

1            **Solid acid catalysts produced by sulfonation of**  
2 **petroleum coke: dominant role of aromatic hydrogen**

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11 **Abstract:** Carbon based solid waste materials have been intensively investigated for the preparation of  
12 solid acid catalysts through sulfonation, but the acidity varies significantly depending on the material. In  
13 this study, the role of aromatic hydrogen in sulfonation with concentrated H<sub>2</sub>SO<sub>4</sub> was investigated using  
14 petroleum coke (petcoke), graphite, and biochar as the carbon materials. Through ball milling and  
15 calcination, the amount of aromatic hydrogen on the petcoke could be increased or decreased,  
16 respectively. After sulfonation at 80 °C with concentrated H<sub>2</sub>SO<sub>4</sub>, the produced acidity (i.e., -SO<sub>3</sub>H  
17 groups) increased as the amount of aromatic hydrogen increased from essentially no acidity on graphite  
18 to 0.55 mmol/g on biochar and 1.25 mmol/g on petcoke (particle sizes of 45-90 μm) indicating the  
19 importance of aromatic hydrogen during sulfonation. Calcination (350 °C for 1 h) of the petcoke before  
20 sulfonation decreased the acidity to 0.59 mmol/g, while ball milling (with isopropanol and silica for 24 h)  
21 increased the acidity to 3.73 mmol/g. The sulfonated petcoke samples were used as catalysts for the  
22 esterification reaction between octanoic acid and methanol at 60 °C and the turnover frequencies were  
23 48-85 h<sup>-1</sup>. The results give insights on the preparation of solid acid catalysts from carbon materials and  
24 highlight the application of petcoke without activation as a feedstock for esterification catalysts.

25 **Keywords:** Petroleum coke; sulfonation; solid acid; aromatic hydrogen; esterification

26

## 27 **1 Introduction**

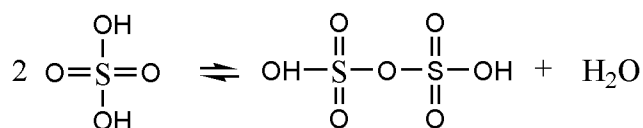
28 Petroleum coke or petcoke is a by-product of the oil sands industry and is mainly a carbonaceous material  
29 (> 80 wt% C) containing some heteroatoms and minerals. The largely stockpiled petcoke - global storage  
30 is increasing at a rate of ~6 million tonnes per year (United Nations Statistics Division, 2019) - has  
31 become a major source of pollutants, including poly aromatic hydrocarbons and molybdenum, and  
32 occupies significant land area even in urban areas (Caruso et al., 2015; Robertson et al., 2019; Zhang et  
33 al., 2016). Depending on the source, the petcoke may contain significant levels (>6 wt%) of sulfur, which  
34 limits its direct use as a fuel for boilers, anodes for the smelting industry, and cement manufacture (Hill et  
35 al., 2014). There is the potential, however, for the direct conversion of petcoke into a solid acid catalyst,  
36 which can be used for esterification and transesterification of acids and lipids into biodiesel (Cheng et al.,  
37 2017; Toda et al., 2005; Wu et al., 2017a, 2017b). Unlike homogeneous acid catalysts, carbon-based solid  
38 acid catalysts can be easily separated and reused (Boz et al., 2015). The sulfonation of activated carbon  
39 from petcoke has been demonstrated by Zeng et al. (2013) who produced a solid acid catalyst with a total  
40 acidity of 5.25 mmol/g. Wu et al. (2016) who produced a catalyst with a  $-\text{SO}_3\text{H}$  acidity of 1.04 mmol/g  
41 (1.21 mmol/g total acidity), and Liu et al. (2019) who produced a catalyst with a total acidity of ~2.0  
42 mmol/g. All of the studies were carried out by first activating the petcoke. Until now, no research has  
43 been reported on the sulfonation of petcoke directly.

44 Solid acid catalysts have been prepared from a variety of carbon materials, including biomass, biochar,  
45 activated carbon, and coal, using concentrated  $\text{H}_2\text{SO}_4$  (Toda et al., 2005), fuming  $\text{H}_2\text{SO}_4$  (Toda et al.,  
46 2005), or chlorosulfonic acid (Cheng et al., 2017). The sulfonation of carbon materials using concentrated  
47  $\text{H}_2\text{SO}_4$  generally requires elevated temperatures (80-200 °C), with the amount of acidity (note, unless  
48 otherwise specified, "acidity" refers to acidity from sulfonic groups,  $-\text{SO}_3\text{H}$ , throughout this paper)  
49 generally decreasing as the temperature increased above 100 °C (Ngaosuwan et al., 2016; Tao et al.,  
50 2015). The actual amount of acidity, however, varied significantly among different studies without a clear  
51 trend for different carbon materials as summarized in Table S1 (supporting information). The acidity

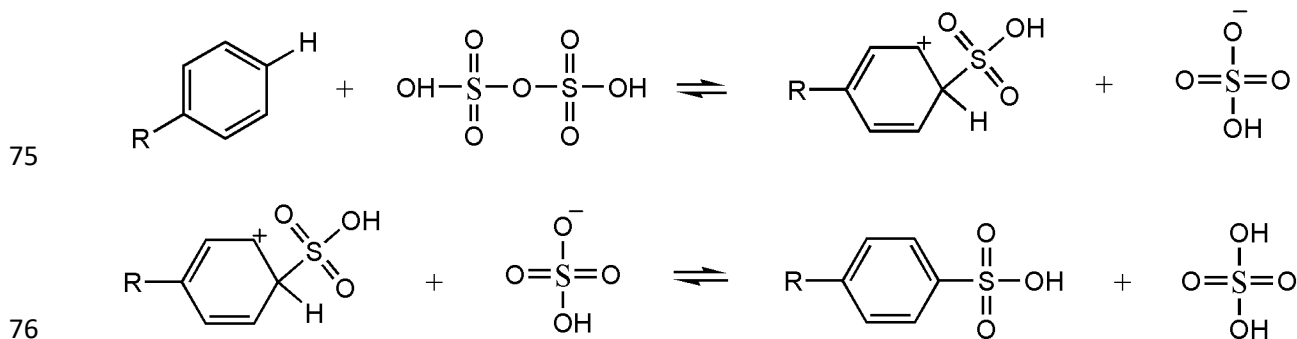
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52 varied from 0.31 mmol/g to 2.1 mmol/g, and although reducing particle size was effective to improve the  
53 acidity (Tamborini et al., 2016), higher surface area did not translate to more acidity (Cheng et al., 2017;  
54 Ngaosuwan et al., 2016; Zhang et al., 2010). Higher carbonization temperatures in the pre-treatment of  
55 the carbon materials before sulfonation, however, did consistently decrease the amount of acidity. For  
56 example, the acidity of sulfonated coal decreased from 1.04 mmol/g to 0.09 mmol/g when the coal  
57 carbonization temperature increased from 350 °C to 550 °C (Yu et al., 2016). Similarly, the acidity of a  
58 silica-carbon composite after sulfonation decreased by 35% when the composite preparation temperature  
59 increased by 200 °C (Zhong et al., 2015). Coupled with the fact that high levels (2.1 mmol/g and 5.0  
60 mmol/g, respectively) of acidity were obtained on mesoporous polydivinylbenzene polymer (Churipard et  
61 al., 2017), and porous aromatic frameworks (Goesten et al., 2016), these results suggest that the presence  
62 of specific functional groups, possibly aromatic groups, is essential for sulfonation of carbon materials by  
63 concentrated H<sub>2</sub>SO<sub>4</sub>.

64 Several reactions may occur during the sulfonation of carbon materials. Aromatic groups are sulfonated  
65 via an electrophilic substitution process - the hydrogen in aromatic rings is substituted by the -SO<sub>3</sub>H  
66 groups - as indicated in Scheme 1 (Kort and Cerfontain, 1968; Olah, 1971). Carbon materials also react  
67 with concentrated H<sub>2</sub>SO<sub>4</sub> through addition of carbon-carbon double bonds to generate alkyl hydrogen  
68 sulfate, which will further hydrolyze to alcohol in hot water (Scheme S1) (Carey, 2000). In addition, in  
69 the presence of fuming sulfuric acid or gaseous sulfur trioxide, alkane structures are sulfonated to produce  
70 sultones and sulfonic acid through hydride abstraction or radical formation followed by addition and  
71 radical reaction (Schemes S2 and S3) (Idage et al., 1996; Ihata, 1988; Kaneko and Sato, 2005).  
72 Considering the activity of these reactions and stability of the products, it is likely that the substitution of  
73 aromatic hydrogen is the main mechanism when concentrated H<sub>2</sub>SO<sub>4</sub> is applied as the sulfonation reagent.



74



Scheme 1. Sulfonation pathways for aromatic groups by concentrated H<sub>2</sub>SO<sub>4</sub>.

78

79 Thus, the hypothesis for this study is that the amount of acidity resulting from the sulfonation of carbon  
80 materials by concentrated H<sub>2</sub>SO<sub>4</sub> is related to the quantity of aromatic hydrogen groups on the carbon  
81 surface. Petcoke was the main carbon material used because this material is proposed to be a dispersion of  
82 micro crystals in condensed aromatic compounds (Berry and Edgeworth-Johnstone, 1944), with a  
83 hydrogen content of ~3.8 wt.% (Hill et al., 2014). For comparison, a selection of other carbon materials -  
84 graphite, mesoporous carbon, and straw char - were also used. The number of surface functional groups  
85 (specifically aromatic hydrogen groups) was decreased through calcination (Yu et al., 2016), and  
86 increased by ball milling to reduce particle size and expose more surface sites (Zou et al., 2008). The  
87 materials were characterized with Fourier-transform infrared spectroscopy and scanning electron  
88 microscopy and used for the esterification of octatonic acid with methanol.

89

## 90 2 Materials and methods

### 91 2.1 Materials

92 Delayed petcoke (PC) from the oil sands industry (Suncor Energy Inc., Alberta, Canada) was ground and  
93 sieved to particle sizes in the range of 45-90 μm before any experiments. The other carbon materials  
94 tested for comparison were graphite (>99.9% carbon, <100 μm, Alfa Aesar), Sigma mesoporous carbon

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95 material (SMC, particle size of <500 nm, Sigma-Aldrich), and char from wheat straw (Alberta, Canada)  
96 which was charred at 600 °C for 0.5 h. Concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, 95-98 wt%, EM Science) was  
97 used for sulfonation. Hydrochloric acid (HCl, 37 wt%, Sigma-Aldrich) was used during washing to  
98 prevent loss of sulfonated carbon. Octanoic acid (> 98%, Alfa Aesar) and methanol (>99.9%, EM  
99 Science) were the reactants in the esterification reaction.

## 100 ***2.2 Pretreatment of petcoke***

101 Petcoke samples were pretreated with different methods to tune the functionalities of the surface. Two  
102 petcoke samples were calcined/oxidized in a muffle furnace in air at 300 °C and 350 °C for 1 h and  
103 denoted as PC-ox-300 and PC-ox-350, respectively. Another two petcoke samples were ground in a  
104 planetary ball mill (Planetary Mono Mill, Pulverisette) using 5 mm zirconia balls with a sample to ball  
105 mass ratio of 4 g to 100 g at 200 rpm for 4 h. The first sample was dry ball milled and named PC-DBM,  
106 while the second sample was wet ball milled by adding 25 mL of isopropanol to the petcoke and zirconia  
107 balls. This sample was named PC-WBM. A third petcoke sample (2 g) was wet ball milled with  
108 isopropanol (25 mL), silica sand (10 g) and zirconia balls (100 g) for 4 h at 200 rpm and named PC-  
109 SiWBM4. A final sample was pretreated as for PC-SiWBM4 except the ball milling time was extended to  
110 24 h; this sample was named PC-SiWBM24. The silica sand particles have a size range of 300-600 µm.

111

## 112 ***2.3 Preparation of sulfonated carbon***

113 The petcoke samples were sulfonated by concentrated H<sub>2</sub>SO<sub>4</sub> as follows: 1 g of sample and 20 mL of  
114 concentrated H<sub>2</sub>SO<sub>4</sub> were placed in an Erlenmeyer flask. The mixture was heated to the desired  
115 temperature on a hot plate and maintained at this temperature for 3 h with continuous stirring (500 rpm)  
116 using a magnetic stirrer. The mixture was washed with deionized water and separated by centrifuging at  
117 6000 rpm for 5 min. This process (i.e., deionized water washing and centrifuging) was done a total of  
118 three times. Further washing the sample with deionized water resulted in the suspension of carbon (see

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119 Figure S1), so the sample was then washed by 50 mL of ~0.6 wt % HCl solution twice to prevent any loss  
120 of soluble carbon materials at higher pH. After centrifugation, the obtained sulfonated petcoke was dried  
121 in a vacuum oven at 65 °C overnight to remove moisture and HCl. Based on the energy dispersive X-ray  
122 spectroscopy (EDX) analysis, less than 0.4 wt% Cl remained on any of the samples. This amount of Cl  
123 corresponds to less than 0.1 mmol/g of acidity. Sulfonated samples have the suffix "-S". For example,  
124 sample PC-S is sulfonated petcoke, while sample PC-SiWBM24-S is petcoke that has been wet ball  
125 milled with silica sand for 24 h and then sulfonated. The other carbon materials - graphite and wheat  
126 straw char - were also ground and sieved to particle sizes in the range of 45-90  $\mu\text{m}$ , before being  
127 sulfonated with concentrated  $\text{H}_2\text{SO}_4$  at 80 °C for 3 h. The SMC carbon sample was sulfonated (with  
128 concentrated  $\text{H}_2\text{SO}_4$  at 80 °C for 3 h) without any pretreatment. After sulfonation, the samples were  
129 washed following the same procedures as for the petcoke samples.

130

#### 131 ***2.4 Characterization of sulfonated carbon***

132 The acidities of the sulfonated petcoke samples were measured by the ion exchange method (Toda et al.,  
133 2005; Yu et al., 2016). Briefly, 0.1 g of sulfonated petcoke was mixed with 5 mL of 1 mol/L NaCl  
134 solution and shaken in an oscillator (VWR Symphony 5000I Shaker, Henry Troemner LLC) at 25 °C and  
135 250 rpm for 4 h. The proton of the  $-\text{SO}_3\text{H}$  group exchanged with  $\text{Na}^+$  and was then released into the  
136 solution. The concentration of  $\text{H}^+$  in solution was then measured by titration with 0.01 mol/L of NaOH  
137 solution. Other acidic functional groups, including carboxyl, lactonic, and hydroxyl groups, were also  
138 measured through a similar process (Boehm, 1994; Budinova et al., 2006). Specifically, 0.1 g of sample  
139 was mixed with 5 mL of 0.1 mol/L  $\text{NaHCO}_3$ ,  $\text{Na}_2\text{CO}_3$ , and NaOH solution. After sufficient mixing and  
140 reaction, the remaining alkali species were titrated by 0.01 mol/L HCl using phenolphthalein as an  
141 indicator (methyl orange was used for titrating  $\text{NaHCO}_3$ ).

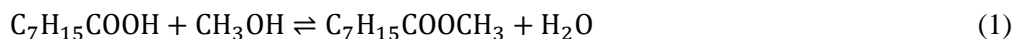
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142 The surface functional groups of the samples were determined by Fourier-transform infrared spectroscopy  
143 (FTIR, Nicolet iS50, Thermo Fisher Scientific) with an attenuated total reflection (ATR) accessory and  
144 scanning from 4000  $\text{cm}^{-1}$  to 400  $\text{cm}^{-1}$ . The surface morphology and elemental compositions of the  
145 samples were determined with scanning electron microscopy coupled with energy dispersive X-ray  
146 spectroscopy (SEM-EDX, Phenom Pro, PhenomWorld) at an acceleration voltage of 15 kV.

147

## 148 *2.5 Esterification reaction*

149 The sulfonated petcoke samples were then tested as catalysts for the following esterification reaction:



150 In the tests, 5 mL (~4.5 g) of octanoic acid and 50 mL of methanol were mixed and heated in a water  
151 bath. After reaching 60 °C, sulfonated petcoke (~0.2 g or 1.2 g for PC-SiWBM4-S and PC-SiWBM24-S  
152 in which the silica could not be separated from the petcoke) was added to the flask. The system was  
153 continuously stirred at 500 rpm using a magnetic stirrer for 3 h. Periodically, ~1 mL of the suspension  
154 was withdrawn from the reactor and filtered using a 0.45  $\mu\text{m}$  membrane (Supor®, Pall corporation). The  
155 solution (0.1  $\mu\text{L}$ ) was analyzed and the composition quantified with a gas chromatography coupled with a  
156 flame ionization detector (GC-FID, 6890N, Agilent Technologies) equipped with a HP-5 capillary  
157 column (5% phenyl methyl siloxane, 30 m  $\times$  320  $\mu\text{m}$   $\times$  0.25  $\mu\text{m}$ ) using toluene as the internal standard.  
158 The injection temperature was 260 °C, while the oven temperature was kept at 50 °C for 2 min and then  
159 heated up to 220 °C with a ramp of 30 °C/min to elute the components of the injected sample from the  
160 column. The reactants and products identified included octanoic acid, methanol, internal standard toluene,  
161 and produced methyl octanoate (Figure S2) using a mass spectrometer (MSD, 5975B, Agilent  
162 Technologies).



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163 The kinetics of the esterification process were interpreted using a pseudo first-order model because an  
164 excess amount of methanol was provided in the system and its concentration [M] was assumed to be  
165 constant throughout the esterification process.

$$\frac{d[OA]}{dt} = k_1[M][OA] = k[OA] \quad (2)$$

$$[OA] = [OA]_0 e^{-kt} \quad (3)$$

166 where [OA] is the concentration of octanoic acid (mmol/mL) with the subscript 0 indicating the initial  
167 concentration,  $k_1$  is the rate constant of the esterification reaction, and  $k$  is the pseudo first-order rate  
168 constant. Turnover frequencies (TOF) were calculated based on the following equation.

$$TOF = \frac{k[OA]_0 V}{m[-SO_3H]} \quad (4)$$

169 where  $V$  is the volume of the reaction solution (mL),  $m$  is the mass of catalyst added (g), and  $[-SO_3H]$  is  
170 the amount of sulfonic acidity on the catalyst (mmol/g).

171 Some of the samples were reused. Because not all of the solid could be recovered, the second reaction  
172 was done on a smaller scale with ~0.04 g of spent catalyst in 10 mL of methanol and 1 mL of octanoic  
173 acid. The reaction conditions (i.e., 60 °C for 3 h) and analysis (GC) did not change. The GC analysis error  
174 was estimated to be <2% from three analyses of several samples.

175

## 176 **3 Results and discussion**

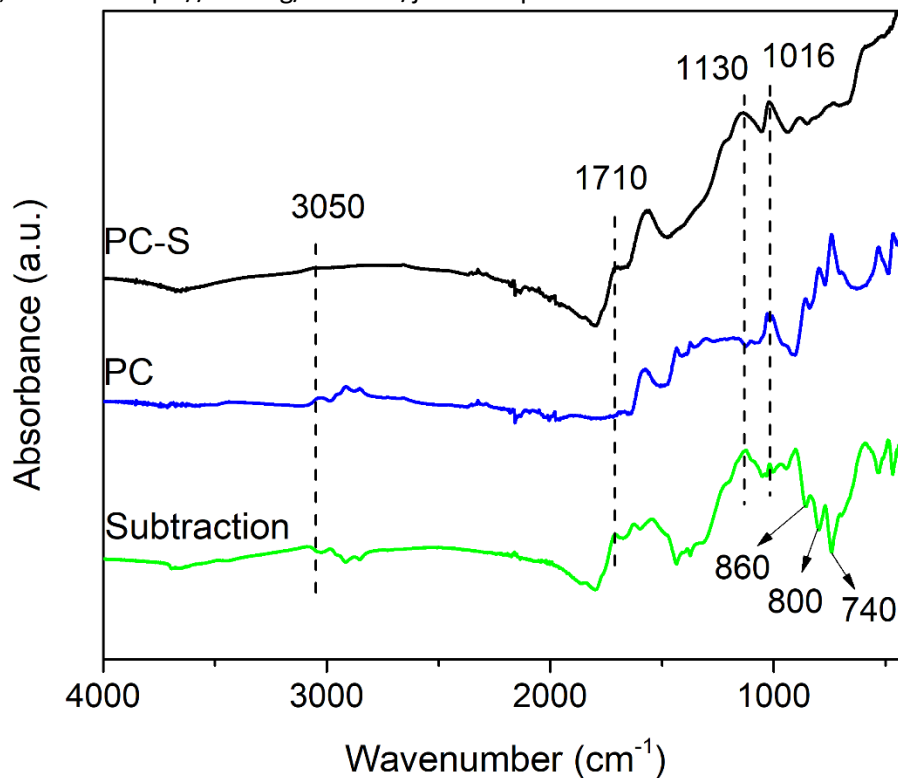
### 177 ***3.1 Characterization of petcoke before and after sulfonation***

178 The FTIR spectra of petcoke (PC) and sulfonated petcoke (PC-S) are shown in Figure 1. After  
179 sulfonation, the spectrum contained peaks at 1016  $\text{cm}^{-1}$  and 1130  $\text{cm}^{-1}$ , corresponding to the symmetric  
180 and asymmetric stretching of O=S=O (Mar and Somsook, 2012; Ngaosuwan et al., 2016), and indicating  
181 the successful introduction of  $-SO_3H$  groups on the petcoke surface. In addition, a peak at 1710  $\text{cm}^{-1}$ ,

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182 corresponding to the C=O stretch vibration, appeared after sulfonation implying the introduction of –  
183 COOH functional groups (Mar and Somsook, 2012). The disappearance of peaks at  $3050\text{ cm}^{-1}$ ,  $860\text{ cm}^{-1}$ ,  
184  $800\text{ cm}^{-1}$ , and  $740\text{ cm}^{-1}$ , which correspond to aromatic hydrogen stretching and bending, is consistent  
185 with the removal of hydrogen after sulfonation (Solomon and Carangelo, 1988), and the proposed  
186 substitution mechanism for the sulfonation process (Scheme 1).

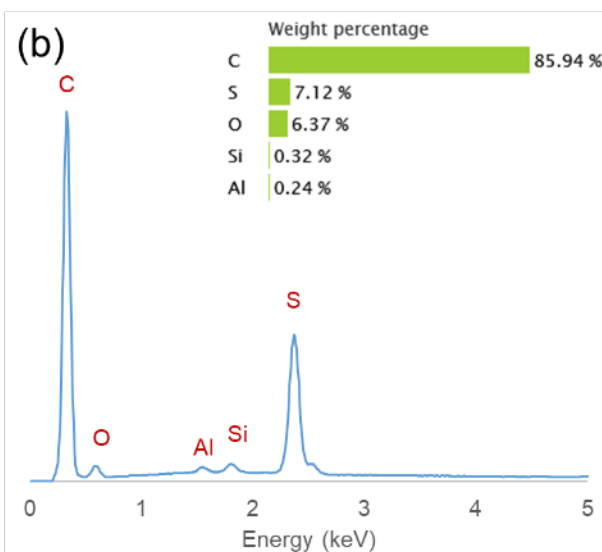
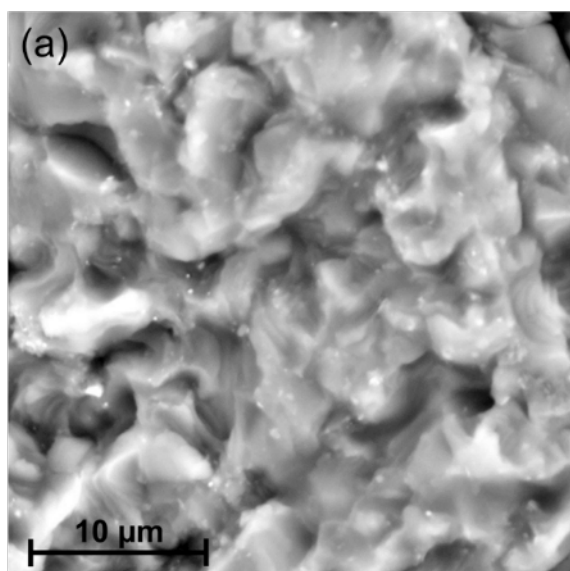
187 The SEM images show similar morphologies for petcoke before and after sulfonation (Figures 2a and c),  
188 indicating that the concentrated  $\text{H}_2\text{SO}_4$  treatment did not substantially change the bulk physical structure.  
189 The surface composition, however, did change substantially (Figures 2b and d). The sulfur content on the  
190 petcoke increased from approximately 7.1 to 12 wt% after sulfonation. This sulfur content is consistent  
191 with an acidity of 1.25 mmol/g determined by titration. The oxygen content also increased, from  
192 approximately 6.4 wt% to 17 wt%, after sulfonation. The petcoke had undetectable amounts of carboxyl  
193 and lactonic groups, and 0.34 mmol/g of hydroxyl groups. After sulfonation, the amounts increased to  
194 0.79 mmol/g, 0.13 mmol/g, and 0.65 mmol/g, respectively. By subtracting the oxygen content added due  
195 to carboxyl, lactonic, and hydroxyl groups, the molar ratio of added sulfur and oxygen was close to 3.2: 1.  
196 These results confirm that with the sulfonation conditions used (i.e., concentrated  $\text{H}_2\text{SO}_4$  at  $80\text{ }^\circ\text{C}$ ),  
197 sulfonic ( $-\text{SO}_3\text{H}$ ) functional groups were added to the petcoke surface.

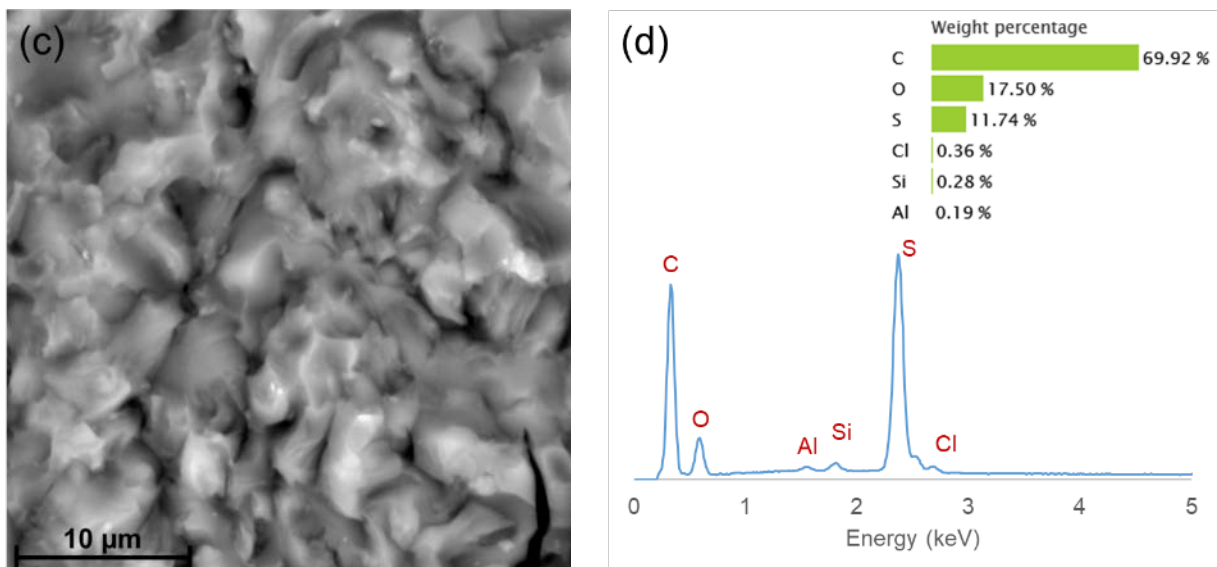


198

199 Figure 1. FTIR spectra of petcoke before (PC) and after sulfonation (PC-S) and the difference between  
200 the spectra (obtained by subtraction).

201

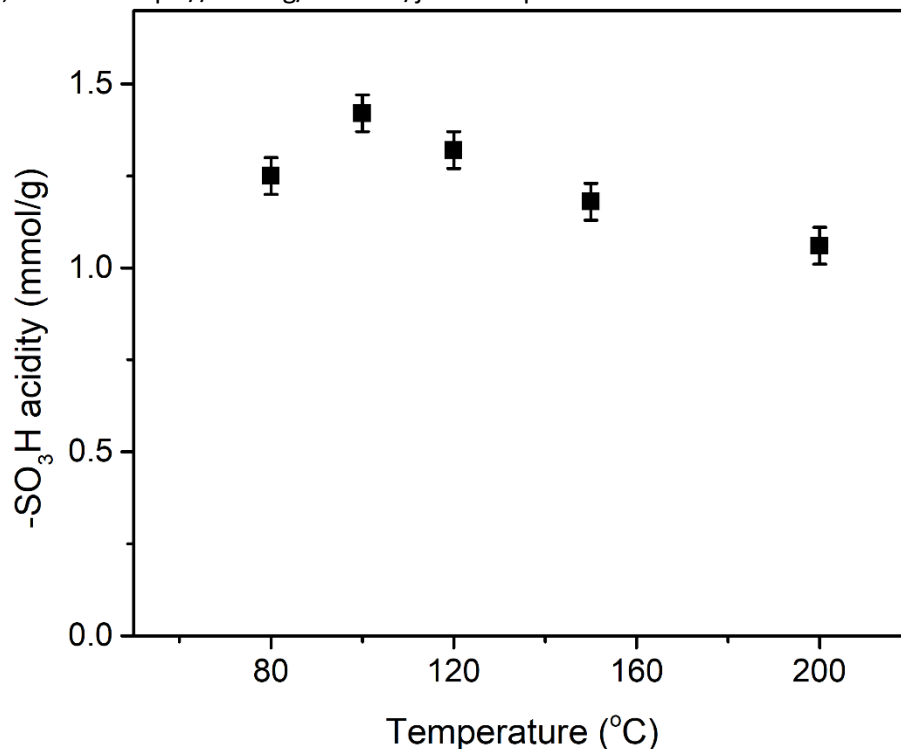




202 Figure 2. SEM images and EDX analyses of petcoke before, PC (a, b) and after sulfonation, PC-S (c, d).

### 203 3.2 Effect of temperature on sulfonation

204 The effect of temperature on the sulfonation of petcoke was investigated within the range of 80-200 °C.  
205 As indicated in Figure 3, the acidity increased from 1.25 mmol/g to 1.42 mmol/g when the sulfonation  
206 temperature increased from 80 °C to 100 °C, and the acidity decreased above this temperature with a  
207 value of 1.05 mmol/g at 200 °C. A similar trend was observed for the sulfonation of carbon derived from  
208 willow catkins with fuming sulfuric acid (15 wt% SO<sub>3</sub>) (Tao et al., 2015), and of activated carbon from  
209 coffee residue with concentrated H<sub>2</sub>SO<sub>4</sub> (Ngaosuwan et al., 2016). As the treatment temperature increases,  
210 surface groups may be removed through hydrolysis, oxidation, dehydration, condensation, and cross-  
211 linking (Lee and Puttnam, 1967; Zhong and Sels, 2018), which reduced the amount of -SO<sub>3</sub>H groups  
212 attached to the carbon surface. Thus, a temperature above 100 °C was not necessary to sulfonate petcoke  
213 with concentrated H<sub>2</sub>SO<sub>4</sub>.



214

215 Figure 3. Effect of sulfonation temperature on the resulting acidity of petcoke; sulfonation conditions  
216 were 1 g petcoke with 20 mL concentrated H<sub>2</sub>SO<sub>4</sub> reacted for 3 h at the temperatures shown.

217

### 218 *3.3 Effect of petcoke pretreatment*

219 The acidities of a variety of carbon materials after sulfonation by concentrated H<sub>2</sub>SO<sub>4</sub> at 80 °C are  
220 summarized in Table 1. Not all sample properties and treatment conditions (e.g., particle size and surface  
221 area) were given in the cited literature but the trend for sulfonation is generally as follows. Pure carbon  
222 materials (graphite and SMC) had little (< 0.1 mmol/g) acidity after sulfonation, implying the inertness of  
223 these materials when exposed to concentrated H<sub>2</sub>SO<sub>4</sub>. Intercalation and oxidation of carbon (graphite) by  
224 H<sub>2</sub>SO<sub>4</sub> requires the presence of stronger oxidants such as KMnO<sub>4</sub>, HNO<sub>3</sub>, and K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (Dreyer et al.,  
225 2010; Hummers and Offeman, 1958; Sorokina et al., 2005).

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226 Carbon materials from biomass had higher acidities of 0.31-0.72 mmol/g. In particular, the acidity of the  
227 sulfonated straw char was 0.55 mmol/g, which was similar to that reported for wood powder char (0.67  
228 mmol/g) (Mun et al., 2017) and sucrose char (0.7 mmol/g) (Toda et al., 2005). The acidities of petcoke,  
229 coal, and resin were in the range of 1.0-1.5 mmol/g. Petcoke oxidized at 350 °C (PC-ox-350) had a lower  
230 acidity of 0.59 mmol/g, while petcoke ball milled with silica for 24 h (PC-SiWBM24) had a higher  
231 acidity of 3.73 mmol/g, which is comparable to the acidity reported for the commercial Amberlyst-15  
232 solid acid catalyst (Wang et al., 2011).

233 For petcoke (particle size of 45-90 μm), an acidity of 1.25 mmol/g was obtained, which was similar to  
234 that obtained from sulfonation of sucrose char by fuming H<sub>2</sub>SO<sub>4</sub> (1.2 mmol/g) under hasher conditions at  
235 a temperature of 150 °C (Toda et al., 2005). The acidity was improved by ball milling the petcoke prior to  
236 sulfonation; acidities of 1.50 mmol/g and 1.58 mmol/g were obtained after dry and wet, respectively, ball  
237 milling. The presence of an additive, such as MgO and silica, improved particle size reduction (Liu et al.,  
238 2003; Yu et al., 2013), which may explain the high the acidity for petcoke wet ball milled with silica sand  
239 for 4 h (2.18 mmol/g) and 24 h (3.73 mmol/g). For the samples wet ball milled with silica, it was difficult  
240 to separate the carbon from the silica and so the acidity was based on the petcoke mass, not the total  
241 sample mass. Silica was not sulfonated under the tested conditions with an acidity <0.01 mmol/g.

242 Oxidation of the petcoke before sulfonation resulted in decreased acidity: 1.04 mmol/g after oxidation in  
243 air at 300 °C for 1 h, and 0.59 mmol/g after oxidation in air at 350 °C for 1 h. Except for those pretreated  
244 by oxidation, the acidities of sulfonated petcoke were among the highest reported in the literature (Table  
245 1) for carbon materials such as char, coal, and activated carbon sulfonated by concentrated H<sub>2</sub>SO<sub>4</sub> (Mun  
246 et al., 2017; Yu et al., 2016; Zhang et al., 2010).

247

248 Table 1. Acidities of different carbon materials after sulfonation by concentrated H<sub>2</sub>SO<sub>4</sub>.

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Carbon Material	Pretreatment	-SO <sub>3</sub> H acidity (mmol/g)	Particle size/surface area	Reference
Graphite	No	0.01	45-90 μm	This study
SMC	No	0.10	<500 nm	This study
Xylose hydrocarbon	Hydrothermal carbonization at 190 °C	0.31	0.8 ± 0.14 μm/95.5 m <sup>2</sup> /g	(Tran et al., 2016)
Porous carbon from resin	Polymerization and then pyrolysis at 800 °C	0.39	695 m <sup>2</sup> /g	(Tamborini et al., 2015)
Straw char	No	0.55	45-90 μm	This study
Activated carbon	Not specified	0.56	506 m <sup>2</sup> /g	(Zhang et al., 2010)
Petcoke (PC-ox-350)	Oxidation 350 °C	0.59	45-90 μm	This study
Wood	Charring at 400 °C	0.67	63 m <sup>2</sup> /g <sup>b</sup>	(Mun et al., 2017)
Coffee residue	Activation at 600 °C	0.72	956 m <sup>2</sup> /g	(Ngaosuwan et al., 2016)
Petcoke (PC-ox-300)	Oxidation 300 °C	1.04	45-90 μm	This study
Coal	Carbonized at 350 °C	1.09	2.6 m <sup>2</sup> /g	(Yu et al., 2016)
Porous carbon from resin	Polymerization and then pyrolysis at 800 °C	1.10	630 m <sup>2</sup> /g	(Tamborini et al., 2016)
Petcoke (PC)	No	1.25	45-90 μm	This study
Petcoke (PC-DBM)	Dry ball-milling	1.50	-	This study
Petcoke (PC-WBM)	Wet ball-milling	1.58	-	This study

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Polydivinylbenzene	Polymerization at 100	2.1	653 m <sup>2</sup> /g	(Churipard et al., 2017)
Polymer	°C			
Petcoke (PC-SiWBM4)	Wet ball-milling with silica for 4 h	2.18 <sup>a</sup>	-	This study
Petcoke (PC-SiWBM24)	Wet ball-milling with silica for 24 h	3.73 <sup>a</sup>	-	This study

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249 <sup>a</sup> determined using the carbon mass in the sample; <sup>b</sup> for the sulfonated material;

### 250 **3.4 Impact of surface groups on sulfonation**

251 Based on the results above, the presence of functional groups aids the sulfonation reaction. Graphite and  
252 SMC had essentially no functional groups as evidenced by the absence of peaks in the FTIR spectra  
253 (Figure S3). The spectrum of straw char contained peaks at ~1700 cm<sup>-1</sup> and ~1100 cm<sup>-1</sup> corresponding  
254 with C=O stretching and C-O stretching, respectively, and consistent with the presence of oxygen  
255 functional groups on biochar (Lee et al., 2017). These peaks were not present in the FTIR spectrum of  
256 petcoke (Figure 1). Given the fact that both biochar and petcoke had acidity after sulfonation, oxygen  
257 functional groups were not necessary for the sulfonation of carbon materials. The common peaks in the  
258 FTIR spectra of petcoke and biochar occurred at ~3000 cm<sup>-1</sup> and 600-900 cm<sup>-1</sup>, which are assigned to  
259 aromatic hydrogen stretching and bending (Lee et al., 2017; Solomon and Carangelo, 1988), respectively.

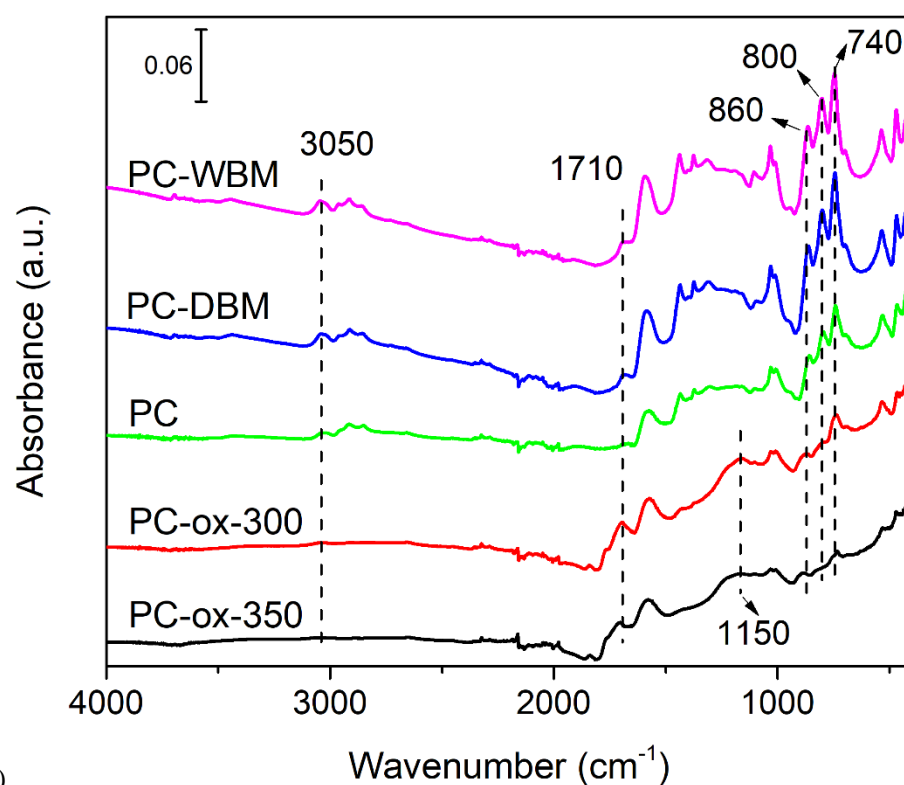
260

261 As shown in Figure 4a, the peaks associated with aromatic hydrogen increased after ball-milling (wet and  
262 dry) and decreased after oxidation, with a higher temperature (350 °C versus 300 °C) removing more of  
263 the groups. Additional oxygen functional groups (C=O at ~1700 cm<sup>-1</sup> and C-O at ~ 1150 cm<sup>-1</sup>) were  
264 added to the petcoke after oxidation. The FTIR spectrum of PC-SiWBM4 and PC-SiWBM24 (Figure S4)  
265 was not included in Figure 4a because the presence of silica in the sample interfered with the peak  
266 associated with the aromatic hydrogen bending vibration. The fact that the FTIR spectra were similar for

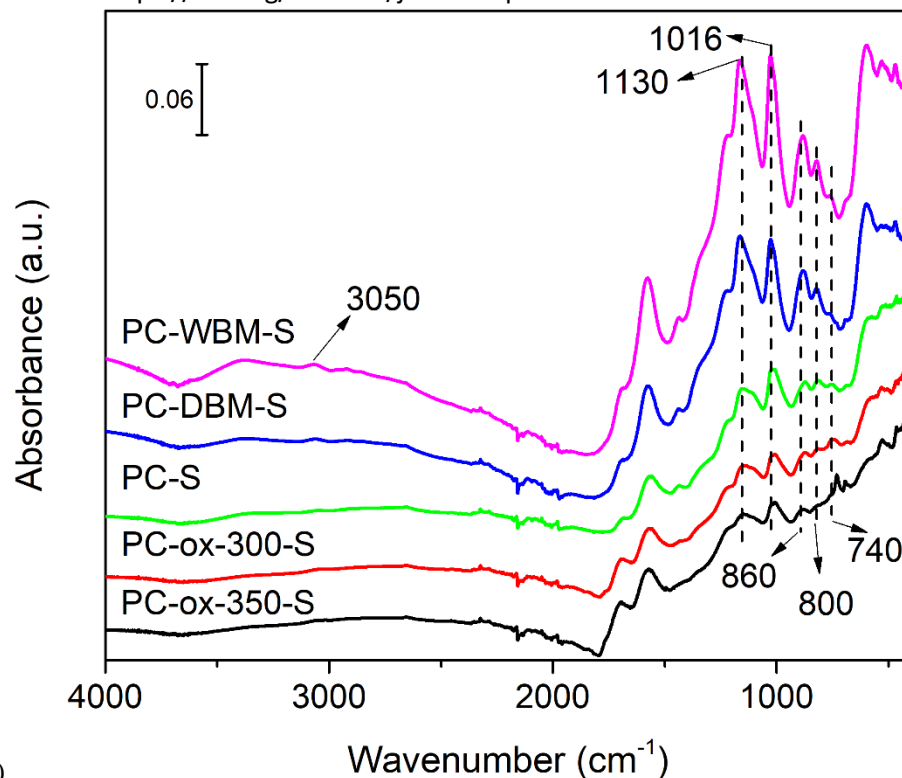


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267 petcoke before and after ball milling (in terms of the location of the peaks) suggests that the ball milling  
268 process did not create new surface functional groups. A rotation speed of 200 rpm was used during ball  
269 milling and according to Yu et al. (2013), at this speed, the energy input was not sufficient to break and  
270 form new chemical bonds. After sulfonation, compared with petcoke (45-90  $\mu\text{m}$ ) without any  
271 pretreatment the peaks assigned to  $-\text{SO}_3\text{H}$  groups at  $1130\text{ cm}^{-1}$  and  $1016\text{ cm}^{-1}$  increased for ball milled  
272 samples and decreased for calcined samples. This trend correlated with the aromatic hydrogen content  
273 before sulfonation.



274 (a)



275 (b)  
276 Figure 4. FTIR spectra of petcoke pretreated with either calcination or ball milling (a) before and (b) after  
277 sulfonation.

278  
279 Further semi-quantitative analysis was done to relate the aromatic hydrogen concentration of each carbon  
280 material with the acidity obtained after sulfonation. The peak at  $>3000\text{ cm}^{-1}$  for aromatic hydrogen  
281 stretching can overlap with the peak corresponding to aliphatic hydrogen stretching as well as be affected  
282 by the oxygen content (Sandford et al., 2013; Solomon and Carangelo, 1988) and so this peak was not  
283 suitable for the correlation. The peak intensities at  $600\text{-}900\text{ cm}^{-1}$  are also affected by the composition of  
284 the sample but corrections can be made using related compounds. Specifically, salicylic acid (SA) and  
285 dibenzothiophene (DBT) were used as model compounds for the aromatic hydrogen in biochar and  
286 petcoke, respectively. Various amounts of the two compounds were mixed with potassium bromide  
287 separately using an agate mortar for 3 min. The mixtures were then analyzed in the FTIR using the ATR

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288 mode and the resulting peak areas plotted versus the aromatic hydrogen content in the samples (Figure  
289 S5). The obtained correlations were as follows:

$$Area = 3.1 * [Aromatic H]_{SA} \quad (5)$$

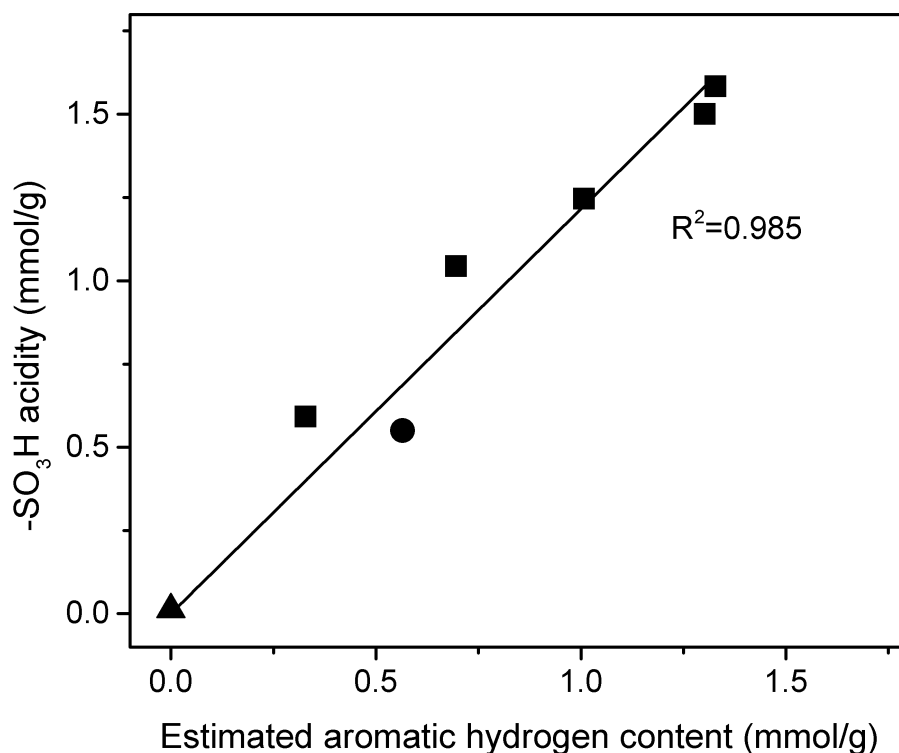
$$Area = 1.5 * [Aromatic H]_{DBT} \quad (6)$$

290 Thus, the resulting peak area was approximately doubled for aromatic hydrogen in SA versus DBT.

291 Particle size also influences the peak areas in the FTIR spectra (Kristova et al., 2015; Udvardi et al.,  
292 2017). The FTIR peak area at 1130 cm<sup>-1</sup> (for asymmetric stretching of O=S=O) for the sulfonated petcoke  
293 samples (Figure 4b) was plotted versus the acidity (-SO<sub>3</sub>H) measured by titration (Figure S6). The  
294 relationship is exponential rather than linear consistent with particle size reduction from ball-milling  
295 increasing the peak area. Assuming that the peak area at 1130 cm<sup>-1</sup> for the sulfonated petcoke samples  
296 should vary linearly with acidity, and that the impact of particle size will be the same for the peaks at  
297 1130 cm<sup>-1</sup> as for the peaks from 600-900 cm<sup>-1</sup>, the latter peak areas (600-900 cm<sup>-1</sup>) were corrected  
298 accordingly and the corrected values plotted in Figure 5. Only the materials tested in this study were  
299 included in the plot as the FTIR peak area information could not be extracted from the literature for the  
300 other materials in Table 2. As indicated in Figure 5, increasing the aromatic hydrogen content in the  
301 carbon material resulted in a linear (with R<sup>2</sup> of 0.985) increase in the acidity with a slope of 1.22. The  
302 results were consistent with the mechanism of sulfonation of carbon materials.

303 As indicated in the literature, during the electrophilic substitution of aromatics, the hydrogen atom is  
304 substituted from the benzene ring by an electrophile (Olah, 1971; Ouellette and Rawn, 2014). The  
305 substitution process follows a two-step mechanism. In the first and rate-determining step, an electrophile,  
306 here H<sub>2</sub>S<sub>2</sub>O<sub>7</sub> for sulfonation by concentrated H<sub>2</sub>SO<sub>4</sub>, attacks the benzene ring to form an σ-complex  
307 (Scheme 1, equation 2) (Olah, 1971; Ouellette and Rawn, 2014), while the second step is deprotonation.  
308 The electrophilic substitution reaction rate increased with increasing stability of the intermediate σ-  
309 complex (Stock and Brown, 1963), with the stability of the ipso σ-complex being low because of steric

310 effects (Douberly et al., 2008). A hydrogen shift to a more stable position was observed prior to the  
311 deprotonation step (Olah, 1971). Therefore, hydrogen was the most easily replaced group during the  
312 electrophilic substitution of aromatics, and aromatic hydrogen was the site where sulfonation took place  
313 to provide acidity to the carbon materials.



314  
315 Figure 5. Relationship between resulting acidity (i.e.,  $-\text{SO}_3\text{H}$  groups) and aromatic hydrogen content of  
316 different carbon materials: ▲ graphite, ● straw char, and ■ petcoke. Sulfonation conditions were 80 °C, 3  
317 h, and carbon:  $\text{H}_2\text{SO}_4$  ratio of 1 g: 20 mL. The acidity was determined by titration, and the aromatic  
318 hydrogen content was estimated by the FTIR peak area from 600 to 900  $\text{cm}^{-1}$  corrected for changes in  
319 particle size after ball-milling.

320

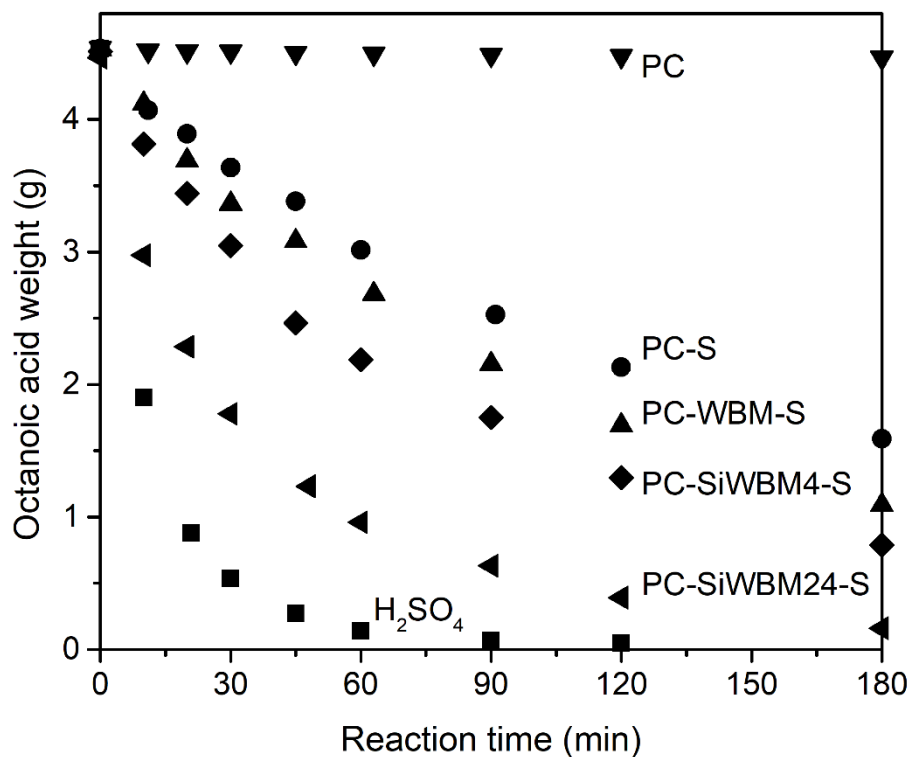
### 321 3.5 Esterification reaction

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322 Some of the carbon samples were used in the esterification reaction between octanoic acid and methanol  
323 to directly probe the acidity and the results are shown in Figure 6. For comparison, the reaction was also  
324 performed with concentrated H<sub>2</sub>SO<sub>4</sub> and this homogeneous catalyst converted >99% of the octanoic acid  
325 in 2 h. Petcoke without sulfonation had essentially no activity for this reaction with less than 2%  
326 conversion of the octanoic acid after 3 h. After sulfonation, however, the activity improved in the order of  
327 PC-S < PC-WBM-S < PC-SiWBM4-S < PC-SiWBM24-S, with conversions of 65%, 76%, 83%, and  
328 96%, respectively, after 3 h.

329  
330 The initial reaction kinetics were fit to a pseudo-first-order model to obtain the rate constants and then the  
331 TOF. The lines of best fit and the residuals are shown in Figure S7. The residuals were randomly  
332 distributed around zero, indicating the proper interpretation of the results by the model. The TOF were  
333 between 48 and 52 h<sup>-1</sup> for PC-S, PC-WBM-S, and PC-SiWBM4-S, suggesting that the -SO<sub>3</sub>H functional  
334 groups were similar on these samples. For petcoke pretreated by ball milling with silica for 24 h (PC-  
335 SiWBM24-S), the TOF was significantly higher at 85 h<sup>-1</sup> and similar to that of the homogeneous H<sub>2</sub>SO<sub>4</sub>  
336 (87 h<sup>-1</sup>). In comparison to other catalysts used for the same reaction at similar conditions (i.e., 60 °C), the  
337 TOF was higher than that of a “nafion”-functionalized mesoporous MCM-41 silica catalyst (TOF of  $9.7 \times$   
338  $10^{-3} \text{ s}^{-1} = 35 \text{ h}^{-1}$ ) (ALVARO et al., 2005), and an order of magnitude higher than that for a commercial  
339 Nafion silica composite (TOF of  $1.1 \times 10^{-3} \text{ s}^{-1} = 3.6 \text{ h}^{-1}$ ) (Alvaro et al., 2004). These results may reflect  
340 that the functional groups were more accessible on the non-porous petcoke than in the pores of other  
341 catalysts (Alvaro et al., 2004; ALVARO et al., 2005), and the accessibility of the -SO<sub>3</sub>H groups were  
342 improved with the decrease in particle size after ball milling. Three of the petcoke-derived solid acid  
343 catalysts were reused for the octanoic acid esterification reaction to verify that the activity did not result  
344 from residual H<sub>2</sub>SO<sub>4</sub> on the catalysts. After three uses, the octanoic acid conversion only slightly dropped  
345 - by 3%, 6%, and 13% for PC-S, PC-SiWBM4-S, and PC-SiWBM24-S, respectively (Figure S7) –  
346 confirming that the attached -SO<sub>3</sub>H groups were responsible for the activity. The stability of these

347 catalysts was comparable and higher than those reported for sulfonated carbon from sugarcane bagasse  
348 (~17% reduction in first reuse) (Flores et al., 2019) and sulfonated carbon from Cacao shell (~19%  
349 reduction in first reuse) (Bureros et al., 2019). The observed deactivation may be from leaching of  
350 polycyclic aromatic hydrocarbons or carbon colloids containing  $-\text{SO}_3\text{H}$  groups (Deshmane et al., 2013;  
351 Wu et al., 2016; Yu et al., 2016).



352  
353 Figure 6. Esterification of octanoic acid using different catalysts. Reaction conditions: 5 mL (~4.5 g)  
354 octanoic acid, 50 mL methanol (methanol: octanoic acid = 40:1 molar ratio), 60 °C, 500 rpm, 0.2 g  
355 petcoke or 0.08 g concentrated H<sub>2</sub>SO<sub>4</sub>.

356 As indicated above, the sulfonation of petcoke could be easily achieved with concentrated H<sub>2</sub>SO<sub>4</sub> (instead  
357 of fuming H<sub>2</sub>SO<sub>4</sub>) under low temperature (80 °C) due to the presence of aromatic hydrogen. The amount  
358 of H on petcoke is ~3.8 wt%, which would correspond to a maximum acidity of 38 mmol/g if all H was  
359 replaced by  $-\text{SO}_3\text{H}$  during sulfonation. Thus, there is room to further improve the sulfonation procedure  
360 for increased acidity. In addition, the process may be improved in terms of environmental impact. For

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361 example, preliminary experiments were done with dilute  $\text{H}_2\text{SO}_4$  for the sulfonation. The addition of 0.70  
362 mmol/g of  $-\text{SO}_3\text{H}$  groups was achieved after wet impregnation using 5 mL of 1 mol/L  $\text{H}_2\text{SO}_4$  with 1 g of  
363 petcoke (procedure given in Figure S8). Thus, the possibility of adding  $-\text{SO}_3\text{H}$  groups on petcoke with  
364 dilute  $\text{H}_2\text{SO}_4$  solution and mild conditions ( $<120\text{ }^\circ\text{C}$ ) demonstrates the potential for petcoke as a raw  
365 material for the preparation of solid acid catalysts, which can be used in the generation of biofuels  
366 through esterification.

367

#### 368 **4 Conclusions**

369 In this study, sulfonation of petcoke by concentrated  $\text{H}_2\text{SO}_4$  was carried out to produce solid acid  
370 catalysts. According to FTIR analysis, SEM-EDX analysis, and titration of the surface functional groups,  
371  $-\text{SO}_3\text{H}$  was successfully added on the petcoke samples after sulfonation at  $80\text{ }^\circ\text{C}$  for 3 h. FTIR (with  
372 ATR) analysis was used to determine changes in surface aromatic hydrogen on the samples, making  
373 corrections for the local environment as well as the particle size. An acidity of 1.25 mmol/g was obtained  
374 for petcoke (45-90  $\mu\text{m}$ ). If the petcoke was oxidized before sulfonation, hydrogen was removed, and the  
375 resulting acidity reduced to 0.59 mmol/g. If the particle size was reduced by ball-milling before  
376 sulfonation, more aromatic hydrogen was accessible, and the resulting acidity increased up to 3.73  
377 mmol/g. The sulfonated petcoke catalysts were active for the esterification of octanoic acid at  $60\text{ }^\circ\text{C}$  with  
378 TOF ranging from 48 to  $85\text{ h}^{-1}$ .

379

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383 esterification reaction to test the sulfonated samples.

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