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Catalytic esterification of fatty acids using solid acid catalysts generated from biochar and activated carbon

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ABSTRACT

Reusable, solid acid carbon supported catalysts were generated from biomass by pyrolysis (400–500 °C) to generate a soft to hard carbon backbone (i.e., biochar) for addition of acidic functional groups. Acid catalysts were synthesized by sulfonating the biochar and wood derived activated carbon using concentrated H_2SO_4 at 100, 150 and 200 °C (12 h) and gaseous SO_3 (23 °C). Attenuated Total Reflectance, sulfur, and NH_3-TPD analysis of the sulfonated carbons indicated the presence of —SO_3H groups on the 100 °C sulfonated biochar and activated carbon (AC), with higher active site densities (SO_3H density) for the SO_3 sulfonated material. The sulfonated carbons were tested for their ability to esterify free fatty acids with methanol in blends with vegetable oil and animal fat (5–15 wt.% FFA). Esterification of the fatty acids was typically complete (~90–100% conversion) within 30–60 min at 55–60 °C (large methanol excess), but decreased with lower methanol to oil ratios using the biochar catalysts (e.g., 70%, 6 h, 20:1). Solid acid catalysts derived from wood based activated carbon had significantly higher activity compared to the biochar derived catalysts (e.g., 97%, 6 h, 6:1). Of the synthesized biochar catalysts, 400 °C pyrolyzedpine chip biochar, sulfonated at 100 °C, resulted in the highest reaction rate and lowest reduction in conversion (or deactivation) when reused multiple times. Drying the biochar catalysts for 1 h at 125 °C between uses maintained esterification activity, allowing the catalysts to be reused up to 7 cycles. For the SO_3 sulfonated AC catalyst, such a regeneration step was not required, as the fractional conversion of palmitic and stearic acid (5% FFA, 10:1, 3 h) remained >90% after 6 cycles.

1. Introduction

Recently there has been renewed interest in the synthesis of solid acid and base catalysts for producing biodiesel – primarily driven by the need to find environmentally benign catalysts to replace waste generating homogeneous acids and bases [1]. The renewed research appears to be driven by a need to replace sulfuric acid and sodium methoxide in the production of methyl esters (i.e., biodiesel) from free fatty acids (FFAs) and triglycerides. In the production of biodiesel, a commodity chemical, the use of acids and bases as unrecoverable catalysts generate large volumes of waste that must be treated, significantly adding to costs and the environmental impact of production.

The economics of biodiesel production are strongly linked to the feedstock cost [2], catalyst cost, and wastewater treatment. The raw material cost of the feedstock (e.g., soybean oil) for biodiesel production is significantly more than that of petroleum based diesel and represents the largest fraction of the cost for biodiesel production [2]. Thus, the high cost of refined vegetable oil, the inability to recover/reuse the catalysts, and waste formation due to use of homogeneous catalysts (e.g., H_2SO_4 and KOH) are all barriers to biodiesel commercialization.

Reusable solid acid catalysts would eliminate these barriers by allowing biodiesel production from low-quality feedstocks high in free fatty acids (FFAs), reducing catalyst cost, and eliminating the need for costly treatment of high and low pH streams. Solid acid catalysts could be used to esterify FFAs in inexpensive sources of triglycerides, such as yellow (<15% free fatty acid or FFA) or brown (>15% FFA) grease, rendered fat, and soapstock, followed by base catalysis to transesterify the glycerides.

This awareness has resulted in research on the synthesis and testing of heterogeneous acid catalysts for esterification. There have been recent reports on the generation of solid acid catalysts. Anion exchange resins (e.g., polystyrenesulfonic acid) have been used to esterify FFAs with a range of alcohols, yet are expensive and

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potentially unstable at high pH [3]. Perfluorinated alkanes supported on silicon oxides catalyze esterification [4], but again are expensive, environmentally unfriendly, unstable at high pH, and are generated from non-renewable carbon sources. Heteropolyacids impregnated/attached on/to zirconia have also been developed, but this support material (i.e., zirconia) is very expensive [5].

An option that has great possibility, but which has not been fully explored is the generation of acid catalysts supported on carbon for catalysis. Carbon supported catalysts have several distinct advantages over alumina or silica supported systems; they are stable under acidic basic conditions, can have very high surface area [200–1500 m^2/g], renewable biomass sources can be used to generate the carbon, and the non-polar nature of the support matrix may reduce adsorption of polar molecules (e.g., water or glycerol) that can deactivate the catalyst.

Functionalized carbon (e.g., attached SO_3H groups) has been generated from refined sugars (pure cellulose, glucose and starch) and was demonstrated to catalyze the transesterification of oleic and stearic acid with ethanol [6]. Acidic functional groups have been attached to wood based activated carbon [7], but there has been limited testing of these materials as catalysts. Recently, solid carbon catalysts derived directly from biomass via fast pyrolysis biochars were explored as biodiesel catalysts, but there is limited data on esterification reaction kinetics and reuse capability of such derived catalysts [8].

The objectives of this research were to develop reusable, porous carbon supported acid catalysts for biodiesel generation using biochar generated from lignocellulosics (by slow pyrolysis) and to contrast esterification rates with activated carbon catalysts. It was theorized that low temperature (400–600 °C), slow pyrolysis of biomass would generate a highly cross-linked, multi-ringed, aromatic structure anchored to lignin that could be easily functionalized with catalytically active acidic groups. Based on the previous analysis of biochar generated by pyrolysis of pure biomass components (cellulose, hemicelluloses, and lignin) and whole biomass, it is theorized that lignin would undergo partial decomposition and hemicellulose and cellulose would undergo a series of thermal homolysis, hydrolysis, dehydration, and molecular rearrangement reactions to form a polymerized aromatic structure. Catalysts derived from biochar or lignocellulosics, contrary to refined carbohydrates, zeolites, and resins would be environmentally friendly (e.g., separation of glucose from biomass, mining required for zeolites, or use of petroleum feedstocks for synthesis of resins would not be required).

The first phase of this research focused on rapid screening of solid acid catalysts generated from biochars for esterification activity, with methanol in large excess. Screening was used to select an optimum biochar catalyst, a sulfonated pine chip biochar, based on fatty acid (FFA) conversion versus time data and reuse activity. Further research was then performed with the pine chip char catalyst in FFA spiked oil at lower methanol to oil ratios; biochars synthesized at 400 °C and sulfonated using H_2SO_4 at 100 °C gave optimum results. Research subsequently focused on biochars synthesized under these conditions and were compared to catalysts synthesized from wood based activated carbon. Although pine chip biochar catalysts generated the highest esterification rates, this particular catalyst was fragile and fragmented into fine powder in the batch, stirred reactions. Since we anticipated this would be problem at an industrial scale (e.g., in a packed-bed reactor), we focused on a biochar form that we theorized would not break down under shear stress and selected a granular peanut hull, smaller in size compared to large pelleted biomass forms to reduce mass transfer limitations. Our overall results, based on esterification reactions rates and turnover frequency or TOF (calculated from the reaction rate and SO_3H density of each catalyst) are presented in tabular form.

Table 1
Compositional analysis of biomass used to generate biochar solid acid catalysts.

Materials properties	Pelletized peanut hulls	Pine pellets	Pine chip char
Cellulose, % (dry basis)	43 ± 0.03	47.3 ± 0.5	51.7 ± 0.9
Hemicellulose, % (dry basis)	4.0 ± 0.2	14.4 ± 1.5	18.7 ± 1.3
Lignin, % (dry basis)	29.2 ± 0.25	24.6 ± 0.42	28.2 ± 0.3
Ash, % (dry basis)	2.6	0.14	0.30
Bulk Density (kg/m^3)	609–720	ND	ND

ND, not determined.

2. Experimental

2.1. Biomass sources and biochar generation

Pelletized peanut hulls and pine logging residues, and wood chips, were used to generate biochar. Pelletized peanut hulls were supplied by Golden Peanut Co. LLC. Pelletized pine pellets and wood chips were purchased from local suppliers. The pelletized peanut hulls were typically 15 mm in length and 8 mm in diameter and the pine chips 4–18 mm in length, 15–30 mm in width, and 1–5 mm in thickness. The composition of biomass materials (cellulose, hemicelluloses, and lignin) was analyzed in labs at The University of Georgia and reported in Table 1.

In addition to pelletized peanut hulls, powdered peanuts hulls were also obtained from Golden Peanut Co., LLC. A product identified as AgForm 200 (http://www.goldenpeanut.com/hullfiber.aspx) was utilized and a sieve analysis of this material indicated that 98% of the ground hulls ranged in particle size from 1.2 to 3 mm. Additives and binders are not present in the pelletized hulls or the AgForm 200 product.

A granular (Nuchar WV-B 20) and pelleted (Nuchar BX-7540) activated carbon (AC) product was obtained from MeadWestvaco and used to synthesize solid acid catalysts. Nuchar WV-B 20 reportedly has an iodine number of 900 (mg/g, minimum), a moisture content of 10% (as packed) and a nominal particle size of 6 × 18 (US Mesh, 8% oversize, 5% undersize), with properties of an apparent density of 240–300 kg/m^3 and a surface area of 1400–1600 m^2/g (nitrogen BET). BX-7540 reportedly has an iodine number of 1000 (mg/g, minimum), a moisture of 5% (as packed) and a nominal pellet diameter of 4 mm, with properties of 9% ash, an ASTM hardness of 95 min, an apparent density of 360–410 kg/m^3 and a surface area of 1100–1300 m^2/g (nitrogen BET).

The pyrolysis unit consisted of a batch reactor (316SS, 23 cm × 23 cm × 23 cm reactor, with a N_2 purge line and exhaust) located inside a furnace (Thermolyne, Barnstead Inc, La., single set point, 1200 °C max, 10 °C/min ramp) followed by a condensation unit (Fig. S-1). Pure nitrogen was used as an inert sweep gas (1/2″ stainless steel tubing) and controlled using a mass flow controller. A thermowell located 2 in. from the bottom of the reactor within the biomass was used to monitor and manually control temperature (type K thermocouple connected to a CR23X datalogger, averaging at 2 min intervals). In this experiment, biochar was prepared over a range of temperatures (400–600 °C) and held for 1 h in the pyrolysis reactor with a N_2 flow at 1–2 L/min. Initial mass loading of the pyrolysis reactor depended on biomass type and ranged from 2 to 5 kg for pine chips and 2–3 kg for pelletized peanut hulls and pine [9].

2.2. Ozone treatment

In some cases, biochar was exposed to ozone in a fixed-bed reactor (1 in. I.D. × 12 in. L, Fig. S-2) packed with a defined mass of the biochar (25 g). Ozone in air was passed downward across the carbon at 1 L/min (total flow) and 33 g m^{-3} O_3 for a period of 6 h (23 °C). An ozone generator (OL100H/DS, Yanco Industries Ltd.,

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B.C., Canada), utilizing a high frequency corona discharge, was used with a medium grade tank of oxygen (99.9%, National Wielders, NC) to generate the ozone required for these experiments [9].

2.3. Catalyst generation – sulfonation methods

Next, the biochar generated above was further reacted to attach strong acidic functional groups on the carbon surface. Acid catalysts included a weak acid functionalized carbon (biochar treated with ozone only) and a strong acid, $-SO_3H$ functionalized carbon. Carbon oxidized using ozone was considered a weak acid catalyst, since this process introduces a high density of weak acidic groups (e.g., carboxylic acids, phenolic, and lactonic groups) throughout the carbon pores [9].

For the strong acid catalyst ($-SO_3H$), the biochars (400 °C, except where noted) and activated carbon were sulfonated based on methods described in the literature [6,7]. First, the biochars generated from pelletized biomass and BX-7540 were ground into smaller particles using a mortar and pestle (pine chip biochar was used as generated and then sieved on 4–12 mesh screen sieves, retaining all carbon particles between in that specific range).

Subsequently, 12.5 g of the previously ozonated biochar or non-ozonated biochar and activated carbon, was placed in a beaker, and contacted with 20 mL of concentrated sulfuric acid (99% H_2SO_4). The acid was mixed with the carbon via periodic stirring (15 min), and then excess acid was decanted. The residual wet solids (carbon plus acid) were then transferred to a ceramic crucible, placed in muffle furnace, and heated for 12–18 h at 100 °C (except where noted). After heating, the char was cooled and rinsed 2–10× with 50–100 mL of deionized water. The pH of the rinsate was measured after each washing and the char was then dried in an oven at 110 °C overnight.

A second sulfonation method using gaseous SO_3 was evaluated for its ability to generate solid acid carbon catalysts. AgForm 200 was selected, since it was granular in form (not a powder) and smaller in size compared to the pelleted peanut hull form. It was theorized that the smaller granular form would result in more complete sulfonation throughout the biochar particle and generate a catalyst form that would not cause a large pressure drop in a packed-bed, compared to the powder form of the pine chip biochar catalyst; we anticipate that a tubular packed-bed reactor would be the best reactor configuration for industrial scale-up. The WV-B-20 activated carbon product was chosen for SO_3 gas sulfonation, since it had the highest catalytic activity of all the carbons at the lowest methanol to oil ratio (Fig. 4). AgForm 200 biochar and WV-B20 (AC) were dried overnight at 110 °C, allowed to cool in a dessicator, and subsequently 5 g of the biochar and AC were weighed and placed in 40 mL glass jars without lids. A total of 4 jars (20 g carbon total) was placed inside a 3.8 L glass jar, exposed to solid SO_3 (20 g – Sigma, 99% non-stabilized) and sealed with a glass top and silicone grease. The contents were kept sealed in the jar for six days at room temperature. Subsequently the jar was opened, vented, the carbon collected and rinsed according to Section 2.4.

2.4. Catalyst washing and IC chromatography

After carbon sulfonation via H_2SO_4 or gaseous SO_3 and initial rinsing, the catalysts were subjected to additional washing. Approximately 50 mL of DI water (preheated to 80 °C) per gram of char was used during washing. The catalyst and hot water were mixed with a stir bar in a beaker mix char and DI water for 1 h. The solution was then allowed to cool, decanted, and the pH of liquid measured. The catalyst was re-washed (same water/char ratio) at room temperature for 15 min, the liquid decanted and the pH measured again. An aliquot of the liquid was saved for Ion Chromatography (IC) analysis to determine the SO_4^{2-} concentration. The catalyst was then dried in an oven overnight at 100 °C. If the SO_4 level was >5 ppm, then the washing steps were repeated until IC analysis indicated a level below 5 ppm (3 times for biochar and 2 times for activated carbon), since sulfur levels in biodiesel must not exceed 5 ppm. Analysis was performed using a Dionex ICS-2000 coupled with a Suppressed Conductivity detector (CD25). The eluent (mobile phase) used was 23 mM KOH (potassium hydroxide). The column used for the analysis was an IonPac AS18 (4 mm × 250 mm) at 30 °C and flow of 1 mL/min. Samples were injected on the column with an auto-sampler at a volume of 20 μL sample size. Standards (sodium sulfate 5, 10, 20 ppm) were analyzed along with the samples to quantify results.

2.5. Catalyst characterization

The physical and chemical characteristics of the biochars, including pH, surface area, bulk density, and the elemental composition were previously determined [9]. Moisture, volatiles and ash content in the biomass, biochar, and treated biochars (i.e., catalysts) were determined by ASTM D5142 using a proximate analyzer (LECO Model TGA701). Ultimate analysis (elemental C, H, N, S, and O (by difference) in % (w/w)) was performed in an ultimate analyzer (LECO, model CHNS-932) following ASTM D3176.

Surface areas of the solid acid catalysts (0.1 g sample size) were measured by N_2 adsorption over a relative pressure range (P/P_0) of 0.05–0.35 using a 7-point BET analysis equation (QuantachromeAUTOSORB-1C; Boynton Beach, FL). Pore size distribution, average pore radius, and total pore volume were estimated from N_2 desorption curves using BJH analysis. All samples were degassed ranging from 100 to 150 °C for 3–4 h before analysis.

Biochar, activated carbon, and subsequently derived solid acid catalysts were analyzed via thermal gravimetric analysis (TGA). Using a Mettler-Toledo 851e Thermogravimetric Analyzer (TGA), samples (approximately 10–15 mg, 0.20 mesh) were raised from room temperature to 900 °C at 10 °C/min and mass loss was recorded versus time and temperature. Helium was used as the carrier gas at a flow rate of 50 mL/min. The TGA analysis was used to design the NH_3 temperature program desorption studies and determine if sulfonation treatment reduced the thermal stability of the carbons.

Ammonia temperature programmed desorption was used to estimate acid site strength of the catalysts. All samples were degassed ranging from 100 to 150 °C for 3–4 h before NH_3-TPD analysis. Samples (0.1 g) were loaded in a quartz U-tube and packed between two quartz-wool layers, degassed at 100 °C for 30 min in helium, saturated with ammonia (pure electronic grade) at 40 °C for 15 min, flushed with helium at 40 °C for 15 min, then desorbed with helium from 40 to 900 °C at 10 °C/min (all flows at 80 mL/min). Desorbed NH_3 was detected using a TCD detector (16× attenuation). TPD measurements were made using a QuantachromeAUTOSORB-1C instrument.

To qualitatively assess the formation of functional groups on the surface of the treated carbon, FTIR analysis (32 scans per sample, 4 cm^{-1} resolution) was performed on the base biochars and AC (i.e., just pyrolyzed and not functionalized) and the sulfonated carbons. The carbon catalysts were crushed to a fine powder and analyzed directly using a Grazing Angle Attenuated Total Reflection Fourier Transform Infrared Spectroscopy (GATR-FTIR, ThermoElectron Nicolet 6700). ATR (Smart Ark – ATR attachment with ZnSe 45° crystal) was used to deconvolute the functional groups on the surface from the bulk phase by using an incident angle with a limited depth of penetration (~150 nm). Our experimental setup allowed

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for a variable angle, so that the incident angle could be optimized for highest sensitivity with different types of samples.

The acid density of the catalysts was estimated by titration and CHNS analysis. One gram of catalyst and untreated carbon was contacted (145 rpm) with 150 mL of a 0.1 N NaOH solution overnight at room temperature and 10 mL of the supernatant solution was back titrated with 1 N HCl (verified each run) until neutral pH (3 replicates). The acid density of the untreated carbons was subtracted from the total acidity of the solid acid catalysts. Sulfonic acid group density was estimated from the sulfur content assuming all S atoms were in the $-SO_3H$ form with baseline sulfur content subtracted.

2.6. Esterification activity

2.6.1. Acid catalyst screening

Each acid catalyst was tested for its ability to form methyl esters using free fatty acids (palmitic and stearic acids) and methanol. The catalysts were tested in a small scale batch reactor system (ReactiTherm, Pierce – Thermo Scientific). The reactor was pre-calibrated to determine temperature output versus setting input and temperature was monitored using a thermocouple. Pure palmitic and stearic acids (99+%) were used as model free fatty acids and purchased for use (Sigma–Aldrich).

A known amount of catalyst (typically 0.2 g) was charged into a vial (5 mL total volume) with a known initial volume of palmitic (C_{16}-saturated FFA) or stearic (C_{18}-saturated, both at 200 ppm) and anhydrous methanol (4 mL, excess methanol). The mixture was then heated at 55–60 °C and sub-samples taken as function of time to determine the formation of methylesters. Control reactions consisted of the untreated char (negative control) or use of HCl (positive control). The liquid sub-samples were analyzed and quantified using a GC/FID or GC/MS and n-hexadecane was used as an internal standard to determine the concentration of methylesters formed. Fractional removal or % conversion of palmitic or stearic acid were based on the defined initial concentrations of the FFAs (maximum theoretical amount of methyl ester that could form) and the concentration of the methylesters of the FFAs that formed during the catalytic reaction, thus %X or conversion = $[C_{final}(\text{FFA-ME})]/C_{initial}(\text{FFA}) \times 100$, where C is concentration, FFA is free fatty acid, and FFA-ME is fatty acid methyl ester.

2.6.2. Acid catalyst testing using simulated feedstocks

The acid catalysts identified as having high esterification activity with palmitic and stearic acid were then tested for activity using spiked soybean oil (Kroger Brand Pure Vegetable Oil) and rendered poultry fat (Fieldale Farms Poultry, LLC Baldwin, GA 30511; %FFA of 2.53 ± 0.11 and moisture content of 0.16 ± 0.05 [%]). Catalytic reactions were performed in a 200 mL (three-neck round-bottom flask [24/40] LabGlass with a thermometer adaptor and RTD probe) or a 50 mL single neck flask equipped with a thermal well and a magnetic stirring bar, both connected to a water-cooled condenser (Liebig Condenser) and an electronic heater/stirrer (VWR model # VMS C7). In some cases reactions were carried out in capped 25 mL Erlenmeyer flasks. Batch reactors were immersed in a water bath and the temperature was maintained at 60–65 °C with the RTP probe. The reaction mixture was rapidly stirred using a magnetic stirring bar (500–800 rpm). Palmitic and stearic acid were added to poultry fat to generate ~10–13.5% FFAs in the fat. This mixture was heated to 60 °C and agitated to generate a clear solution and the temperature then raised to 65 °C. The solid acid catalyst (3 and 6 wt.%) was then mixed at a methanol to FFA molar ratio of 37:1 and 54:1, and transferred to the batch reactor where the esterification reaction was allowed to proceed for 2 h at 65 °C under agitation. After cooling the mixture was filtered into a graduated cylinder and allowed to separate into two layers – a top layer (methanol) and bottom layer (fat, FFA-methylesters). Both layers were analyzed by gas chromatography using ASTM Method D6584-07 and by potentiometric titration for total acids using ASTM Method 664-07. When calculating percent conversion using the ASTM Method 664, Eq. (1) was used and based on the measured total acid number (TAN).

$$\text{Conversion}(\%) = \frac{\text{Initial acid number} - \text{final acid number}}{\text{Initial acid number}} \times 100, \quad (1)$$

where

$$\text{the acid number}(\text{mg KOH/g}) = \frac{(A - B) \times M \times 56.1}{W}, \quad (2)$$

and M is the concentration of the KOH solution (mol L^{-1}); A the volume of KOH standard solution used in the titration (mL); B the volume of KOH standard solution used in the titration of the blank (mL); 56.1 the molecular weight of KOH (g mol^{-1}); and W the sample weight (g).

In similar experiments, solid acid catalysts were tested for the capability of esterifying palmitic and stearic acid in soybean oil. Defined amounts of palmitic and stearic acid were added to a known amount of soybean oil to generate 5–15 wt.% FFAs in the oil. This mixture was heated to 60 °C and agitated to generate a clear solution and the temperature then raised to 65 °C. A defined amount of solid acid catalyst (2–8 wt.%) was then mixed with methanol (6:1–30:1 MeOH:oil + FFA ratio) and transferred to the batch reactor where the esterification reaction was allowed to proceed for defined periods at 65 °C under agitation. Liquid subsamples (0.1 mL) were taken as a function of time to determine FFA and methylester concentrations.

2.7. Analytical methods

2.7.1. Standards and quality control

Standard stock solutions were prepared from certified analytical reference materials (Matreya Company, Pleasant Gap, PA) which included, n-hexadecane, methyl pentadecanoate, methyl hexadecanoate (palmitic acid, methyl ester), methyl octadecanoate (stearic acid, methyl ester), methyl heneicosanoate, hexadecanoic acid, and octadecanoic acid (10,000 ppm, dissolved in a 1:1 mixture of dichloromethane and heptane). Each standard was analyzed in triplicate to determine standard deviations (SD) and relative standard deviations (RSD) of response factors.

2.7.2. Solid acid catalyst reactions with palmitic and stearic acids

Standard curves for methyl hexadecanoate (palmitic acid, methyl ester) and methyl octadecanoate (stearic acid, methyl ester), using n-hexadecane as a quantitative internal standard, were prepared and used to quantify palmitic and stearic acid methyl esters. Conversion of palmitic and stearic acid to methyl esters was quantified using GC/FID or GC/MS methods.

Methyl ester concentrations were determined using the GC/FID with direct on-column 1 μL injections under conditions specified in ASTM Method D6584-07. An SRI Model 610 gas chromatograph equipped with an FID detector and capillary column (Restek MXT widebore metal column, 15 m) was used with the following temperature program; 50 °C for 1 min, ramped to 180 °C at 15 °C/min, ramped to 230 °C at 7 °C/min, ramped to 380 °C at 30 °C/min and held 10 min.

In some cases methyl hexadecanoate and methyl octadecanoate concentrations were determined using GC/MS. An Agilent 6890 chromatograph operated with split injection (50:1) and equipped with a MS detector (Agilent 5973) and capillary column (HP-5, 0.25 mm I.D., 0.25 μm film thickness, 30 m) was used, with the

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following conditions and temperature program; solvent delay of 2.8 min, inlet 230 °C, detector 280 °C (MS interface temperature), 1 mL/min He, 50 °C for 1 min followed by a ramp at 25 °C/min to 200 °C, and then a ramp at 3 °C/min to 240 °C and held for 15 min. Masses were scanned from 30 to 500 mass units and the injection volume was 1 μL. The methyl esters were identified based on retention times with standards and mass spectral analysis (MSD ChemStation D.03.00.611 and NIST 98 database). Quantification was made using n-hexadecane as an external standard (500 ppm) and single concentration standards of methyl hexadecanoate and methyl octadecanoate (500 ppm).

2.7.3. Solid acid catalyst reactions with rendered poultry fat

Conversion of palmitic and stearic acid to methylesters in poultry fat was quantified using GC/FID and ASTM Method D6584-07, and by potentiometric titration using ASTM Method D664-07 with a KEM Model AT-610 automatic potentiometric titrator.

In the GC method a 100 μL sample (original, spiked, and reacted samples) was prepared for gas chromatographic analysis by adding 100 μL of tricaprin standard (internal standard for quantifying glycerides) and 100 μL of N-methyl-N-trimethylsilyltrifluoracetamide (MSTFA) to derivatize the glycerides. After 20 min at room temperature, 8 mL of n-heptane was added and to 2.0 mL aliquots of the derivatized solutions was added 100 μL of 10,000 ppm solutions of n-hexadecane, methyl pentadecanoate and methyl heneicosanoate standards to make a 500 ppm internal standard for quantifying methyl palmitate and methyl stearate. The samples were analyzed using conditions listed for oil analysis by ASTM D6584-07 (Section 2.7.1).

Free fatty acid levels (original, spiked, and reacted samples) using potentiometric titrations were performed in the following manner using ASTM 664. Samples (~20 g of unfortified control sample oils or ~2 g of biodiesel reaction products) were dissolved in a mixture of 50% toluene and 49.5% 2-propanol containing 0.5% water and titrated potentiometrically using a solution of 0.1 N potassium hydroxide in 2-propanol (the electrode was a glass combination electrode with a saturated lithium chloride solution). The meter readings are plotted automatically against the respective volumes of titrating solution and the end points are recorded at well-defined inflections in the resulting curve. The Total Acid Number (TAN) was determined based on Eq. (2).

2.7.4. Solid acid catalyst reactions with spiked soybean oil

Conversion of palmitic and stearic acid to methylesters in soybean oil was quantified using the methods as reported in Section 2.7.2.

3. Results

3.1. Char characterization

Significant differences in biomass composition, which ultimately may have affected char structure, were observed. Peanut hulls had a significantly higher ash content and lower hemicellulose concentration compared to pine pellets and chips (Table 1). The high ash content of the peanut hulls is reflected in high levels of calcium and potassium in the biochars (Ca, 4000–4600 mg L^{-1}; K, 15,000–20,000 mg L^{-1}). Biochars formed at low temperature (<600 °C) and relatively short holding times (<1 h) typically have low surface area. The generated biochars had surface areas ranging from 1 to 4 m^2/g and nonexistent pore structure, much lower than the activated carbons (1000–1900 m^2/g – Table 2). These surface areas are similar to chars previously used to synthesize solid acid catalysts and generated from cellulose, sucrose, and glucose via low temperature pyrolysis [4–7 m^2/g]; [10]. However, it is interesting to note that sulfonation using H_2SO_4 significantly increased surface area and pore structure formed in the biochars, suggesting activation/oxidation of the carbon also occurred with sulfonation (Table 2). Additionally, the resulting surface areas were significantly larger than those reported for sulfonated biochars generated from fast pyrolysis char [8]. This effect was not observed in the activated carbon (H_2SO_4 and SO_3 sulfonation) or biochar when using SO_3 (Table 2).

Table 2
Physical characteristics of solid acid carbon catalysts.

Biochar/catalysts properties	Surface area (m^2/g)	Total pore volume (cm^3/g)	Pore radius (Å)
PHC-400C	1–4[a]	ND	ND
PHC-400C-SO4	242	0.13	10.5
PPC-500C	10	0.0048	9.57
PPC-500C-SO4	BD	ND	ND
AgForm 400C	1.13	0.0007	12
AgForm 400C-SO4	338	0.18	10.6
AgForm 400C-SO3	1.23	0.0005	7.8
AgForm 400C-SO3-6×	0.77	0.0005	13.8
PCC 400C	BD	ND	ND
PCC 400C-SO4	365	0.20	10.5
WVB-20	1944	1.2	12.2
WVB-20-SO4	1391	0.76	11.0
WVB-20-SO3	1137	0.63	11.1
WVB-20-SO3-6×	587	0.34	11.5
BX-7540	1165	0.36	6.1
BX-7540-SO4	967	0.34	7.1

PHC, peanut hull char; PCC, pine chip char; PPC, pine pellet char.
AgForm: AgForm 200 biohcar, 400 °C; pyrolysis, 1 h.
WVB-20: MeadWestvaco, wood activated carbon; BX-7540 MeadWestvaco, wood activated carbon.
SO_4, H_2SO_4 sulfonated; SO_3, gaseous SO_3; ND, not determined; 6× catalyst used 6 times.
BD, below detection limit, area too low to measure.
[a] Based on the previous analysis of biochars generated between 400 and 600 °C and 1 h [9].

Sulfonation clearly increased the acid density as measured by base titration and the sulfur content of the carbon (Table 3). The acid density measured by base titration was significantly larger than that indicated by the sulfur content, suggesting that sulfonation using H_2SO_4 and SO_3 not only created sulfonic acid groups (Fig. 1), but created additional weak acid groups (e.g., —COOH). The presence of weak acid groups was also indicated by the formation of an IR absorption band at ~1725 cm^{-1} (carbonyl stretching, —COOH – see Fig. 1 and Table 1, supplemental information). Two trends in acid density were observed – H_2SO_4 sulfonated biochars had higher acid densities than AC (based on CHNS) and SO_3 sulfonation generated higher acid density carbons (Table 3).

3.2. ATR, TGA, and TPD analysis

ATR analysis of the sulfonated carbons confirmed the formation of a sulfonic acid functional group (1035, 1200 cm^{-1} [11,12]) on the biochar and AC surface. AgForm biochar (400 °C) and AC when sulfonated with H_2SO_4 at 100 °C formed a distinct peak at 1050–1100 cm^{-1} and this peak was qualitatively larger using SO_3 (Fig. 1 and Table S-1; other biochars not shown).

Thermal gravimetric analysis was used to define the NH_3-TPD method and understand the impact of carbon sulfonation on the thermal stability of the solid acid catalysts. Sulfonation of the biochars either by H_2SO_4 or by SO_3 lowered the temperature at which mass loss occurred in the TGA analysis. Using the first derivative of the mass loss versus time data, the onset of thermal decomposition was initiated between 200 and 250 °C for sulfonated biochars, compared to 350–400 °C for untreated biochars (data not shown). Similarly, sulfonation of the activated carbon using H_2SO_4 lowered the temperature at which mass loss occurred in

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Table 3
Compositional analysis and acid density of the solid acid carbon catalysts.

Catalysts	Carbon (%)	Nitrogen (%)	Sulfur (%)	SO_3H density (mmol/g)[a]	Acid density (mmol/g)
WVB-20	82.6 ± 0.82	0.39 ± 0.07	0.05 ± 0.02	0.0	0.23
BX-7540	87.9 ± 0.22	0.49 ± 0.04	0.01 ± 0.01	0.0	0.144
AgForm-400C	68.4 ± 1.7	2.3 ± 0.15	0.10 ± 0.01	0.0	0.605
PCC-400C	65 ± 0.38	1.8 ± 0.6	0.10 ± 0.03	0.0	0.41
PHC-400C	64 ± 1.7	2.0 ± 0.30	0.14 ± 0.05	0.0	0.14
PPC-500C	76.2 ± 0.15	0.62 ± 0.065	0.10 ± 0.0	0.0	ND
AgForm-400C-SO4	60.4 ± 0.70	2.26 ± 0.05	1.50 ± 0.06	0.45 ± 0.001	5.87
AgForm-400C-SO3	62.44 ± 0.38	2.55 ± 0.04	2.82 ± 0.13	0.86 ± 0.02	ND
AgForm-400C-SO3-6×	61.96 ± 0.34	2.34 ± 0.04	2.04 ± 0.13	0.62 ± 0.025	ND
PHC-400C-SO4	68 ± 1.1	2.0 ± 0.10	2.1 ± 0.04	0.61 ± 0.03	5.65
PPC-500C-SO4	62 ± 0.76	0.40 ± 0.08	1.2 ± 0.11	0.34 ± 0.01	ND
PCC-400C-SO4	58 ± 0.23	0.39 ± 0.13	2.30 ± 0.08	0.69 ± 0.006	4.40
WVB-20-SO4	75.8 ± 2.2	2.26 ± 0.05	0.68 ± 0.02	0.20 ± 0.01	2.59
WVB-20-SO3	64.0 ± 0.85	0.56 ± 0.04	2.63 ± 0.08	0.81 ± 0.01	2.23
WVB-20-SO3-6×	61.96 ± 0.34	0.62 ± 0.06	1.80 ± 0.04	0.55 ± 0.002	ND
BX-7540-SO4	90.0 ± 0.42	0.71 ± 0.09	0.34 ± 0.02	0.10 ± 0.002	0.641

AgForm: AgForm 200 biochar, 400C pyrolysis at 400 °C; 100 °C sulfonation temperature; see Table 2 for other abbreviations.
P, pyrolysis temperature; S, sulfonation temperature; ND, not determined (not enough material for SO_3 treatment).
[a] Calculated from sulfur content assuming all S atoms are in the —SO_3H form with baseline sulfur content subtracted.

the TGA analysis (~250–300 °C). Contrary to the biochars, sulfonation of activated carbons using SO_3 did not lower the onset of thermal decomposition, which remained at 500–550 °C (data not shown). These data indicated that sulfonation of the biochars partially oxidized the structure, reducing thermal stability, and provided a rational for limiting our TPD desorption temperature to 300 °C.

Three acid sites, a weak acid (90–100 °C), a medium acid (150–170 °C), and strong acid (210–225 °C) were observed in the NH_3-TPD experiments (Fig. 2). Sulfuric acid treatment of the biochar appeared to generate a higher density of acid sites compared to SO_3 treatment (assuming peak area is proportional to acid site density, Fig. 2). Gaseous SO_3 treatment of the activated carbon appeared to generate a higher density of acid sites compared to H_2SO_4 treatment (assuming peak area is proportional to acid site density – Fig. 2B). Both of these trends were observed in the SO_3H density measurements as well (Table 3).

3.3. Esterification catalytic activity

Control studies clearly indicated that sulfonation of the carbons was required for catalytic activity and esterification did not take place without the catalysts. Controls consisted of a method blank (methanol plus palmitic or stearic acid) and catalyst blank (non-sulfonated carbons). Reactions (0.20 g peanut hull char, 5 mL methanol, and 200 ppm of palmitic or stearic acid) conducted at 50 °C for 4 h (data not shown) or 58 °C for 1 h (Fig. 3) indicated no formation of methylesters, contrary to positive controls using

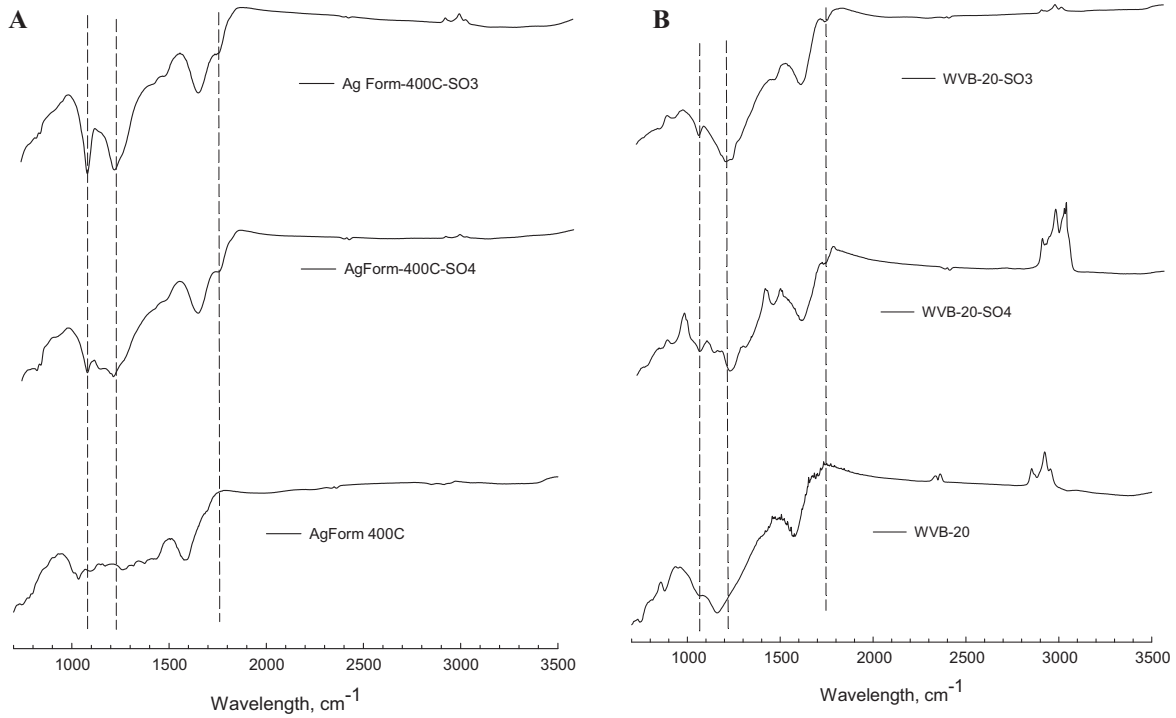

Fig. 1. ATR analysis of AgForm biochar (A) and WVB-20 (B) char sulfonated using H_2SO_4 or SO_3.

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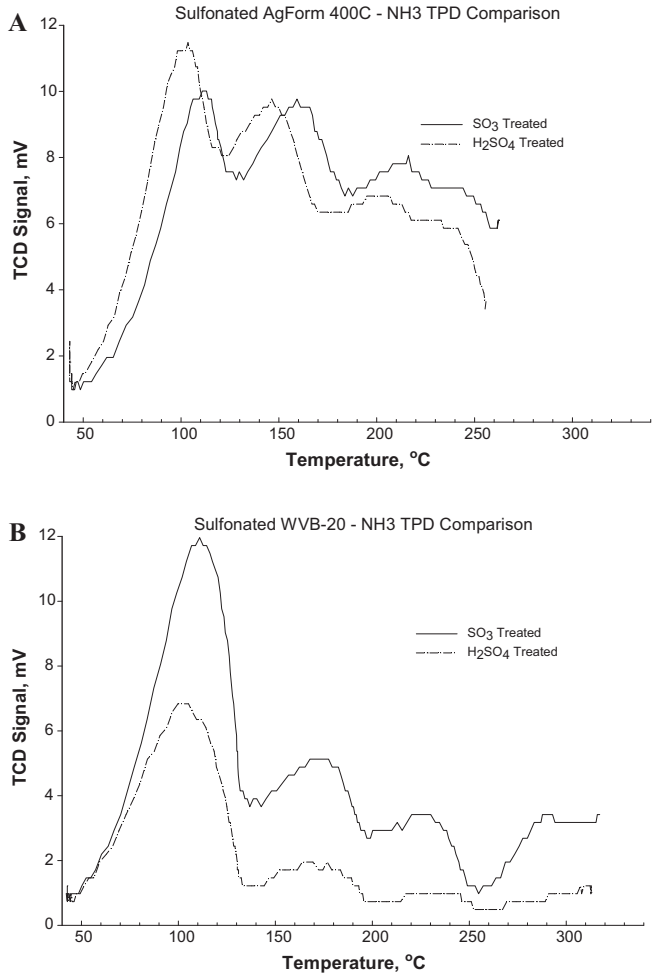

Fig. 2. Ammonia TPD analysis of AgForm biochar (A) and WV-B20 (B) char sulfonated using H_2SO_4 or SO_3.

HCl (1 drop ~ 38% HCl) under identical conditions, which resulted in 100% conversion of the fatty acids to methylesters (data not shown).

All sulfonated biochars were demonstrated to be catalytically active for esterification of palmitic and stearic acid with methanol. Biochars treated with ozone only (i.e., weak acid functional groups on the surface, e.g., carboxylic acid groups) were not active and chars ozonated followed by sulfonation resulted in esterification activities similar to chars that were directly sulfonated (Fig. 3). The esterification rate and fractional conversion of palmitic and stearic acid were similar, but in the case of stearic acid appeared to be reduced when using granular catalysts (Fig. S-3). Solid acid catalysts generated from pelletized peanut hulls had higher catalytic activity when compared to pine pellets, except in the case of stearic acid esterification using granular forms of the catalysts (Fig. S-4). Biochars synthesized at lower temperatures and sulfonated at lower temperatures (400 °C for pyrolysis, 100 °C for sulfonation) had the highest activity (Fig. S-5). Additionally, sulfonated biochar generated from pine chips (not pellets) appeared to maintain higher esterification activity upon reuse relative to peanut hull char (e.g., after 4 uses 95% conversion of palmitic for PCC compared to 75% for PHC) and repeated reuse of the catalysts indicated a reduction in activity, but not a complete loss in activity (after 6 uses, 65% conversion of palmitic, compared to 45% – Fig. S-6).

Solid acid catalysts derived from wood based activated carbon, particularly WV-B20, had significantly higher esterification activities than the biochar catalysts (Fig. 4 and Table 4). A series of batch kinetic studies were conducted in which the esterification rates were compared between the two types of sulfonated carbons at methanol to oil ratios of 6, 20 and 30 to 1, and 13.2% total FFAs (in spiked soybean oil, Section 2.6.2). After a 3 h reaction time, 80% of the fatty acids were converted, compared to 40% or less for the biochar catalysts (Fig. 4A and B). Increasing the methanol concentration clearly increased conversion for the biochar catalyst, yet did not approach the levels achieved by WV-B20 even at a 30:1 methanol to oil ratio (Fig. 4D). Interestingly, increasing the methanol concentration did not affect the conversion rates using WV-B20 (Fig. 4C).

Given the significantly higher esterification rates for WV-B20 compared to the other solid acid catalysts (Fig. 4 and Table 4) it was decided to compare catalytic activity between H_2SO_4 and gaseous SO_3 WV-B20 sulfonated carbons. Sulfur trioxide treated WV-B20 had significantly higher esterification activities. For example, a reaction time of 6 h was required for complete conversion of the free fatty acids using H_2SO_4 WV-B20, compared to 2 h for SO_3 sulfonated carbon (Fig. 5). Correspondingly, the average esterification rate during the course of the reaction (Eq. (3)) was ~20 times higher for SO_3 sulfonated carbon (Fig. 5). Esterification reaction rates were calculated from the batch data at different points,

$$-r = \frac{VC_{AO}}{W} \times \frac{\Delta K}{\Delta t} \quad (3)$$

where r is the rate of esterification (mg g^{-1} min^{-1}), V the volume (L), C_{Ao} the initial concentration of fatty acid (mg L^{-1}), or $C_{Ao}V$ the initial mass of fatty acid (mg), W the mass of catalyst (g), ΔX the change in fractional conversion over Δt, and Δt the change in time (min).

3.4. Acid catalyst regeneration and reuse

Since catalytic activity declined with repeated use, different regeneration techniques were explored to determine if activity could be regenerated. Rinsing the biochar catalyst with methanol in between batch reactions was not effective, since this resulted in declining activity (Figs. S-5 and 6). Subsequently, contacting the char catalyst with heptane and then drying at 125 °C or 250 °C was determined to significantly increase catalytic activity of the char catalyst (Fig. 6). Finally, drying the acid catalyst at 125 °C (1 h) between uses, without solvent contact, resulted in a consistent, high catalytic activity with repeated uses of the char catalyst (Fig. 6).

Since the previous catalyst reuse studies were conducted with a large excess of methanol and SO_3 sulfonated carbons demonstrated high esterification activity, additional reuse tests were conducted using the SO_3 sulfonated carbons at 10:1 methanol to oil ratios (10 wt.% catalyst, 60 °C, 3 h reaction). As in the previous studies the biochar catalysts declined in activity if not regenerated between uses, yet such a regeneration step was not required for the SO_3 sulfonated WV-B20 catalyst; fractional conversion of palmitic and stearic acid (not shown) remained >90% after 6 cycles (Fig. 7).

3.5. Solid acid esterification activity in fats and oils

Catalytic testing of the solid acid catalyst generated from biochar indicated that sulfonated biochar (100 °C, 12 h) generated from 400 °C pine chip biochar had the most robust esterification activity and thus, was tested for activity in fats and oils. Conversion of FFAs in oil or poultry fat (10–14%) ranged between 50 and 80% (65 °C, 2 h) measured using GC/FID methods and approached 100% when measured using the total acid number (Table S-2). Increasing the methanol to FFA ratio also increased the measured conversion of

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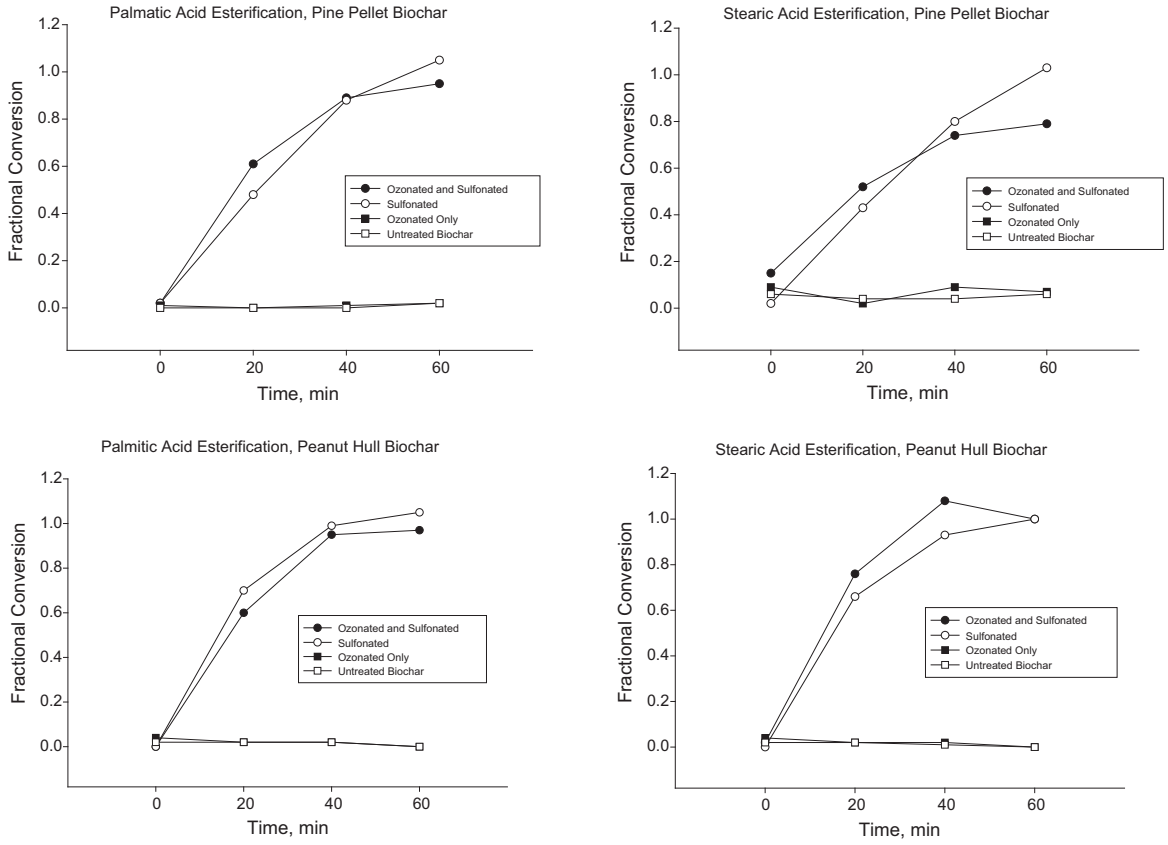

Fig. 3. Comparison of esterification catalytic activity between sulfonated (H_2SO_4) pelletized peanut hull and pine biochar (500 °C pyrolysis, sulfonation 250 °C). Reaction conditions were 200 ppm palmitic or stearic acid in methanol (32,000:1), 4 wt.% biochar, and 58 °C.

FFAs to methyl esters. Given the limited supply of SO_3 sulfonated catalyst and poultry fat, we were not able to test esterification activity in poultry fat, yet the high activity of WV-B20-SO3 in spiked soybean oil suggests esterification activity would be high at industrially relevant methanol to oil ratios (<10:1).

4. Discussion

Solid acid carbon catalysts (e.g., attached —SO_3H groups) have recently been generated from refined sugars (e.g., pure cellulose, glucose and starch) and demonstrated to catalyze esterification reactions [6]. In order to generate the solid acid catalysts, the refined carbohydrates are pyrolyzed at low temperatures (400–500 °C) to generate a cross-linked, polyaromatic polymer that is subsequently sulfonated using concentrated H_2SO_4 (or other sulfonation agents). Our results indicate that solid acid catalysts can be generated from crude biomass, contrary to refined carbohydrates, using a slow, low temperature pyrolysis process (1–20 °C/min, 400–500 °C) or directly from biomass derived activated carbon.

It is clear that the type of sulfonation process and carbon structure affected acid density and catalytic activity. Sulfonation of the biochar using H_2SO_4 increased biochar surface area and generated acid densities higher then observed in activated carbon (AgForm 400C-SO4 vs. WVB-20-SO4); yet, esterification rates and yields were higher using activated carbon. We attribute this difference in activity to the larger pore size and volume in the activated carbon, thus increasing diffusion rates and accessibility

Table 4
Comparison of initial batch esterification rates between different solid acid catalysts.

Catalysts	MeOH:oil + FFA ratio	Catalyst (wt.%)	T (°C)	FFAs (wt.%)	Palmitic acid reaction rate (mg g^{-1} min^{-1})	SO_3H density (mmol/g)	TOF (min^{-1})
AgForm-400C-SO4	6	7.5	57	11	0.7	0.45 ± 0.001	0.006
	20	5.0	57	7.5	4.7	–	0.04
PHC-400C-SO4	6	5.0	57	7.5	5.9	0.61 ± 0.03	0.04
	20	5.0	57	7.5	23.3	–	0.15
WVB-20-SO4	6	7.5	57	11	6.1	0.20 ± 0.01	0.12
	10	6.5	57	10	7.0	–	0.13
	20	5.0	57	7.5	9.2	–	0.18
BX-7540-SO4	6	7.5	60	11	4.0	0.10 ± 0.002	0.16
	20	8.6	60	11	14.3	–	0.56
WVB-20-SO3	10	2.0	60	10	37	0.81 ± 0.01	0.18

TOF, turnover frequency based on palmitic acid reaction rate and SO_3H density.

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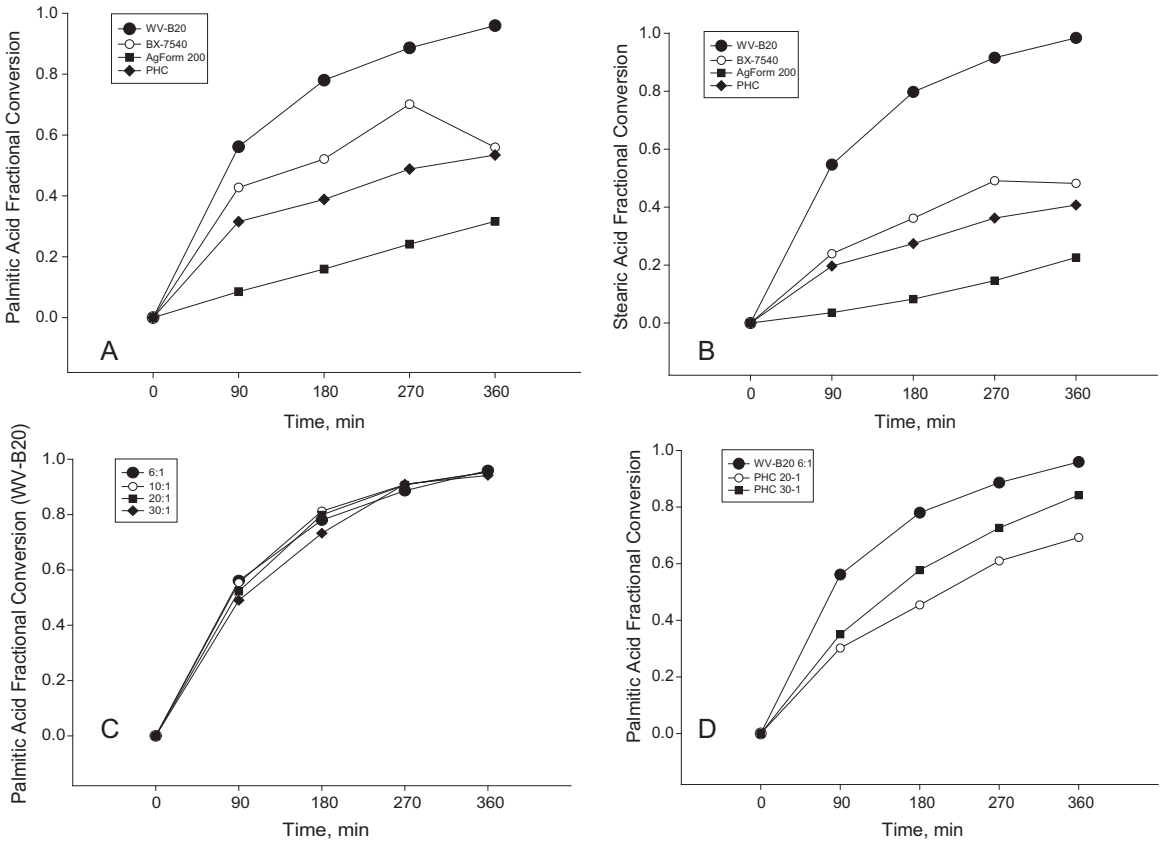

Fig. 4. Comparison of esterification catalytic activity between sulfonated (H_2SO_4, 100 °C) WV-B20 and various biochars under reaction condition of 5 wt.% palmitic and stearic acid spiked (10 wt.% total FFA) in soybean oil and methanol (A and B, 6:1 molar ratio), 4–7.5 wt.% catalyst at 57–59 °C.

to active sites. The lower acid densities in the activated carbon using H_2SO_4 sulfonation can be attributed to higher cross linking and degree of polymerization in the AC (900–1000 °C) compared to biochar (400 °C), thus reducing sulfonation efficiency [12,13]. The increased acid density in the SO_3 sulfonated carbons at significantly lower temperatures then H_2SO_4 can be attributed to the fact that SO_3 is much more reactive and selective than H_2SO_4, since the entire SO_3 group is inserted into the carbon backbone [14].

Overall, our results are comparable to the literature for solid acid catalysts derived from refined carbohydrates. The surface area of the H_2SO_4sulfonatedbiochar (350 m^2/g) is significantly larger than the 1–8 m^2/g reported for carbonized and sulfonated refined carbohydrates [10,15], but pore volume was similar (0.1–0.2 vs. 0.4–0.8 cm^3/g [10]). Acid density based on elemental sulfur analysis (Table 3) was significantly higher in the pine chip char and potentially accounted for the higher esterification activity of this solid acid catalyst. The measured acid density in our catalysts were on average lower (0.2–0.9 mmol SO_3H/g), but comparable to solid acid catalysts derived from glucose (0.7–1.5 [10,15,16]), starch (1.8 [10]), glucose impregnated carbonized polymer (0.7–2.4 [17]), and cellulose (1.7 [10]). The higher acid density in the sulfonated pine chip char and overall lower acid density compared with acid catalysts prepared from refined carbohydrates may have been due to the larger particle size of the starting biomass (8 mm dia., peanut hull pellets; 1–5 mm thick pine chips). The biomass particles we have used may not be conducive to uniform or complete pyrolysis (due to temperature gradients within the particles) and complete formation and cross linking of the polycyclic aromatic sheets from cellulose and lignin in the biomass may not have occurred. These aromatic sheets are the anticipated sites for sulfonation and active sites in the catalysts.

Key to industrial use of solid acid catalysts is their ease of recovery and reusability. Repeated reuse of biochar solid acid catalysts (H_2SO_4 sulfonated), without regeneration between steps, resulted in a decline in activity. Catalytic activity continued to decline or was not fully recovered even after washing with solvents such as methanol and heptane, indicating bound fatty acids were not inhibiting the reaction. However, when the catalysts were dried between use (125 °C), activity remained >90% (Fig. 6). These results suggest that water adsorption may have caused the decline in activity in our catalysts and/or could have inhibited the esterification reaction. The difference between the total acid density and SO_3H group density was significantly higher in the H_2SO_4biochars compared to the SO_3 sulfonated AC indicating a much higher density of weak acid sites that would provide hydrogen bonding sites for water (e.g., carboxylic acids). In addition, the reduction in acid density after 6 uses indicate that leaching of active sites (loss of sulfonated aromatic fragments) also contributed to the decline in activity and was due to particle attrition during agitation (evident by the significant reduction in surface area and pore volume after 6 uses – Table 2).

Similar to our results, Mo et al. [17], synthesized a solid acid carbon catalyst via glucose impregnation of Amberlite XAD1180, followed by low temperature pyrolysis (300 °C) and sulfonation (concentrated H_2SO_4 was added prior to pyrolysis). This catalyst when recovered and dried at 100 °C between uses maintained catalytic esterification activity for 6 cycles, unlike sulfonated amorphous carbon generated from glucose [10]. Similarly, solid acid catalysts generated from pyrolyzed expanded starch (Starbon®) or

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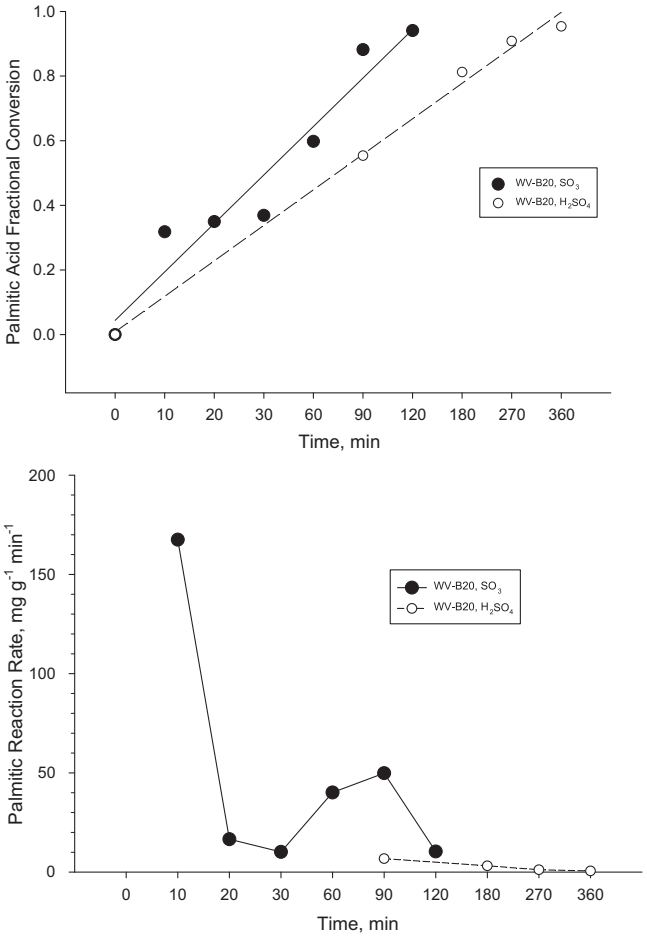

Fig. 5. Comparison of esterification catalytic activity between SO_3 and H_2SO_4 sulfonated WV-B20 carbons under reaction condition of 11 wt.% FFAs in soybean oil and methanol (10:1 molar ratio), 2 wt.% SO_3 catalyst, and 7.5 wt.% H_2SO_4 catalyst at 57–59 °C (results were similar for stearic acid).

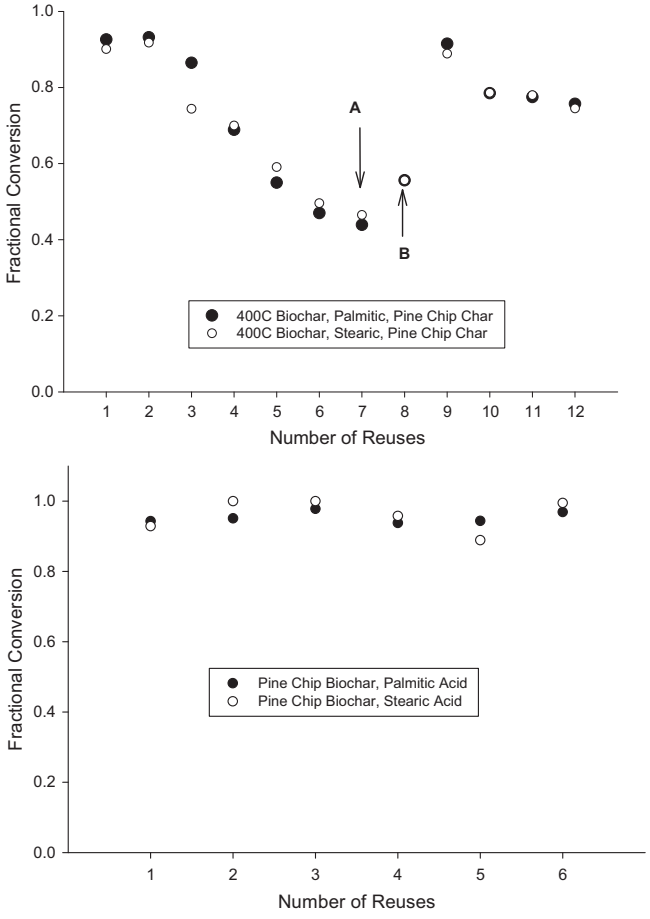

Fig. 6. Effect of heating the acid catalyst in heptane (top, 250 °C) or heating only (bottom, 125 °C) on esterification activity (550 and 454 ppm palmitic and stearic acid; 15,470:1 molar methanol to FFA ratio) during reuse. The period before A indicates methanol rinsing only, after A indicates heptane rinsing following by heating at 250 °C, and after B represents heptane rinsing followed by heating 125 °C (top). The catalyst was generated from pine chip biochar pyrolyzed at 400 °C and sulfonated at 100 °C for 12 h. All reactions were performed at 60 °C with 14 wt.% catalyst 1 h.

ordered mesoporous carbon (OMC), when washed in acetone or water and dried between reuse maintained activity for at least 3–5 cycles [18].

However, three research groups recently reported maintaining esterification activity of solid acid catalysts without regeneration (the catalysts were simply filtered from the reaction mixture and reused). Refs. [10,15] report that solid acid carbon catalysts generated from starch and glucose, respectively, can be reused multiple times without a regeneration step in the esterification of oleic acid with ethanol and waste cooking oils with methanol. Ref. [19] reports similar results using a newly synthesized Amberlyst BD20 solid acid catalyst. All of these researchers performed their catalytic reactions at 80 °C (significantly higher than our work and others at 55–65 °C – Table S-2), which may account for the different regeneration requirements. Reaction temperatures at 80 °C may have prevented (or minimized) significant adsorption of water on the catalyst surface, thereby preventing reaction inhibition. Interestingly, the Amberlyst BD20 catalyst was treated with distilled water, 50, 70, and 95 wt.% ethanol, ethanol, acetone, and petroleum ether in series before catalytic testing. It is not clear why this solvent pretreatment was performed, whether it is needed to activate the catalyst, nor has the chemical structure of the catalyst been reported [19].

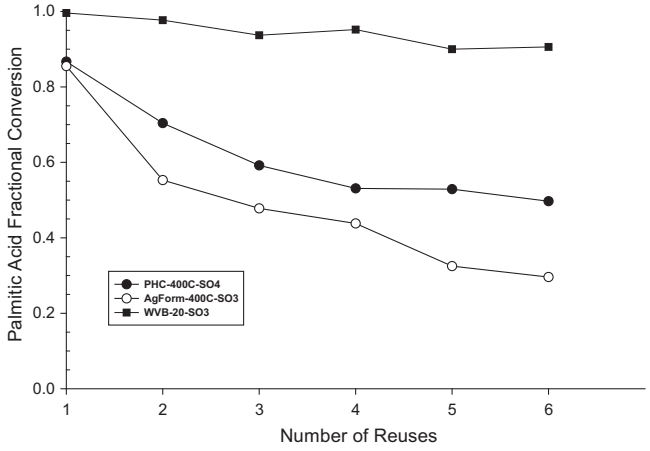

Fig. 7. Effect of sulfonation method on solid acid catalyst re-use (palmitic acid esterification) activity [10 wt.% catalyst, 60 °C, 3 h, 10 wt.% FFAs (5% palmitic and stearic acid), spiked in methanol and soybean oil at 10:1].

5. Conclusions

Both biochar generated by biomass pyrolysis and wood based activated carbon were successfully sulfonated using H_2SO_4 and

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SO_3, yielding solid acid carbon supported catalysts catalytically active for esterification. H_2SO_4 sulfonation of the biochar clearly increased surface area and pore structure of the biochars, yet did not generate acid densities as high as SO_3 sulfonation. Wood based activated carbon sulfonated using SO_3 generated a solid acid catalyst with the highest esterification activity and reuse capability due to a combination of particle strength, hydrophobicity (difference between total acid density and SO_3H group density), and high surface area (1137 m^2/g) and sulfonic acid group density (0.81 mmol/g). The significant decline in esterification activity for the biochar catalyst upon reuse was due to water adsorption, particle attrition during agitation and strong acid site leaching as evidenced by the measurable reduction in surface area (338–1.2 m^2/g) and sulfonic acid group density (0.86–0.62 mmol/g).

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cattod.2012.02.006.

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