Original Article

Impact of hydrolysis on surface area and energy storage applications of activated carbons produced from corn fiber and soy hulls

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HIGHLIGHTS

- Hemicellulose extracted fibers produced activated carbons (ACs) with higher surface areas.
- The surface area of the AC from pre-hydrolysis DDG was only $10 \text{ m}^2/\text{g}$ compared to $689 \text{ m}^2/\text{g}$ for soy hulls.
- The surface area of AC from post-hydrolysis DDG and soy hulls increased dramatically to $1700 \text{ m}^2/\text{g}$ and $1300 \text{ m}^2/\text{g}$ respectively.
- TEM images indicated exfoliation in the post-hydrolysis fibers leading to higher surface area in AC.
- Under the same current density ($500 \text{ mA/g}$) the cycling performance of the AC increased as the surface area increased significantly.

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ABSTRACT

Complete utilization of lignocellulosic biomass through the creation of value-added coproducts is one of the key strategies of the Bioenergy Technologies Office (BETO) for the cost-effective production of biofuels and bio-chemicals. A green approach to producing lightweight and high specific surface area (SSA) activated carbons (ACs) from sustainable biomass sources is of great interest to producers and users of energy devices such as batteries and supercapacitors. While direct conversion from biomass has been studied extensively, AC with relatively high surface areas can be produced more cost-effectively when leveraged as a co-product from a biorefinery. In this paper, we discuss the production of high specific surface area activated carbons from residual fiber (fiber remaining after extraction of C5-sugars) generated as part of a C5 biorefinery. The surface, morphological characteristics using SEM and TEM, and energy storage behavior of ACs produced using the C5 extracted residual fiber were evaluated in the present study. The ACs produced from the residual fiber delivered an order of magnitude higher surface area than the one directly from corn pericarp fiber and soy hulls. The surface area of the ACs produced from pre-hydrolysis DDG was only $10 \text{ m}^2/\text{g}$ compared to $689 \text{ m}^2/\text{g}$ for soy hulls whereas after hydrolysis these values increased significantly (DDG: $1700 \text{ m}^2/\text{g}$ and soy hulls: $1300 \text{ m}^2/\text{g}$). TEM images indicated high exfoliation, explaining the change in surface area values. Under the same current density ($500 \text{ mA/g}$) the cycling performance of the ACs increased as the surface area increased significantly.

1. Introduction

New energy-storage material development is gaining a lot of importance. There is an ever-growing need for high energy and high power, especially for emerging large-scale applications such as electric cars and next-generation wireless communication devices. Supercapacitors (SCs) are attracting considerable research interest as high-performance energy storage devices that can contribute to the rapid growth of low-power electronics (e.g., wearable, portable electronic devices) and high-power military applications (e.g., guided-missile techniques and highly sensitive naval warheads). Currently, supercapacitors (SCs) are one of the most promising devices for energy storage due to their high-power density, fast charge/discharge rate, and long cycling life [24]. The success of portable energy storage systems such as Li-ion batteries, Li-S batteries, symmetric and asymmetric supercapacitors, hydrogen storage mechanisms, and solar devices are...
dependent on sustainable and low-cost electrode materials. Various researchers have tested biomass for production of activated carbon for energy applications. Activated carbons (ACs) are a promising material for SCs application as they exhibit large surface area, good electrical performance, and are affordable [25]. ACs are usually made from various carbonaceous materials (i.e., waste, coal, nutshells, and wood) via physical (thermal) or chemical steps [26]. Thermal pretreatment is performed at high temperatures (700–1200 °C) in the presence of reducing and oxidizing agents (i.e., air, CO2, and steam) while the chemical treatment is conducted in lower temperature conditions (400–700 °C) using chemical agents such as oxaycid, potash, hydroxide, or metal chloride [27]. Considerable technical advances have been achieved to enhance the surface area of ACs up to 3000 m² g⁻¹ and improve their electrochemical properties (total capacitance, real-time constant, gravimetric capacitance, energy density, and electrical conductivity). One of the major challenges of using activated carbons is the cost of precursor materials. Activated carbons derived from low cost, sustainable resources using low energy-consuming processes can deliver such energy storage materials at a reduced cost, encouraging industrial-scale use. To meet this challenge, residual agricultural biomass from biomass processing has been tested for its effectiveness in producing high surface area carbons. This is a logical choice as agricultural biomass is an abundant resource that comes at low cost and avoids the use of non-renewable sources such as anthracites for carbon production. Biomass materials such as rice husks [1], coconut fibers [2], peanut shells [3], hemp [4], and banana peels [5] have all demonstrated the effective formation of high surface area carbons. However, most of the materials tested are only used for the purpose of creating activated carbons. The application of these materials for energy storage is not widely studied.

Several economic models have been developed to guide cost-effective production of bioproducts from lingo-cellulosic biomass in a biorefinery format [6–11]. One common conclusion from these models is the high cost attributed to the biomass starting material and its handling. Cardona and Sanchez [12] and Solomon et al. [13] estimated the share of feedstock to be about 40–70% of the overall production cost. Therefore, the choice of appropriate lignocellulosic biomass is imperative to a cost-effective biorefinery and, subsequently, the production of activated carbons. Fonseca et al. [14] discussed an integrated CS-based biorefinery approach using corn fiber from dried distiller’s grains (DDG) as a starting material. DDG is highly available from both the fuel ethanol and beverage alcohol industries. Taking advantage of the high hemicellulose composition of corn fiber, they presented a hydrolysis process to selectively extract hemicelluloses from the corn fiber biomass. Further research also demonstrated the extraction of CS sugars from soy hulls. This process (using both biomass types) generates a cellulosic residual fiber with higher surface areas than pre-hydrolysis fibers that have the potential to make an excellent precursor to produce high surface area activated carbons.

1.1. The activation process

An ample amount of research has been done on understanding the chemical and physical activation methods used for carbons. Since energy storage is the goal, the activation process must provide carbons that produce high surface areas and a well-developed micro-porosity. Both types of activation have been proven to provide these qualities [15]. Product yield is also a concern when it comes to developing an activation process. The chemical process is often chosen over the physical due to its higher yields and lower activation temperature. Chemical activation occurs when an activating agent permeates the structure of the biomass and then reacts with the various carbon and oxygen compounds to prevent the collapse of the structure. This develops a porous structure and, consequently, a higher surface area. There are three main types of activating agents used in chemical activation. Strong concentrated acids (Phosphoric acid – H₃PO₄), strong bases (Potassium Hydroxide - KOH), and salts (Zinc Chloride - ZnCl₂) have been proven to yield high surface area carbon fibers and a well-developed porosity that could prove useful for energy storage [15,16,18,19]. KOH has also been shown to provide pore size adjustability based on concentration. This characteristic in combination with the abundance of KOH as a lab chemical made it a logical choice for the main activating agent during the carbonization process in the present work.

1.2. Objectives

Initial studies on the activation of CS extracted residual fiber was reported by Herde et al. [20]. These authors provided details regarding the activation method and initial results in terms of surface characteristics and energy storage application. The initial results indicated that the AC produced from the residual fiber after dilute acid hydrolysis delivered an order of magnitude higher surface area than the one directly from corn pericarp fiber and soy hulls. Based on these results, a more detailed study was conducted to understand the effect of hydrolysis on the quality of the activated carbon and its application for energy storage.

The overall objective of the work is to use the hemicellulose-rich residual biomass as a starting material, to produce carbon materials, which can be created as a value-added co-product; improving process sustainability and potentially improving the overall process economics through an array of co-products taken from a single source. In this study corn fiber (DDG) and soy hulls from corn processing and soybean processing plants are used as starting materials for the production of AC. The fiber used is the residual fiber (post-hydrolysis) as prepared per Fonseca et al. [14]. Fiber without any hydrolysis (pre-hydrolysis) is used for comparison (Control). The corn fiber used was a pre-sieved fiber from DDG as suggested by Fonseca et al [14]. The specific objective of the project is a) pre and post hydrolysis of fibers and fiber characterization b) understand the impact of KOH activation of surface area and pore size, c) surface characterization of the activated carbons using TEM and d) evaluation of the activated carbon for energy storage applications.

2. Materials and methods

2.1. Materials

The DDG was obtained from the Brown Forman Corporation (Louisville, KY) and the soy hulls were obtained from Owensboro Grain Company (Owensboro, KY). KOH solution was made from > 85wt. % KOH pellets (Sigma-Aldrich) in deionized water. Per Wang and Kaskel (2012) [15], the KOH–carbon mass ratio ranges from 2 to 5. In the present study, we chose to use a 1:1 mass ratio of KOH to residual fiber (please see Table 1). The methods used for carbonization and for analysis of the carbon produced are discussed below. Fig. 1(a & b): Processing schemes used for straight carbon production and biorefinery [20].

2.2. Sample preparation

2.2.1. Pre-hydrolysis samples

Distillers grains were screened using a No. 20 (0.85 mm opening) sieve. The coarse fraction retained on the screen was used for hydrolysis purposes. The coarse fiber was then mixed with 1 L of water and sonicated for 30 minutes at 200 W power using a UP200S transonic homogenizer (Hielscher Ultrasonics, Germany) with a 40 mm diameter probe. It was then dewatered using a 40-mesh screen. Soy hulls were used as-is in the present study.

2.2.2. Post hydrolysis samples

The grain samples were hydrolyzed in a 6 L percolation reactor with liquid recirculation (M/K Systems Inc, Peabody, MA). The samples used...
in this work were hydrolyzed at 120 °C using 0.4% sulfuric acid concentration [14]. The remaining residual fiber was dried at 110 °C for use in the activation process.

2.2.3. Chemical activation

Five grams each of soy and corn fibers from pre-hydrolysis as well as post-hydrolysis were mixed with a KOH solution consisting of desired concentration of KOH and 15 ml of deionized water. For example, 5 g of KOH in solution would yield a 1:1 ratio with 5 g of grains. They were then mixed using a vortex mixer until they formed a thick paste. This paste was then allowed to dry at 80 °C. Control samples of carbon were obtained from the MWV Corporation.

2.2.4. Carbonization

The resulting samples were then carbonized in a horizontal tube furnace under a Nitrogen blanket at 950˚C for one hour. The ramp rate was 10 °C/min until 500 °C and then was increased to 20 °C/min up to the final temperature of 950 °C. The sample was then allowed to cool naturally under the Nitrogen blanket before removing it from the furnace. The samples were washed thoroughly with deionized water and air-dried. Figs. 2 and 3 indicates the activated and carbonized soy hulls and DDGs.

2.3. Surface area analysis and material characterization

Table 1

<table>
<thead>
<tr>
<th>KOH Concentration</th>
<th>Average Pore Width (nm)</th>
<th>BET Surface Area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control DDG – S1</td>
<td>8.39</td>
<td>0.47</td>
</tr>
<tr>
<td>0.17:1 KOH to DDG – S2</td>
<td>2.11</td>
<td>774.34</td>
</tr>
<tr>
<td>0.17:1 KOH to DDG Blended – S3</td>
<td>2.08</td>
<td>744.07</td>
</tr>
<tr>
<td>1:1 Mass Ratio KOH to DDG – S4</td>
<td>2.92</td>
<td>1705.575</td>
</tr>
</tbody>
</table>

The samples were analyzed using a BET surface area analyzer (Micromeritics, TriStar 3000). This was done using Nitrogen gas as the adsorbed gas at 77.3 K. The samples were degassed before the analysis at 160°C for two and a half hours. Raman spectroscopy was performed to determine the spectra of each sample using a Renishaw inVia Raman Microscope. Transmission Electron Microscope (TEM) with a combination of a single line EDAX analysis was performed to look at graphitization and composition of the sample (Tecnai G2 F30). Scanning Electron Microscope (SEM) images (Vega 3 Tescan) were also taken to show the differentiation in pore size, fiber structure, and surface defects for both post and pre-hydrolysis biomass and carbon samples. This would allow visual confirmation of the BET data that was collected from the surface area analyzer.

3. Results and discussion

The minimum benchmarks set for this work were 1000 m²/g BET surface area and average pore widths in the mesoporous range (between 2 nm and 50 nm) as these have been shown to be effective for high energy density applications [15,16]. The post-hydrolysis fibers are already acid-activated; when they were carbonized “as is” in our first attempt, the resulting AC yielded a surface area of 900 m²/g – which is lower than our target of 1000 m²/g. We chose to further activate the residual fibers using KOH. Both pre hydrolysis and post hydrolysis samples were prepared with KOH in the same manner and then carbonized to demonstrate the differences in the surface areas.
Fig. 2. Process for the production of high surface area activated carbon from DDG.

Fig. 3. Process for the production of high surface area activated carbon from soy hulls.
KOH activation is a complex process that involves multiple reactions taking place within and on the surface of the biomass structure. The process also involves characteristics of physical activation which includes the expansion of the material via gas release during heating. This results in three main explanations for the change in the structure of the material [19]. Surface area increases due to etching of the surface by the various redox reactions that occur between the potassium compounds and the increasingly free oxygen atoms available in the fiber structure. Water vapor and carbon dioxide result from surface reactions and decomposition of material at high temperatures. These vapors increase the pore volume and develop the porosity in a form of physical activation. Finally, the material is expanded due to metallic potassium layering itself into the structure of the fiber and then is removed during the washing process. The resulting material is a less dense, expanded carbon structure with a higher surface area that is dependent mainly on the physical structure of the precursor [19]. SEM images showing surface differences between the pre and post-hydrolysis residual fiber and of carbonized fiber samples produced from non-activated and KOH activated DDG (both post-hydrolysis) are included in Fig. 4. In the case of the DDG and soy fibers used, the post hydrolysis fibers for both biomass types showed an increased surface structure, as shown in Fig. 4. This is due to the acid activation during the hydrolysis process and removal of the hemicellulose and other structural compounds from the original fiber. In the case of both the DDG and the soy, there are drastic differences in surface morphology. The pre-hydrolysis fibers (Fig. 4a and c) show both flatter and smoother surfaces, while the post-hydrolysis fibers, as shown in (b) and (d), reveal an expanded / exploded surface that can be taken advantage of during activation. Carbonized sample from non-activated fiber (Fig. 4e) has a smooth obsidian-like surface, whereas, as shown in (f), the KOH activated

Fig. 4. SEM images showing differences in surface structure between pre and post-hydrolysis DDG fibers (a), (b); pre and post-hydrolysis soy hulls (c), (d); and between carbon made without KOH activation and with KOH activation (e), (f).
three curves are all representative of Type II isotherms, showing re
surface and therefore less surface area for application purposes. These
little potential for adsorption beyond the monolayer formed on the
where all of the surface area is found within those pores. This allows for
KOH both show curves typical of material with exposed micropores
absence of pores. The two carbons activated with 0.17:1 mass ratio of
Treatments, preliminary work was done with DDG residual fiber to give a
data profile that demonstrated the effect of concentration of KOH and
fluffing of fibers on both surface area and pore size. Fluffing was done
to aerate sample and ensure maximum surface area. Four samples were
and described in the literature [21], the surface area increased with increased KOH concentration (Table 1) as well as pore
volume as confirmed by the isotherms presented in Fig. 5 (adsorption
isotherms from KOH activated DDG). The non-activated sample shows
little to no adsorption in any range, representing an almost complete
absence of pores. The two carbons activated with 0.17:1 mass ratio of
KOH both show curves typical of material with exposed micropores
where all of the surface area is found within those pores. This allows for
little potential for adsorption beyond the monolayer formed on the
surface and therefore less surface area for application purposes. These
three curves are all representative of Type II isotherms, showing re
versible adsorption of a monolayer on a non-adsorbent or macroporous
material [28]. The 1:1 mass ratio of KOH yielded a Type IV isotherm,
visible adsorption of a monolayer on a non-adsorbent or macroporous
material [28]. The 1:1 mass ratio of KOH yielded a Type IV isotherm,
increased with increased KOH concentration (Table 1) as well as pore
width. At higher pressures, there is a sharper uptake representing adsorption beyond the
initial monolayer and multilayer adsorption into capillary condensation
[21,30].

3.2. Surface area of pre and post hydrolysis fibers

The surface areas of activated carbons produced from pre and post
hydrolysis fibers are compared in Table 2. The corresponding isotherms
are given in Fig. 6. KOH to fiber ratio of 1:1 was used as the activation
recipe. Pre-hydrolysis fibers were carbonized with KOH mixture, hy
drolyzed fibers were run as described in the experimental section before
being carbonized, control sample comes from an industrial activation
process.

As shown in Table 2, the surface areas of carbonized fibers from pre
hydrolysis DDG and soy are drastically different. The AC from pre-hy
drolysis DDG is only 10 m²/g compared to 689 m²/g for soy. However,
the surface area of AC from post-hydrolysis DDG increased dramatically
to about 1700 m²/g compared to a moderate value of about 1300 m²/g
for post-hydrolysis soy. This discrepancy is most likely due to the less
dramatic change in surface structures of the soy after it goes through
the hydrolysis process (Fig. 4). The pre-hydrolysis soy already has an
intricate and defined surface structure which explains the relatively
high surface area of 600 m²/g after carbonization. The change in the
surface structure of soy seems to only provide enough surface change to
achieve 1300 m²/g post hydrolysis carbons.

The corn fiber presents a very different surface structure. Corn fiber
in its natural state has a tough protective layer that is selectively hy
drophobic. As shown in Fig. 4(a), this provides a smooth structure made
up of small, rectangular, interlocking units that provide a barrier from
outside elements in nature [17]. This can prevent the development of
the surface area and therefore prevent the production of higher surface
area carbons if the fiber alone is used as a precursor. Fig. 4(b) is an
image of post-hydrolysis fiber showing a highly etched surface. The
pericarp, being removed, leaves behind cellular block structures with
obvious depth. This provides a very small surface area of 0.7844 m²/g
but high potential to increase due to its jagged surface. The soy fibers
present pentagonal cells that form a honeycomb-like structure. This
structure and the observed lack of an outer protective coating like the
DDG would explain the larger surface area value for carbonized, pre-
hydrolysis soy compared to the DDG.

The isotherms in Fig. 6 show little to no multi-layer adsorption in
the pre-hydrolysis samples. This is indicated by the Type II isotherm.
Surprisingly, the post-hydrolysis soy also showed a Type II isotherm in
spite of its higher surface area. Because of this adsorption pattern, we
can speculate that the only added pores to the post-hydrolysis are large
surface pores, increasing the overall surface area, but not showing in-
creased adsorption beyond the monolayer. This could also help explain

Table 2

<table>
<thead>
<tr>
<th>Sample (1:1 KOH to Grains)</th>
<th>BET Surface Area (m²/g)</th>
<th>Langmuir SA (m²/g)</th>
<th>External Surface Area (m²/g)</th>
<th>Average Pore Width (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DDG: Pre-Hydrolysis</td>
<td>10.44</td>
<td>15.47</td>
<td>7.35</td>
<td>9.533</td>
</tr>
<tr>
<td>DDG: Post-Hydrolysis</td>
<td>1705.58</td>
<td>2440.36</td>
<td>1245.13</td>
<td>2.922</td>
</tr>
<tr>
<td>Soy: Pre-Hydrolysis</td>
<td>689.03</td>
<td>972.92</td>
<td>262.15</td>
<td>2.652</td>
</tr>
<tr>
<td>Soy: Post-Hydrolysis</td>
<td>1316.34</td>
<td>1860.06</td>
<td>533.21</td>
<td>2.202</td>
</tr>
<tr>
<td>Control: MWV</td>
<td>1226.71</td>
<td>1751.39</td>
<td>797.18</td>
<td>3.620</td>
</tr>
</tbody>
</table>
the discrepancy between the differences in surface areas between the two precursors. DDG clearly gains micropores upon hydrolysis and carbonization as indicated by its Type IV isotherm, adding to its overall surface area by forcing condensation of Nitrogen at higher pressures [28]. This behavior is most similar to the MWV carbon control, an indication that it may be the most effective for energy storage purposes. This would imply a potentially more effective transfer of ions in capacitors. The post-hydrolysis DDG sample in and of itself would probably be an effective carbon to use in many renewable energy applications, but the goal would be to continue to increase the surface area so that a maximum amount of energy could be stored.

As demonstrated by the data, there is a dramatic increase in the surface area of the carbons produced from pre and post-hydrolysis fibers. This is an expected result as the chemical activation process is dependent on the surface structure of the precursor. The fibers that had variant and fibrous surface defects provided a good medium for KOH to react with the surface. Both residual fibers from DDG and soy were able to produce carbons that exceeded 1000 m²/g in terms of surface area as well as maintained an average pore size of around 2 nm. This shows that both could be used as a viable fiber starting material for AC.

3.3. Structure of the activated carbons produced

In order to explore the physical and chemical structure of the activated carbons, transmission electron microscopy (TEM) and Raman techniques were used to look at the arrangement of the carbon and the types of bonds between the carbons.

TEM images (Fig. 7) and corresponding selective area electron diffraction patterns (Fig. 8) for carbons derived from pre and post-hydrolysis fibers are typical of amorphous carbon materials. Fig. 7 shows variations in the exfoliation between the pre and post-hydrolysis DDG and soy, but no real organization of the material into a crystalline structure seen in graphene. Both pre-hydrolysis samples (Fig. 7a and c) show the similar graphitic planes, as seen toward the edges of the image subject. The higher density of planes within the post-hydrolysis samples are indicative of a more exfoliated carbon-revealing how structures at the nm scale could be impacting overall surface areas. This change in exfoliation seems to appear more drastic in the DDG sample as indicated by the stronger organizational lines and lesser density of planes in Fig. 7a. However, this could be due to the specific area of the material that was imaged at the time.

SAED patterns for all the samples were diffuse, indicating minimal crystallinity for all four samples [29]. The absence of bright points along the rings reveals little lattice structure that might be expected from graphene compounds [32]. This does not disqualify it from its use as an energy storage material, it merely suggests that conductive properties of a system that uses these carbons might be minimal (as shown in Fig. 8).

Raman spectra were then obtained to help determine the structure and to compare the spectra to samples of commercially available activated carbons. The spectra are presented in Fig. 9. As shown in Fig. 9(a), all three of the spectra show traditional peaks found in most carbon results from the literature. When discussing carbon materials, these spectra are divided into 3 main peaks; The G peak, which is found at 1580 cm⁻¹ in disordered carbons and looks at the sp³ hybridization [22], the D peak at 1350 cm⁻¹ which is indicative of the clustering of the sp² hybridized carbons, and the 2D peak which represents an overtone of the vibration from the D peak at around 2690 cm⁻¹ [23]. The presence of a D peak in all three samples and a G peak generally represent two different characteristics of the structure. The G peak presence represents a lack of graphitic organization meaning that in terms of the three carbons tested, the best for graphitic capabilities would be the DDG carbon. Because the G peak is greatly reduced in comparison to the D peak in the DDG sample, more order would be expected of its carbon structure.

Fig. 9(b) shows the D and G bands with a Lorentzian curve fit. The intensity ratio (R = ID/IG) of the D and G bands calculated for all three samples is 0.21, 0.86, 1.25 for wood, DDG, and soy hulls ACs.
respectively. The intensity ratio, \( R = \frac{I_D}{I_G} \) is related to the structure of carbon materials and implies that the wood-derived sample has the highest degree of disorder. The most ordered sample based on \( R \) would therefore be the soy carbon. Additionally, for the soy-derived sample a strong 2D peak could indicate layering of carbonaceous materials, contributing to its higher intensity ratio. The structural parameter, \( L_a \) of the fibers is related to the intensity ratio, \( R \) as \( L_a = C/R \), where \( C \) is a constant. \( L_a \) is also another measurement of the crystallinity and order of the structure. As \( L_a \) increases, layered stacking becomes more disordered, usually due to burnoff during the carbonization process [31]. From our Raman results, it can be concluded that \( L_a \) is largest for the wood-derived sample and the smallest for soy-derived samples again implying higher disorder in the wood and lower disorder in the soy.

3.4. Impact of the high surface area activated carbons on energy storage

One of the potential applications for the high surface area AC produced from the sustainable agricultural sources is in renewable energy storage devices; e.g., supercapacitors, which require materials that provide high energy density. Such AC can be produced at a relatively low cost by incorporating abundantly available and less expensive agricultural biomass precursor. This lowered cost can lead to large rates of manufacture and increased consumption. As discussed in later sections with TEM imaging, the carbons produced are graphitic in nature, making them potentially conductive. This combined with the porosity and high surface area would, in practice, allow the carbon matrix combined with a binder to form electrodes in supercapacitors leading to batteries and capacitors with high energy density.
Electrochemical measurements were conducted for the use of ACs in a supercapacitor structure. For this, the electrodes were prepared using the various surface area ACs prepared after activation with varying ratios of KOH in Table 1. The electrode materials for both the cathode and anode are prepared using 90 wt% active material (ACs) with 2 wt% AB (acetylene black) and 8% PVDF (Polyvinylidene fluoride) binder distributed in NMP (N-Methyl-2-pyrrolidone) solvent. The well-mixed slurry is coated onto an aluminum foil using the doctor blade method. The electrodes were then dried at 180 °C for 3 h under vacuum.

Fig. 10(a) shows preliminary results of supercapacitor characteristics for both electrodes comprising high surface area AC (produced with 1:1 KOH activation) as the active material when the full cell is charged and discharged between 0 and 3.5 V at the current density of 500 mA/g. The electrolyte was 1.5 M TEAPF₆-PC (Tetraethylammonium hexafluorophosphate in propylene carbonate). Almost linear voltage–time relation (discharge) is characteristic of electric double-layer capacitance. There is a slight distortion of the curves presumably caused by the pseudo capacitance of functional groups. The specific capacitance of the electrode was calculated by the equation, \[ C = \frac{\Delta I \Delta t}{m \Delta V} \], where I, \( \Delta t \), m, and \( \Delta V \) are the applied current, discharge time, mass of the active material, and the voltage change, respectively. First cycle capacity was found to be ~100 F/g. Fig. 10(b) compares the supercapacitor performance of the four samples produced with varying ratios of KOH (Table 1) under same current density (500 mA/g) including the non-activated sample as the control (S1). The cycling performance of the AC increased dramatically as the surface area increased from S1 to S4. The capacitance value is seen to range from 4 F/g to 100 F/g; interestingly, the capacitance varied linearly with the surface area as seen in Fig. 10(c). This variation of capacitance may stem from the fact that it has the varying pore sizes compared to the triethylamine cation, TEA⁺ and hexafluorophosphate anion, PF₆⁻ thereby affecting the effective accessibility of electrode/electrolyte interface areas. In general, proper matching of pores with the ions can allow full utilization to form the double layer and contribute to the higher capacity values. The low capacitance for ACs with high specific surface area is believed to be mainly due to their low mesopores and, in turn, low electrolyte accessibility. For microporous carbon or mesoporous carbon fibers, to efficiently host the electrolyte ions, the pore size should be more precisely tuned.

4. Conclusions

The present work shows that residual fiber (fiber remaining after extraction of C5-sugars) generated as part of a C5 biorefinery are very effective biomass starting materials to produce high surface area activated carbons. Residual fibers after hydrolysis of corn pericarp fibers from dried distillers’ grains (DDG) and soy hulls were carbonized and activated to produce activated carbons (AC). Our work showed that the AC produced from the residual fiber delivered an order of magnitude higher surface area than the one directly from corn pericarp fiber and soy hulls. The surface area of the AC from pre-hydrolysis DDG was only 10 m²/g compared to 689 m²/g for soy hulls. However, the surface area of AC from post-hydrolysis DDG and soy hulls increased dramatically to 1700 m²/g and 1300 m²/g respectively. Isotherms from BET measurements demonstrated that most of the pores were in the micro and mesoporous ranges – optimal sizes for many electrolytes in energy storage. TEM imaging of the activated carbons from pre and post hydrolysis biomass shows thin layers of non-amorphous carbon, indicating a potential for graphene formation which would be beneficial for applications requiring conductivity.

When used to make double plate capacitors, the sample with the highest surface area AC (produced with 1:1 g/g KOH activation)
showed the highest capacity ~100 F/g which is comparable to standard activated carbon capacitors. Further, the capacity is seen to vary linearly with the surface area. Based on these results, further exploration of these carbons from a production standpoint can lead to the increased use of sustainable low-cost agricultural biomass-based activated carbons as components in energy storage devices such as supercapacitors. When leveraged as co-products from a C5 sugar-based integrated biorefinery, such as lightweight and high specific surface area (SSA) activated carbons (AC) can improve the overall economics of a biorefinery.

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