campus community, with the long-term goal of becoming financially self-sufficient by selling biodiesel (Alemzadeh et al. 2012). The campus currently produces approximately 60,000 litres of WVO a year that could be turned into biodiesel (Alemzadeh et al. 2012). Recently, the club produced 150 L of biodiesel through the catalytic transesterification of vegetable oils with sodium hydroxide (NaOH) (Butler 2012). The use of a heterogeneous catalyst for pretreatment of the WVO by the CHBE Sustainability Club would reduce the environmental impact and financial cost of

biodiesel production by reducing by-product production, catalyst usage, and additional treatment steps.

1.3 Research Objectives

The objectives of this thesis are to continue the work done by West (2006), Dehkhoda (2010), and Januan (2012) by preparing a heterogeneous catalyst that can be used for the pretreatment of WVOs in the UBC Biodiesel Project. Previous work on the catalyst has determined the most effective method to develop the surface area and porosity of the biochar, and established relationships between surface area, porosity, acid density and catalytic activity (Dehkhoda 2010, Januan 2012). The primary focus of this thesis is how three different methods of functionalization affect the catalyst's acid density and catalytic activity. The catalysts' activity and acid density will be examined through the esterification of oleic acid with methanol. The main objectives are:

- Investigate the effect of functionalization by liquid phase sulfonation, capour phase sulfonation and ozonation on the development of the acid density of the catalyst;
- Analyze the effect of functionalization steps on the esterification activity of the catalyst

SECTION 2 Literature Review

2.1 Solid Acid Catalyst Selection

While a variety of solid acid catalysts are being studied, carbon-based catalysts have shown the highest catalytic activity (Dehkhoda 2010) as shown in Table A-1, in Appendix A. In addition, carbon based catalysts are stable under acidic conditions, are renewable, stable at high temperatures (200-300°C), inexpensive, and have a large surface area and a non-polar support matrix that may reduce deactivation by reducing adsorption of other polar molecules (*i.e.* water or glycerol) (Lotero et al. 2005). Among carbon-based catalysts, there is extensive research on activated carbon, glucose, and biochar based catalysts. Biochar is a by-product of pyrolysis process, the heating of biomass to 450-500°C in the absence of oxygen to produce bio-oil. In addition to biochar, the pyrolysis process produces bio-oil and non-condensable gases (Mohan et al. 2006). Biochar is an excellent choice as a catalyst support because it is inexpensive and its conversion into a catalyst will add value to the bio-oil production process.

2.2 Catalyst Characteristics

The surface area, porosity and acid group density largely determine a heterogeneous catalyst activity (Nykulyshyn et al. 2012). The surface area and porosity are important for two reasons: 1) the larger the surface area, the more room is available for acid groups, thus more reactions can be catalyzed; and 2) pores containing acid groups may be blocked by glycerol or water preventing further reactions (Januan 2012). The acid groups are the active sites on the catalyst that catalyze esterification. Figure 2-1 illustrates the variety of acid groups that may form

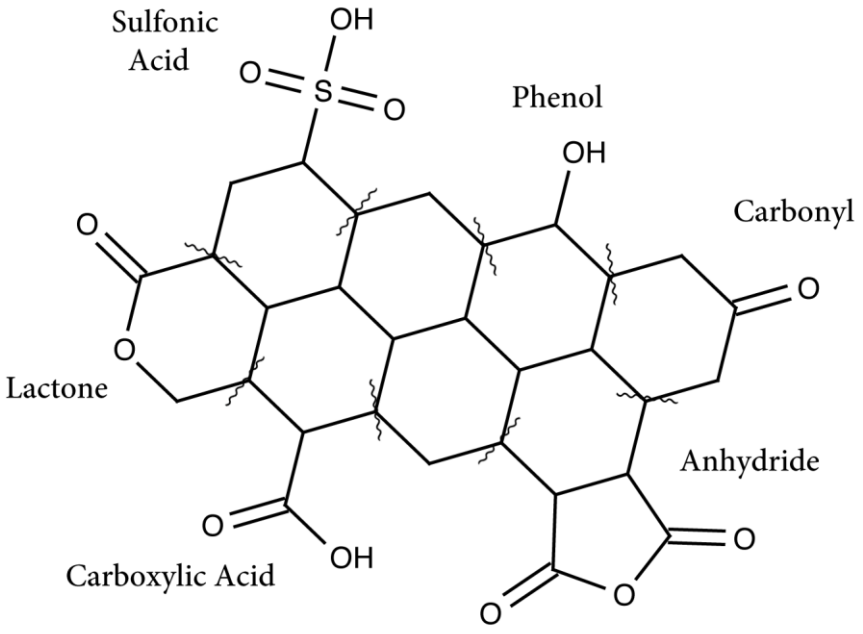


Figure 2–1 Various functional groups attached to carbon structure adapted from Fictorie et al. 2011

on the biochar. Acid groups bond to the biochar by reacting with the edges of the polycyclic aromatic rings, which have high concentrations of unpaired electrons (Marsh et al. 1997). The acid groups are classified as either strong or weak Brønsted acids (Liu et al. 2006). The weak acid group includes carbonyl, phenol, lactone, and carboxylic acid, among others. The density and type of the acid groups controls the rate at which the esterification can occur (Liu et al. 2006). The sulfonic group contributes much to transesterification and esterification reactions because it is a strong Brønsted acid (Mo et al. 2008). The affects of the other acid groups upon catalytic activity have not been well documented.

Figure A-1 (in Appendix) illustrates the mechanism by which the esterification is catalyzed. The mechanism begins with protonation of the carboxylic acid, located on the FFA, by the acid catalyst. This activates the carboxylic acid for reaction with non-protonated methanol, which yields a tetrahedral intermediate. Through decomposition of this tetrahedral an ester and water are formed (Liu et al. 2006). All of these steps are reversible, but increased concentration of alcohol, beyond stoichiometric ratios, shifts the equilibrium point of the reaction and the reaction can go virtually to completion. Deactivation or acid group leaching prevents this reaction from achieving high conversions (Januan 2012). Without an acid to protonate, the esterification of FFA proceeds very slowly (Liu et al. 2006).

2.3 Surface Area and Porosity Development

The activity of a carbon catalyst is largely due to its surface area and pore distribution (Lotero et al. 2005). There are two methods of developing surface area and porosity: physical and chemical. Table 2-1 compares the two methods. During chemical activation, the biochar is treated with a chemical agent, the most common being potassium hydroxide (KOH),

Table 2-1 Comparison between chemical and physical activation adapted from Dehkhoda 2010

Activation Conditions	Chemical Activation	Physical Activation
Activation Temperature (°C)	500-800	600-900
Mass Ratio of Oxidizing Agent/Biochar	0.25-3	0.4-2
Nitrogen Flow (mL/min)	80-250	-
Activation Time (h)	-	0.9-4
BET Surface Area Range (m^2/g)	180-1500	300-950
Average Pore Diameter	13-15 A^o	13-26 A^o

phosphoric acid or zinc chloride. The mechanism by which the surface area is increased is not well understood, but it is thought that the chemical agent dehydrates the biochar and inhibits tar and volatile compound formation thereby enhancing the carbonization process (Azargohar and Dalai 2008). Physical activation can be achieved with steam, air, CO_2 or by utilizing silica templates. High temperature steam removes carbon atoms from the surface of the biochar thus increasing the surface area (Azargohar and Dalai 2008). The silica template method is a common means for the development of surface

area of carbon material (Hu et al. 2006). A porous template of silica is formed and the carbon is introduced to the template, the mixture is carbonized after which time the template can be removed and the surface area of the biochar will have been increased. The chemical activation by KOH requires the least complicated procedure and is the least time consuming. In addition, chemical activation has been shown to generate the largest increase in surface area, pore size and pore volume. For these reasons, the chemical activation procedure described by Dehkhoda (2010), will be used to develop the catalyst's surface area and porosity in this study.

2.4 Functionalization

In addition to the surface area and pore size, the acid sites attached to the biochar determine the catalyst's activity (Lotero et al. 2005). Acid sites develop on biochar by bonding acid groups with the polycyclic aromatic rings of the biochar. The effectiveness of a variety of methods for generating acid groups on biochar has been tested. This thesis will focus on three: ozonation, liquid phase sulfonation, and vapour phase sulfonation.

Recently, wastewater has been treated with the combined methods of ozonation and activated carbon. It was found that exposure to ozone generated acid groups on the active carbon and altered the geometry of the active carbon. Mawhinney and Yates (2001) proposed the following mechanism (Figure 2-2) for the production of carboxylic groups on the edges of polycyclic aromatic ring. Kastner et al. (2012) demonstrated that ozone treatment also effectively transformed basic sites into acidic

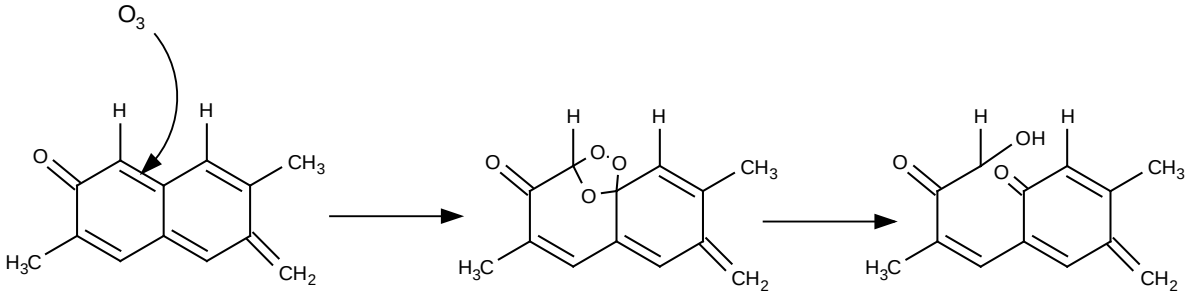


Figure 2–2 Formation of carboxylic group on carbon sheet through ozonation (Mawhinney and Yate 2001)

sites.

Figure 2-3 illustrates the effect of ozonation over the period of one hour. The resultant carbon has significantly higher acid density mainly due to groups such as

anhydride, lactones, and carboxylic bonding to the carbon (Valdés et al. 2002). Kastner et al. (2012) has experimented with the ozonation of biochar for biodiesel production, but their results have shown negligible catalytic activity for esterification. This result warrants further investigation, as this author feels even biochar that has not been functionalized should report some catalytic activity.

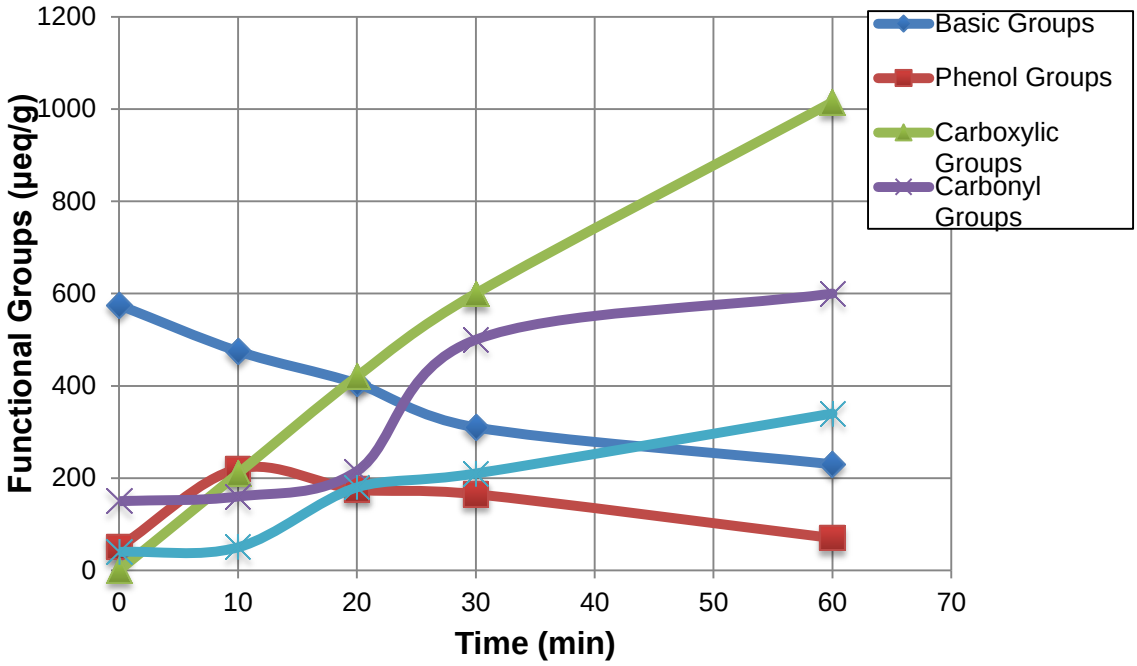


Figure 2–3 Effect of ozonation on carbon adapted from Valdés et al. 2002

By treating biochar with sulfuric acid, sulfonic, phenolic, and carboxylic groups form on the surface of the biochar and act as catalysts for transesterification and esterification. The sulfonic group is thought to contribute the most to transesterification and esterification due to its high acid strength (Mo, et al. 2008). Direct contact with fuming sulfuric acid (20wt.% free SO_3) produced a catalyst with total acid density between 1.17-7.30 mmol/g (Januan 2012). This method appears frequently in the literature (Dehkhoda 2010; Januan, 2012; Kastner et al, 2012). It is the simplest and fastest to perform, but significantly reduces the surface area and porosity of the catalyst due to direct contact with a strong acid. Because of the simplicity of liquid sulfonation and its frequent use throughout the research community, it will be utilized in this thesis. Vapour phase sulfonation of a carbon catalyst is a relatively novel approach for developing a functionalized carbon catalyst. In previous literature the resulting catalyst, produced using liquid phase sulfonation,

had a total acid density of 3.20 to 4.15 mmol/g (Januan 2012). Januan (2012) and Kastner et al. (2012) each used separate methods to produce a functionalized catalyst through vapour phase sulfonation. Kastner introduced biochar to fuming sulfuric in a sealed container for six days, while Januan utilized a heated mantle to fume SO_3 over biochar for four hours (Januan 2012; Kastner et al. 2012). Januan's method, discussed in Section 3, is faster and appears to provide greater control over variables that may affect the functionalization process. For these reasons, vapour phase sulfonation is performed using Januan's method.

SECTION 3 Materials and Methods

3.1 Materials

Biochar was used as a starting material for the catalyst. The biochar was generated through the fast pyrolysis process, the quick heating of biomass in the absence of oxygen to a high temperature (~500°C), of a mixture of hard and soft wood. Dynamotive Energy Systems Corporation, (Vancouver, BC) conducted the pyrolysis of the char. Oleic acid will be used as a feedstock for esterification along with methanol. Catalyst activation will require potassium hydroxide and hydrochloric acid (HCl). To functionalize the catalyst, fuming sulfuric acid (20wt.% free SO_3) and a canister of high purity (99.9993%) oxygen (Praxair) will be required. For analysing the acid density of the catalyst, HCl and NaOH will be needed. The gas chromatography analysis requires methyl oleate standard to be obtained from Sigma-Aldrich.

To ensure the catalyst is comparable to previous studies conducted by Dehkhoda (2010) and Januan (2012), two sieves, a 38 μm and 250 μm, must be obtained, as well as a shaker to conduct the sieving. A Thermolyne F21100 tube furnace is required to reach the needed temperature for the carbonization, and a nitrogen canister will be needed to prevent the combustion of the char within the tube furnace. For the sulfonation procedures a variety of glassware will be used, as well as a heat exchanger (Jubalo F12) to maintain the temperature of the bed.

3.2 Experimental Methods

3.2.1 Preparing the Biochar

The biochar was first dried in an oven (Sheldon Manufacturing Inc.) at ~110°C for five days. In this phase the moisture in the biochar evaporated and the mass and

volume of the biochar decreased significantly. Following the drying, the catalyst was sieved and ground to between +38 μm and -250 μm to be consistent with previous research. Upon sieving the biochar, it was stored in an oven at ~110°C until activation.

3.2.2 Surface Area and Porosity Development

Chemical activation with potassium hydroxide was performed to increase the biochar's surface area and porosity. The biochar was mixed with a 7 M solution of potassium hydroxide for two hours at room temperature, with a mass ratio of KOH to biochar of 3.55:1. The biochar was recovered by filtration and stored in the oven at ~110°C until carbonization. In the first stage of carbonization, ~18 g of biochar was placed in the tube furnace and a constant flow of nitrogen 258 mL/min was introduced as the temperature was raised to 300°C at 3°C/min. This first stage removed any remaining water/contaminants from the biochar. The furnace was held at 300°C for one hour and then the temperature was increased to 675°C and held for two hours to re-carbonize the biochar. This process alters the structure of the biochar by forming carbon sheets. These sheets provide additional edge area for acid groups to attach to the catalyst. At higher temperatures the polycyclic aromatic carbon rings will break apart leading to reduced acid group density (Dehkhoda 2010). After carbonization, the biochar was washed with distilled water at ~90°C until the pH of the wash water was neutral. Then the biochar was demineralized through treatment with 250 mL of 0.1 M hydrochloric acid. Heated distilled water was utilized again to wash the catalyst a second time to remove any soluble salts and potassium compounds remaining from chemical activation. The biochar was then dried for 12 hours at ~110°C to prepare the biochar for functionalization (Azargohar and Dalai 2008). All biochar that was activated was labelled as BC-A.

3.2.3 Functionalization

Ozonation

Ozone treatment of the biochar was used to increase the density of the weak acid groups (phenol, carboxylic, lactone and carbonyl) while decreasing the density of any basic groups found on the biochar (Valdés, et al. 2002). 7 g of biochar were exposed to ozone in a fixed bed column using the apparatus shown in Figure 3-1. The ozone generator (VMUS-2, Azco Industries) produced ozone from a canister of high purity oxygen (99.993% oxygen). The biochar was placed at the bottom of a flask and ozone was passed over the catalyst in a downward flow at 1 L/min (total flow) with an ozone

concentration of 45 g/m^3 for 6 hours at 25°C and 1 atm in accordance with the literature (Valdés, et al. 2002; Kastner, et al. 2012). After treatment, the catalyst was oven dried at 110°C overnight and stored in a desiccator until used. The biochar that

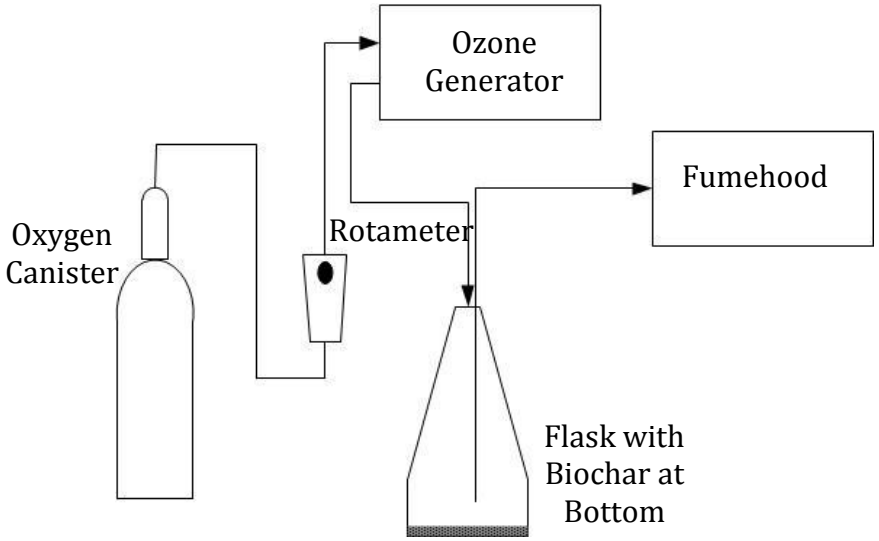
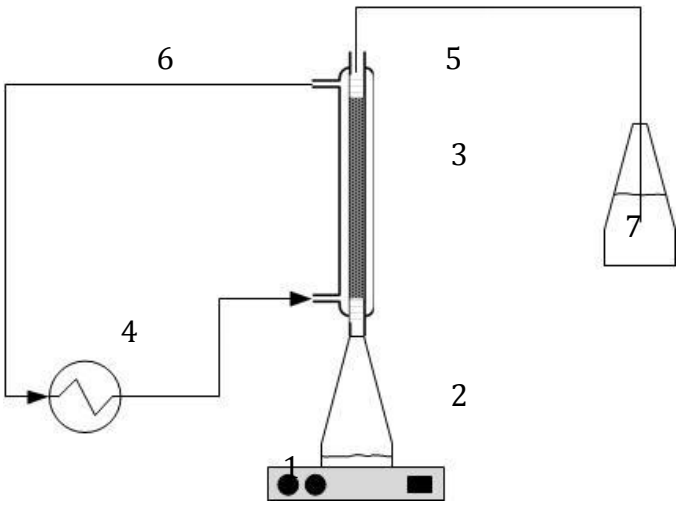


Figure 3–1 Ozone generator setup



1. Temperature Controlling Stir Plate
2. Erlenmeyer Flask
3. Condenser with Biochar
4. Heat Exchanger
5. Quartz Wool
6. Silicone Tubing
7. 1 M NaOH

underwent this procedure was abbreviated as BC-A-O.

Vapour Sulfonation

The vapour phase sulfonation was performed using the experimental setup shown in Figure 3-2. A 1000mL Erlenmeyer flask was placed on a temperature controlled heating plate and filled with 100 mL of fuming sulfuric acid (20 wt.% free SO_3). 7 g of biochar was placed in a glass condenser (6 mm inner tube diameter and 30 mm height); quartz wool above and below the biochar held the bed in place. The glass condenser was connected to the Erlenmeyer flask and its other end was connected with silicon tube, which was dipped into a 1M NaOH. The NaOH was used to neutralize the fuming sulfuric acid vapour before it was released in the fume hood. The temperature in the condenser was not directly measured, but was maintained at 60°C by a heat exchanger (Julabo F12) using R134a as the refrigerant. The sulfuric acid was vapourized at 225°C and the vapour passed through the biochar bed for four hours. Upon completion, the char was withdrawn from the condenser and washed repeatedly with distilled water at ~90°C until the pH of the wash became neutral. The catalyst was then dried at ~110°C overnight and stored. The biochar that underwent this procedure

Figure 3–2 Vapour phase sulfonation setup

was abbreviated as BC-A-VS.

Liquid Sulfonation

The liquid phase sulfonation was conducted in a batch reactor (STEM-Omni Reaction Station 6100) at 150°C ±2°C under reflux, stirred at 425 rpm. The ratio of fuming sulfuric acid to char was 16.5 mL fuming sulfuric for each gram of biochar. The char was added first to the reactor vessel then the fuming sulfuric was added slowly. The reaction was conducted under nitrogen flow of 50 mL/min. A photograph of the liquid sulfonation setup can be found in the Appendix A (Figure A-2). The reaction was conducted over a 15 hour period, after which the products were cooled to room temperature and water was added to the reactor vessel to dilute the remaining sulfuric acid. The biochar was then washed with 500 mL of pre heated (~100°C) distilled water until the pH of the wash water was neutral. Then the catalyst was dried for one day in the oven at ~110°C and stored in a desiccator. The biochar that underwent this procedure was defined as BC-A-LS.

3.3 Catalyst Characterization

3.3.1 Esterification

To evaluate the activity of the biochar as a catalyst, esterification was conducted with oleic acid, as a substitute for long chain fatty acids, and methanol as alcohol reagent. The reaction was conducted in a batch reactor (STEM-OMNI Reaction Station 6100). The temperature was maintained at 60°C ±2°C, under reflux, and stirred at 450 rpm. The molar ratio of methanol to oleic acid was 10 to 1, and 3 wt.% catalyst loading with respect to the oleic acid was used. The amount of reactants used was 250 mmol of methanol, 25 mmol oleic acid, and 0.21 g of catalyst. The catalyst was pre-dried in an oven at ~110°C for approximately two hours prior to reaction. After drying, the catalyst was weighed out and mixed with the methanol for 15 minutes. The mixture was then combined with oleic acid, which had been preheated to 65°C. The reaction time was set to 10 hours and once completed the products were filtered to remove the catalyst, and the resultant solution was sealed with plastic wrap and stored at room temperature. This was repeated three times for each catalyst.

3.3.2 Gas Chromatography (GC) Analysis

Gas chromatography was used to quantify the conversion of the esterification reaction. GC operates on the separation of the different compounds in a mixture based on their partitioning between a stationary liquid phase (the sample) and a moving gas phase (the carrier gas). Each component in the sample has a specific retention time in the column before being reaching the detector. The signal intensity from the detector is proportional to the concentration of components.

A total of 50 µL of sample was taken from the bottom layer of the filtered esterification products, diluted with heptane, and mixed using a digital vortex mixer (Fischer Scientific) at 3000 rpm for 10 seconds. The samples were analyzed by GC/MS (Varian CP-3800) using a fused silica 60 m x 0.25 mm x 0.25 µm with CPWax52CB coating column. The temperature program was ramped at 20°C/min from 150 to 240°C, using helium as the carrier gas with a column flow of 2 mL/min. The diluted samples were analyzed three to six times. A calibration curve for the GC was obtained prior to sample analysis using four different dilutions of pure GC grade methyl oleate. The calibration curve is given in Figure A-4 in the Appendix.

3.3.3 Back Titration

The total acid group density of the catalyst samples was determined using the back titration method. The catalysts were pre-dried in the oven at 110°C for at least two hours prior to analysis, then ~0.1 g of catalyst was added into 60 mL 0.0080 mol/L NaOH and mixed for 30 minutes. Back titration was conducted with 0.02 M HCl, and due to an absence of an indicator, a pH probe (Metrohm AG) was used. The samples were then titrated to a pH of 7. Since there was a delay in the pH meter reading, the titration of 1 mL at a time allowing the pH meter to reach a constant value before continuing the titration.

SECTION 4 Results and Discussion

4.1 Experimental

After drying, sieving, and soaking the biochar in KOH, 200 g of it remained. The chemical activation of the surface area reduced the sample mass to 45 g of activated char remaining. The large reduction in mass was consistent with past experiment (Dehkhoda 2010) and was primarily due to biochar loss during the filtration and washing steps to remove KOH and tar formations from the biochar. The biochar's surface area was not measured; however, a previous study using the same procedure and a similar biochar resulted in a surface area increase from >0.5 m^2/g to ~200 m^2/g (Dehkhoda 2010). The biochar was then divided so that ~10 g each of catalyst would be functionalized by each of the methods described above, and ~10 g of activated biochar would remain, with 5 g remaining.

The vapour phase sulfonation procedure was initially setup following Januan's method, displayed in Figure 4-1. A small hole in the thermometer well went unnoticed until the fuming sulfuric acid had started heating in the round bottom flask. By this time

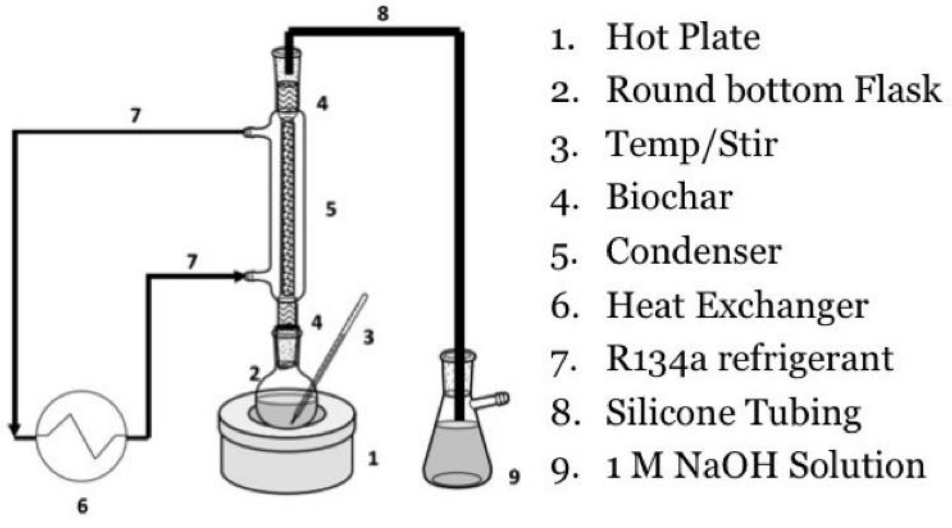


Figure 4-1 Proposed vapour phase sulfonation setup (Jidon 2012)

acid vapours had escaped from the thermometer well and dripped onto the heating mantle, effectively disabling it. The fume hood was closed for two days to allow for the remaining sulfuric acid to fume off. The biochar and heating mantle were disposed of. Since another round bottom flask was not available this procedure had to be adjusted. An Erlenmeyer flask was used instead. Only ~5 g of biochar could fit in the condenser at one time so two separate runs were conducted. During sulfonation some of the char was forced out of the condenser and into the NaOH solution by fumes. After drying the two runs were mixed together and weighed, the 9.450 g of initial biochar had been reduced to 7.201 g.

The setup for the ozone also had to be adjusted from that reported by Kastner et al. (2012). Initially, 3.332 g of biochar was packed into a column and held in place with quartz wool as a fixed bed reactor. Upon starting the oxygen flow and activating the ozone generator a spark and small flame were observed in the column. This was most likely due to unreacted oxygen being ignited by sparks generated from biochar producing static electricity. The biochar that had ignited was thrown out and 6.6094 g of activated char was placed in a thin layer over the bottom of an Erlenmeyer flask. The ozone was then passed over the char and out a tube to the fume hood. No significant loss of biochar was observed in this procedure.

Two batch reactors conducted the liquid sulfonation procedure simultaneously. 4.331 g of activated biochar was loaded into each reactor, and the temperature and stir functions were activated. Due to the long procedure time (15 hours) the procedure was run overnight. At some point overnight a fuse blew on the STEM-OMNI Reaction Station and the reaction conditions were not maintained. Unfortunately, the procedure could not be repeated as there was insufficient activated biochar left. Rather than omitting liquid sulfonation, and disposing the biochar, the biochar in the reactors was filtered, dried, and weighed. This resulted in 7.583 g of liquid sulfonated biochar being produced.

4.2 Esterification Activity

Table 4-2 shows a comparison of the average activities of the four prepared catalysts on the esterification of oleic acid and methanol at 65°C in terms of the concentration of methyl oleate produced. The conversion was calculated based on the reaction between oleic acid and methanol to produce methyl oleate and water. The conversion of oleic acid is defined as the difference between the final and initial concentration of oleic acid divided by the initial concentration oleic acid. The catalyst with the greatest activity was the one prepared through vapour sulfonation. The catalyst functionalized with ozone and liquid sulfonation were the next best with similar catalytic activity, 21.37% and 25.15%, respectively, and the catalyst which had not been functionalized preformed the worst.

Table 4-1 Acid densities and conversion for each prepared catalyst

Catalyst	Run #	Average X	Overall Average X	Acid Group Density (mmol/g)
BC-A	1	3.80%	6.52%	0.29 ± 0.024
	2	11.46%		
	3	4.30%		
BC-A-O	1	25.50%	21.57%	0.44 ± 0.031
	2	8.06%		
	3	31.16%		
BC-A-LS	1	*	25.15%	0.50 ± 0.022
	2	27.48%		
	3	22.83%		
BC-A-VS	1	21.45%	38.09%	0.78± 0.023
	2	20.11%		
	3	72.72%		

* = Run 1 for BC-A-LS was spilled during the filtration process

The similarity between the ozonated biochar and the liquid sulfonated biochar was unexpected. Kastner et al (2012) reported the activity of ozonated biochar demonstrated negligible activity in the esterification of palmatic acid. Additionally, the activity of liquid sulfonated biochars created under similar reaction conditions (10:1 vs. 18:1 alcohol to oil ratio and 3wt.% verse 5wt.% catalytic loading) has been reported to be much higher, ~90% (Dehkhoda 2010). The reason for the large discrepancy between these values and ones from the literature in liquid sulfonated activity may be due to equipment failure during the sulfonation process. This prevented the reaction from being run at the desired temperature and mixing regime.

The activity of the vapour sulfonated biochar was comparable to that created by Januan (2012), ~40%. The standard deviation of three was 48.9%, which is far too large for these values to be accurate. A reason for the large variability of the catalytic activity between different runs is that some of the samples, after the reaction was complete, appeared to have decreased in volume significantly. The reactions were ideally run in batch under reflux conditions, but samples BC-A-O Run 2 and BC-A-VS Run 1 appear to have decreased in volume by more than 50%. This is most likely due to the evaporation of methanol that may have occurred due to a reactor vessel not being properly sealed. It may also explain the large standard deviations for both of these catalysts. Table A-3 in the Appendix show the results of the GC analysis with the same sample tested up to six times. Finally, the uncatalyzed yield of the esterification reaction under these conditions was not investigated. Esterification is generally limited by the low equilibrium conversion and slow reaction rate, but the addition of excess alcohol and higher temperatures shift the equilibrium conversion (Liu, Lotero and Goodwin 2006). Without a control it is impossible to know how much oleic acid would have converted to methyl oleate without a catalyst.

4.3 Total Acid Density

The acid density of biochar before any treatment and the catalysts was found through back titration as described in Section 3.3.3. The acid density of the biochar, before treatment was found to be 0.22 mmol/g. Figure 4-2 shows the acid density of the catalysts with their respective catalytic activity. The ozonation procedure yielded a catalyst with similar acid density to what was produced through liquid sulfonation. The total acid density is significantly lower than that reported by Dehkhoda (2010), Januan (2012), or Kastner (2012) but higher than that reported by West (2003). A possible reason for this is the surface area of the char was never confirmed. Dehkhoda (2012) has shown that the acid density is largely dependent on porosity and surface area. Due to time constraints and equipment malfunctions, the BET surface area was not determined.

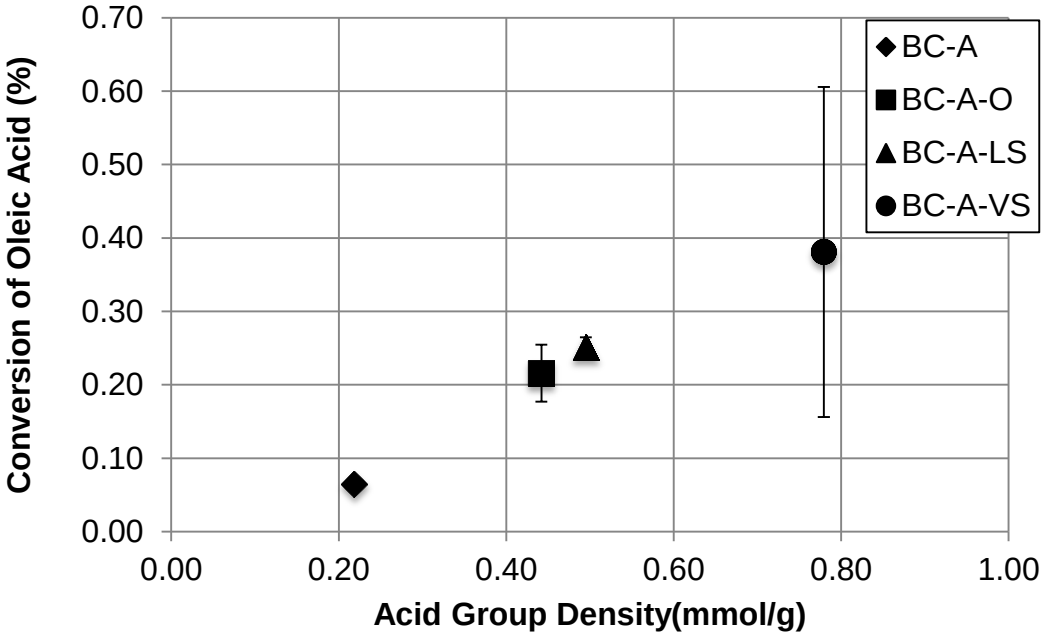


Figure 4–2 Conversion of oleic acid as a function of acid density

Despite the various sources of error, it is encouraging that there does appear to be a positive relationship between acid density and catalytic activity. This is consistent with the literature (Januan 2012; Kastner, et al. 2012). The results also confirm the importance of the sulfonic group. Both catalysts that underwent sulfonation preformed the best. However, the small difference between the ozonated char and liquid sulfonated char indicates that a weak acid group such as carboxylic may perform similarly in high acid densities.

SECTION 5 Conclusion and Recommendations

5.1 Conclusions

A heterogeneous catalyst for biodiesel production was prepared by exposure to fuming sulphuric acid and ozone. It was assumed the surface area and porosity of the biochar samples was increased by chemical activation with KOH. The chemical activation technique with KOH involves the reaction of specific amount of biochar with the highly concentrated solution of KOH (7 mol/L) followed by carbonization under nitrogen (258 mL/min). The surface area of the biochars prepared was not measured, but the procedure followed in this thesis was identical to that of Dehkhoda (2010). The catalyst then underwent three separate forms of functionalization.

To examine the effects of the functionalization procedures the activity of the

biochar-based catalysts was assessed for esterification of oleic acid with methanol. BC-A, BC-A-O, BC-A-LS, and BC-A-VS had oleic acid conversion of 6.5, 21.6, 25.2, and 38.1%, respectively. The acid density of each catalyst and the un-activated biochar was evaluated through back titration. BC had the lowest acid density of 0.22 mmol/g, increasing the surface area also increased the acid density to 0.29 mmol/g. The samples that had been functionalized: BC-A-O, BC-A-LS and BC-A-VS had acid densities of 0.44, 0.50, and 0.70 mmol/g, respectively. The difference in the catalytic activity among the catalysts tested was attributed to the density of acid sites per gram of catalyst and the different acid groups present. There is a large error associated with BC-A-O and BC-A-VS which maybe due to a variety of experimental errors. In conclusion, three successful catalysts have been prepared through separate functionalization procedures. Their catalytic activities vary which is most likely due to the different acid densities of the catalyst. Further investigations are required to verify the accuracy of the findings reported here.

5.2 Recommendations

To understand the behaviour and explore the application of the carbon-based catalysts further investigations are recommended, such as:

- Understanding the effect pyrolysis conditions have on the structure and composition of the biochar would help optimize the catalyst production.
- Boehm titration of the catalyst following (Fictorie et al. 2011), procedure would help quantify the amount of each functional group on the catalyst.
- Determining the strength of the different active sites would create a better understanding of the functional groups and their effect on catalytic activity.
- Further studies could be preformed on the development of the catalyst. Using different functionalizing reagents such as fuming acids with a higher percentage of free SO_3, other strong acids, or super acids as suggested by Dehkhoda (2010).
- Study of reusability and regeneration of carbon-based catalysts.
- Examining the changes in composition and structure of the biochar following the chemical activation or functionalization steps would be useful.

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Appendix A – Tables and Figures

Table A-1 Comparison of different solid acid catalysts used for esterification/transesterification adapted from Dehkhoda 2010

Catalyst	Reaction			Yield (%)	Reference
	Type	Temperature (°C)	Time (h)		
Sulfated Zirconia	Transesterification/Esterification	80	9	63	(Zong, et al. 2007)
Amberlyst-15				33	
Niobic Acid				10	
Carbon-Based				85	
Nafion SAC-13	Transesterificatio	60	1	72	(Mo, et al. 2008)
	Esterification			30	
Carbon-Based	Transesterification Esterification	60	1	91	
				41	

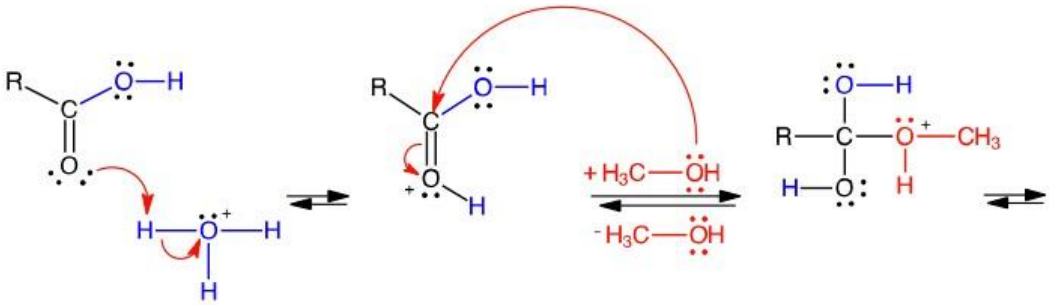


Figure A–1 msan et al. 2010)

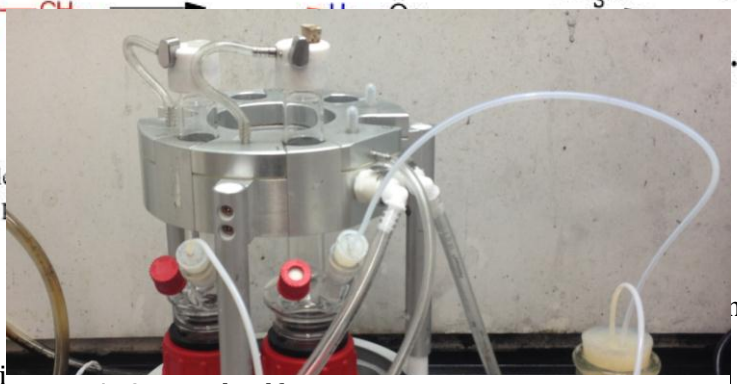
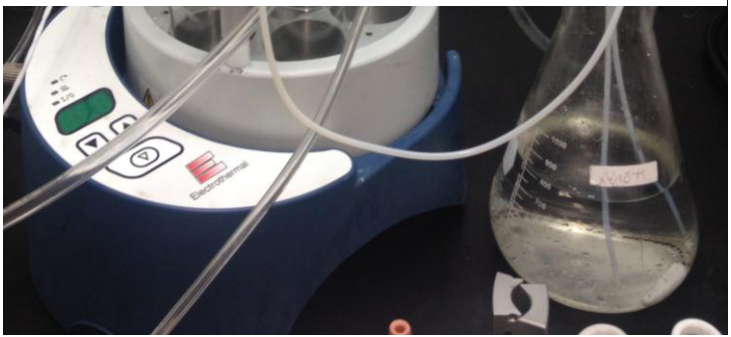


Figure A–3 Liquid sulfonation setup



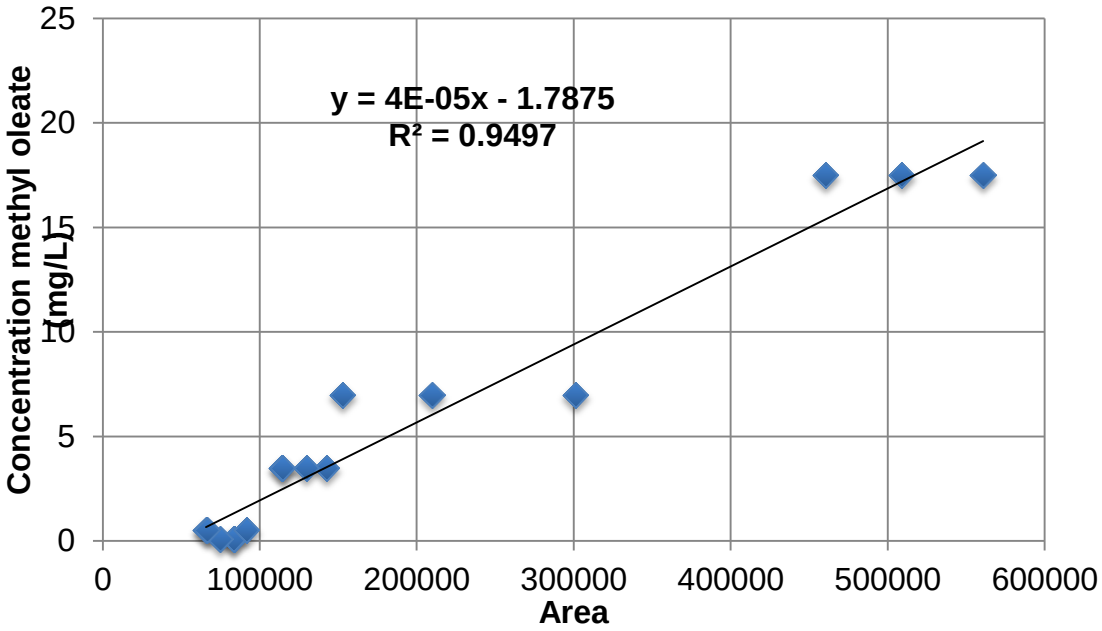


Figure A–2 Calibration curve developed with methyl oleate standard

Table A-2 Average concentration of oleic acid between experimental runs and the standard deviation over the three runs

Sample	Concentration of Oleic Acid (mg/L)					
	Run 1	Run 2	Run 3	Average	SD	SD%
BC-A	1.18	1.07	1.17	1.14	0.060	5.22%
BC-A-O	0.88	1.12	0.83	0.94	0.154	17.92%
BC-A-LS	-	0.85	0.92	0.88	0.046	5.17%
BC-A-VS	0.93	0.95	0.22	0.70	0.416	59.20%

Table A-3 Concentration of oleic acid with the same experimental runs and the standard deviation from GC trials

Catalyst Type	Run #	Oleic Acid Concentration After Reaction (mol/L)						Average	SD	%SD
		Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Trial 6			
BC-A	1	1.370	1.330	1.345	1.317	1.323	1.327	1.335	0.019	1.4%
	2	1.345	1.209	1.134	1.276	1.180		1.229	0.083	6.8%
	3	1.362	1.345	1.278				1.328	0.044	3.3%
BC-A-O	1	0.990	1.090	1.022				1.034	0.051	5.0%
	2	1.289	1.264					1.276	0.018	1.4%
	3	0.985	1.100	0.884	0.853			0.955	0.112	11.7%
BC-A-LS	1									
	2	0.906	1.076	0.958	1.086			1.007	0.089	8.8%
	3	1.266	0.884	1.0897	0.8605	1.255		1.071	0.19	18.2%
BC-A-VS	1	1.017	1.087	1.114	1.133	1.101		1.090	0.044	4.1%
	2	1.173	1.005	1.148				1.109	0.091	8.2%
	3	0.290	0.196	0.276	0.308	0.892	0.312	0.379	0.255	67.3%