Effects of FeCl₃ Catalytic Hydrothermal Carbonization on Chemical Activation of Corn Wet Distillers’ Fiber

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ABSTRACT: Corn wet distillers’ fiber (corn fiber) is a byproduct of the corn-ethanol production process, with high potential as a precursor for activated carbon due to its moderate nitrogen content and availability. However, there has been limited investigation into activated carbons from the corn fiber. In this work, we produce activated carbons from the corn fiber using three procedures, including direct KOH activation, hydrothermal carbonization (HTC) followed by KOH activation, and FeCl₃-catalyzed HTC followed by KOH activation. Catalytic HTC with FeCl₃ was found to slightly increase the degree of carbonization relative to uncatalyzed HTC while also removing the nitrogen content at increasing concentrations and slightly increasing the porosity. The resulting activated carbon samples are then characterized by thermal gravimetric analysis, Fourier transform infrared spectroscopy, scanning electron microscopy, and nitrogen analysis. The two-step process resulted in activated carbon with substantially higher surface areas than the one-step process (1220 vs 789 m²/g), as well as much higher thermal stability and nitrogen content (up to 1.20%). The results show that the corn fiber has potential for activated carbon production, with the two-step HTC followed by the activation process producing more favorable material properties than direct activation.

INTRODUCTION

Hydrothermal carbonization (HTC) is a thermochemical processing method for biomass in which the sample is submerged in water, sealed, and heated under autogenous pressures to produce a char, whereas traditional carbonization involves heating the material in an inert environment such as nitrogen gas. Relative to traditional carbonization, which can approach temperatures of 1000 °C and in which the biomass must be first dried, HTC operates at closer to 200−300 °C and does not require predrying. HTC has been tested extensively in the literature under a variety of conditions and with various biomass sources. HTC has also been shown to decrease the ash content of biomass. HTC is especially useful for processing biomass with a high moisture content, which would otherwise be energy intensive to dry, and the relatively low operating temperatures have been shown to maintain nitrogen, sulfur, and oxygen contents. The maintenance of heteroatoms gives HTC an advantage over traditional carbonization for activated carbons for applications such as supercapacitors. Super-capacitors require a large chemically active surface area with a hierarchically interconnected pore structure [containing micro (<2 nm), meso (2−50 nm), and macro (>50 nm) pores]. The addition of heteroatoms, such as oxygen, nitrogen, and sulfur, can increase wettability or pseudo-capacitance behavior and result in substantially higher performances. As such, activated carbons produced from the hydrochar have performed better than commercial activated carbons in some instances.

Corn wet distillers’ fiber (corn fiber) is a biomass stream produced as a byproduct of the corn-ethanol production process and is currently used as part of a combined stream (fiber with syrup) for cattle feed supplement. However, with crop contamination being a substantial issue which may grow with climate change, alternative high-value applications are needed. Due to the high nitrogen and moisture contents of the corn fiber, it is well suited for hydrothermal treatment. In addition to the benefits of HTC, catalytic HTC can produce hydrochars with a higher level of carbonization, an increased nitrogen or sulfur content, or increased porosity. One catalyst which has had limited investigation is FeCl₃. The catalyst FeCl₃ has been used as an activating...
agent, with moderate success, in a number of studies.\textsuperscript{19−21} FeCl\textsubscript{3} has also been investigated separately as a catalyst for HTC, showing a moderate increase in hydrochar quality, including increased surface area, through increased bond cracking of cellulose.\textsuperscript{22} Despite the preliminary potential of the catalyst, to the authors knowledge, no studies exist which have tested FeCl\textsubscript{3}-catalyzed HTC followed by activation.

KOH activation is among the most common methods for producing activated carbons in the literature, with optimal reaction temperatures between 700 °C\textsuperscript{23} and 900 °C,\textsuperscript{3} KOH-to-biomass mass ratios of 2:1\textsuperscript{24} to 4:1,\textsuperscript{25} and residence times of either 60 min\textsuperscript{26} or 120 min\textsuperscript{4} Washing after activation is done using distilled water\textsuperscript{24} or HCl of 0.1 N\textsuperscript{10} or higher concentration,\textsuperscript{4} followed by distilled water. Impregnation of the biomass with the activating agent is either accomplished by liquid mixing followed by evaporation or mechanical mixing, with mechanical mixing being simpler but resulting in a slightly reduced quality.\textsuperscript{27} The mechanism by which KOH activation takes place has not been well understood; however, a few main mechanisms have been widely accepted, including etching of the carbon framework, partial gasification of carbon, and intercalation of metallic K into the carbon lattices which creates porosity after removal of potassium by washing.\textsuperscript{28} Jin et al. (2014) produced activated carbon for supercapacitors by KOH activation of a similar product of the corn-ethanol process to the corn fiber, distillers dried grains with solubles, and found it to be suitable for high-performance supercapacitor electrodes.\textsuperscript{29}

The purpose of the following study is to investigate the potential of FeCl\textsubscript{3} to act as a hydrothermal catalyst for the corn fiber, as well as the potential of these hydrochars and raw corn fiber to produce high-surface-area activated carbons. The main novel investigations of the following study are the utilization of a previously untested material in a two-step HTC and chemical activation procedure, a unique investigation of FeCl\textsubscript{3} catalysis in HTC and its application as a pretreatment to activation, and the proposal of possible chemical reactions for an integrated system based on FeCl\textsubscript{3}-catalyzed HTC and KOH activation. New observations are made relative to previous studies on FeCl\textsubscript{3} catalysis in HTC, and a high-value alternative application for the corn fiber is identified.

\begin{table}
\centering
\caption{Ultimate Analysis and Ash Content of the Raw Corn Fiber and Catalyzed HTC Hydrochars}
\begin{tabular}{|l|c|c|c|c|c|c|}
\hline
source & C (%) & H (%) & N (%) & S (%) & O (%) & ash (%) \\
\hline
raw fiber & 49.48 ± 1.40 & 6.93 ± 0.22 & 2.96 ± 0.88 & 0.19 ± 0.07 & 38.58 ± 2.58 & 1.85 \\
HTC-0 & 67.28 ± 0.38 & 7.32 ± 0.19 & 2.82 ± 0.21 & 0.22 ± 0.018 & 21.78 ± 0.80 & 0.56 \\
HTC-10 & 69.81 ± 0.31 & 6.77 ± 0.18 & 2.54 ± 0.07 & 0.29 ± 0.01 & 19.51 ± 0.58 & 1.08 \\
HTC-20 & 72.19 ± 0.21 & 7.02 ± 0.12 & 1.84 ± 0.05 & 0.29 ± 0.011 & 18.56 ± 0.40 & 0.09 \\
HTC-50 & 70.38 ± 0.44 & 6.49 ± 0.10 & 1.02 ± 0.016 & 0.24 ± 0.016 & 21.28 ± 0.57 & 0.57 \\
HTC-100 & 70.53 ± 0.52 & 6.64 ± 0.04 & 0.758 ± 0.0014 & 0.202 ± 0.007 & 20.98 ± 0.57 & 0.88 \\
HTC-200 & 69.66 ± 0.06 & 6.57 ± 0.03 & 0.60 ± 0.01 & 0.19 ± 0.014 & 19.54 ± 0.12 & 3.44 \\
\hline
\end{tabular}
\end{table}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{Figure1.png}
\caption{TGA and DTG curves for the raw corn fiber and catalyzed HTC hydrochars.}
\end{figure}
RESULTS AND DISCUSSION

The pressure of the reactor over time during the experiments was monitored, with the maximum pressure increasing substantially with higher concentrations of FeCl₃. In the case of HTC-200, the maximum pressure during the reaction reached 134.1 bar, whereas for HTC-0, it reached a maximum of 43.4 bar. This pressure change may be due to the presence of HCl and may be noteworthy as the pressure increases the system energy and is known to have a small effect on HTC reactions such as dehydration and decarboxylation.³⁰ The moisture content of the raw fiber was determined to be 63.6 ± 0.12 percent through four trials. CHNS–O and ash contents for the raw material and hydrochars are shown in Table 1. There appears to be a slight increase in the degree of carbonization with the addition of the catalyst; however, increased concentration of FeCl₃ did not appear to increase carbonization further and the carbon content decreased slightly after a peak at 20%. This effect could also be due to the presence of HCl, which has been shown to catalyze the reaction as well.⁵¹ The ash content appears to have increased in the case of HTC-200. The most severe effect of increasing the concentration of FeCl₃ was the reduction in the nitrogen content of the biomass. This nitrogen leaching effect has not been mentioned in previous studies testing either HCl³² or FeCl₃.²² Given that the nitrogen content is generally seen as advantageous in many applications of hydrochar, this effect is undesirable. While there was a slight change in the H/C and O/C atomic ratios due to the addition of FeCl₃, increasing the concentration further had little to no effect on these ratios.

Thermal gravimetric analysis (TGA) and derivative thermogravimetry (DTG) curves for the raw sample and hydrochars can be seen in Figure 1. Hydrothermal treatment resulted in a substantial increase in the thermal stability and residual weight. The large peak in the DTG curve around 250–300 °C in the raw sample was removed for all hydrochars. This is likely due to the removal of hemicellulose during HTC. The addition of higher concentrations of FeCl₃ appeared to increase the thermal stability and residual weight of the samples. This is also seen in the variations of the DTG curves for the uncatalyzed and catalyzed HTC hydrochars as the catalyzed hydrochars have a substantially less intense peak around 400 °C relative to the uncatalyzed samples. This may be due to the increased hydrolysis reactions causing the alteration of cellulose content to alternative and more thermally stable forms of carbon as FeCl₃ is a Lewis acid and thus may increase the rate of cellulose breakage through hydrolysis and aromatization reactions during HTC.²²

Fourier transform infrared (FT-IR) spectra for the hydrochars are shown in Figure 2. A broad band in the region of 2400–3400 cm⁻¹ for the hydroxyl or carboxyl group is observed more prevalently in the catalytic hydrochars, which is assigned to the increased presence of carboxylic acid. The weak band at 3300–3500 cm⁻¹ attributed to OH stretching is only present in the noncatalytic and raw sample, confirming that the catalytic HTC creates carboxylic acid in comparison to the raw and noncatalytic HTC hydrochar. There was a steady decrease in the intensity of O–H with the increase of the reaction temperature, indicating that the HTC process improved the
dehydration, consistent with the elemental analysis results. Strong peaks at 1700 cm\(^{-1}\) in all samples are attributed to the C\(\equiv\)O stretch suggesting the abundant existence of these functional groups on the surface. The two intense peaks in the 2850–2960 cm\(^{-1}\) range are attributed to an alkyl C–H stretch, with a small peak just above 1500 cm\(^{-1}\) due to the alkenyl C–H stretch, and the intensity of this is reduced in the samples from high catalyst concentration HTC.\(^{33}\) Additionally, the peaks at 1600 and 875–750 cm\(^{-1}\) are attributed to C\(\equiv\)C vibrations and the aromatic C–H vibration and are most intense in the catalytic samples as a result of the reaction that can be ascribed to the breakdown of cellulose/hemicellulose and partial decomposition of the stable lignin and demonstrates that the aromatization reaction happened during the HTC process.\(^{34}\)

The C–O–C vibration band in the region of 1400–1100 cm\(^{-1}\) diminished, whereas the growth of bands at 1600 cm\(^{-1}\) indicates progressive development of aromatization in the carbon skeleton through the postcarbonization treatment.

Scanning electron microscopy (SEM) image of the raw material is shown in Figure 3. SEM images for the HTC-0, HTC-20, and HTC-200 hydrochars can be seen in Figure 4. HTC-0 was chosen as the baseline; HTC-20 was chosen as it had the most optimal properties; and HTC-200 was chosen to see if the high catalyst loading had an effect on the hydrochar structure. It can be seen from the images that the hydrochars have a more amorphous structure than the raw material. Additionally, the images for HTC-20 appear to have some carbon microspheres, and the HTC-200 sample has many more holes on the surface. It is possible that a more severe treatment (above the melting temperature of FeCl\(_3\) of approximately 300 °C) may have a more significant effect on the structure, although the corrosive nature of the catalyst limits the ease at which this may be tested.

In addition, while no characterization tests were done on the process water from the hydrothermal reaction, it was observed that the HTC-200 test, which reached a substantially higher pressure than the other reactions, had a green-colored process water in contrast to the dark brown color of all of the other reactions. To give a better indication of the cause, a solution of KOH was prepared by mixing 10 g of KOH powder with 500 mL of water, and 150 mL of the solution was slowly added to 25 mL of the HTC-200 process water. The process water solution turned from a dark green translucent liquid to a brownish opaque liquid. The solution was then filtered into a solid (brown wet solid) and light green liquid which was more transparent than the original process water. Finally, the light green transparent liquid was mixed with the remaining KOH solution quickly, and the mixture formed two phases, one clear solution and another an insoluble green solid. The green solid in the solution, if removed and brought into ambient air, quickly reacted to turn reddish brown. See Figure S1 for the appearance at each state. It is thought that the high pressure of the reactor in the case of HTC-200 resulted in the conversion of some of FeCl\(_3\) to FeCl\(_2\), which resulted in the green color of the process water. Adding KOH slowly while mixing allowed for the reaction with atmospheric oxygen and thus the formation of Fe\(_2\)O\(_3\) or its hydrates. When mixed quickly, there was no time to react with atmospheric O\(_2\), and thus Fe(OH)\(_2\) precipitated to form a dark green solid. The water acted as a protective layer to limit reactions with atmospheric O\(_2\), but when taken out of solution, the solid would again form Fe\(_2\)O\(_3\). The suspected reaction of FeCl\(_3\) with KOH and the reaction of Fe(OH)\(_2\) with O\(_2\) are shown in eqs 1 and 2.

\[
\text{FeCl}_3 + 2\text{KOH} \rightarrow \text{Fe(OH)}_2 + \text{KCl} + \text{HCl}
\]

\[
4\text{Fe(OH)}_2 + \text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3 + 4\text{H}_2\text{O}
\]

Activated carbons produced from the raw corn fiber, HTC-0, and HTC-20 samples were chosen to be analyzed. Only HTC-20 was chosen as the catalytic samples as it was considered to have the best properties. The TGA and DTG curves for the activated samples are given below in Figure 5. The TGA graph clearly shows that the hydrothermal treatment of the biomass prior to activation increases the thermal stability and residual mass of the activated carbon. This effect may be due to an increased removal of volatile components through the two-step process. The DTG curve shows some surface moisture loss (below 105 °C), with the greatest weight loss rate occurring at approximately 520 °C for the activated carbon from the raw corn fiber and a wider curve peaking at approximately 650 °C for the activated carbons from the hydrochar. The transition from weight loss peaks at approximately 300–400 °C to weight loss peaks in the range of 500–700 °C has been shown previously to signify the transition from amorphous carbons to carbon nanotubes in an atmosphere with some oxygen availability.\(^{35}\) Alternatively, a similar weight loss was seen in other studies on biomass-derived activated carbons.\(^{36}\) The later peak for hydrochar-derived activated carbons may be an indication of increased carbonization of these samples. While the activated carbon produced from the raw biomass was relatively soft, the hydrochar-derived activated carbons were much harder.

FT-IR spectra for the activated carbon samples are presented in Figure 6. Minor peaks at 1890 cm\(^{-1}\) in each sample were attributed to C–H bond stretching vibrations, and the peak at 1580 cm\(^{-1}\) was attributed to C\(\equiv\)C aromatic ring stretching vibrations.\(^{37}\) No C–OH or carboxylic acid stretch is visible, and only a very weak peak at 1700 cm\(^{-1}\) is visible where C\(\equiv\)O
stretching is found. Reduction reaction is expected during the thermal treatment and the reaction between free radicals generated by breakdown of carbonaceous chains and oxygen-forming groups such as carboxylic acids. This is evident from a comparatively lower intensity of peaks between 800 and 3000 cm\(^{-1}\) representing aromatic structures, for example, 880 cm\(^{-1}\) in all samples, at 754 cm\(^{-1}\) in the AC-Raw sample, or C–C rings in the range of 1400–1600 cm\(^{-1}\).

SEM images of the activated samples over a range of magnifications can be seen in Figure 7. Each set of SEM images clearly shows substantial changes to the surface morphology relative to the raw material or hydrochar.

The quality of the three activated carbon samples is more specifically defined by their specific surface area (SSA), pore volume, pore size distribution, and heteroatom presence. The raw isotherm data are presented in Figure 8. The adsorption curve appears to be an IUPAC type 1 curve for microporous materials, with a small hysteresis at a relative pressure of 0.5. However, without data for the range below \(P/P_0\) of 0.1, any type determination or pore analysis will have a high degree of uncertainty. However, an isotherm analysis was still performed to provide a comparison between the three samples.

Table 2 outlines the key properties as per the Quanta chrome 5.0 software and the nonlocal density functional theory (NLDFT) method, as well as provides the nitrogen content from the LECO FP-528 Nitrogen Determinator. The pore size distributions of the activated samples are presented in Figure 9.

The hydrothermal treatment created a moderately increased quality in the activated carbon with respect to pore development. In addition, the catalytic treatment with FeCl\(_3\) further increased the surface area and pore volume relative to the noncatalytic sample, as well as increased the average micropore radius. The hydrothermal treatment substantially increased the nitrogen content of the final activated carbon; however, the sample produced by the catalytic HTC did not have this benefit. The slight variations in the micropore size distribution may be an important aspect to maximize performance. Since the FeCl\(_3\)-catalyzed hydrochar produced
activated carbon with a larger average micropore size, it may be more suited for use in supercapacitors with a slightly larger electrolyte ion size. As such, this factor should be considered when deciding to use or exclude FeCl₃ in the preprocessing step.

In order to propose a mechanism for an integrated system based on FeCl₃-catalyzed HTC and KOH activation, the literature was comprehensively reviewed, FT-IR analyses were interpreted in detail, and experimental chemical tests were designed. Figure 10 shows a possible chemical reaction pathway of KOH activation during pyrolysis of Fe-treated hydrochar. As can be seen from the FT-IR spectra, the hydrochar obtained from FeCl₃-catalyzed HTC holds large amounts of functional groups (Figure 2). According to the literature, during the KOH activation, carboxylic, carbonyl, hydroxyl, and aldehyde functional groups attached to the hydrochar surface chemically react with KOH to release H₂, CO, and CO₂ gases and form K and K₂CO₃ (eqs 3 and 4).³⁸,³⁹ Meanwhile, KOH may undergo a reaction with carbon fragments (eqs 5 and 6). Since the temperature is set to a high temperature of 800 °C, K₂CO₃, which is the prevalent product of the KOH activation process, can be further converted to K₂O and K, along with the release of CO and CO₂.

KOH + (−COOH)/(−O−CaO)
→ K₂CO₃ + K + H₂ + CO₂

KOH + (−CaO)/(C−O−C)
→ K₂CO₃ + K + H₂ + CO

KOH + (−O−CH₃) → K₂CO₃ + K + H₂ + CH₄

KOH + (C−OH) → K₂CO₃ + K + H₂O + H₂

KOH + (C−H) → K₂CO₃ + K + H₂

6KOH + 2\(\text{C}_2\text{K}_2\text{CO}_3\) + 2K + 3H₂

K₂CO₃ + ČK₂O + 2CO

K₂CO₃ → K₂O + CO₂

2K + CO₂ → K₂O + CO

K₂O + Č2K + CO

Mineral acids such as hydrochloric acid, sulfuric acid, and phosphoric acid have been widely used in the HTC of various natural biomass and model compounds. Many studies showed that these homogeneous activators could accelerate the carbonization process via dehydration of simple sugars like furfural, fructose, sucrose, and xylose to form carbon basic structural units. In other words, this phenomenon fabricates a hollow carbonaceous microsphere providing a substrate for carbonaceous particles (i.e., hydrochar) formed later due to the repolymerization. The mechanism of HTC in the presence of such acids has been previously proposed and discussed in
detail by Kang et al. With this in mind, a mechanism for FeCl₃-catalyzed HTC was proposed. Fe cations (Fe³⁺ and Fe²⁺), being electron acceptors, as Lewis acids could accelerate the dehydration reactions by protonation of glycosidic oxygen followed by scission of natural polysaccharide consisting of linear chains of fructose units with glycosidic linkage. This is in agreement with the FT-IR spectra presented in Figure 2. It can be seen that the higher concentration of Fe³⁺ caused the less absorption peak intensity of the C=O group at 1700 cm⁻¹.

Afterward, dehydrated intermediates such as oligosaccharides, phenolic, and furan compounds undergo repolymerization due to the C=C bonds produced by keto–enol tautomerization and intramolecular dehydration.

**CONCLUSIONS**

FeCl₃-catalyzed HTC has been shown to increase the degree of carbonization slightly; however, this effect did not increase with higher catalyst loading, and nitrogen content was removed from the material. The addition of FeCl₃ appears to have also caused the removal of OH functional groupings. A small amount of pore development may have occurred in the material with FeCl₃ use; however, the level of porosity is small. In addition, pressure build-up at higher catalyst loadings has shown evidence of the conversion of FeCl₃ to FeCl₂. These results are in line with previously reported HTC catalyzed by FeCl₃, which was found to increase carbonization and carbon microsphere development, although the nitrogen content leaching was not reported in previous studies.

Activated carbons produced from the corn fiber and corn fiber hydrochars showed a major structural change through SEM images and surface area and pore volume measurements and substantially increased thermal stability. The thermal stability of the hydrochar-derived activated carbons was substantially higher than that of the raw corn fiber-derived activated carbon, increasing from 48 to 85% residual weight after TGA, indicating a higher degree of carbonization. The SSA of the activated carbon from the raw corn fiber produced a moderate SSA of 789 m²/g, which increased to 1046 and 1220 m²/g for the HTC and FeCl₃-catalyzed HTC pretreated samples, respectively. However, the nitrogen isotherms used did not measure adsorption at low partial pressures, which will be needed to accurately determine the surface areas and porosities. The HTC treatment step substantially increased the nitrogen content of the final activated carbon product from 0.74 to 1.20%; however, the catalytic treatment did not have this benefit.

Overall, corn fiber has shown potential as a source material for activated carbon production, with noticeable pore development, moderate nitrogen content, and high thermal stability when first pretreated with HTC. Further study is needed to provide a stronger isotherm analysis with a lower relative pressure test range, to optimize the process parameters to maximize product quality, and to perform electrochemical testing to identify its practical performance.

**EXPERIMENTAL SECTION**

Corn fiber was obtained from IGPC Ethanol on October 7, 2019. Ferric chloride (40% W/V FeCl₃, 12.8–14.7% W/V Fe and 3.9–6.6% W/V HCl) solution and 0.1 N HCl solution were purchased from Fisher Scientific, Canada and used as received. KOH pellets were purchased from Emplura (≥ 84% KOH, ≤ 2% carbonate and trace amounts of others) and ground into a powder for use. It should be noted that FeCl₃ is highly corrosive, especially at elevated temperatures, and
Figure 7. SEM (10 kV) images of (a) AC-Raw, (b) AC-HTC-0, and (c) AC-HTC-20.
results in elevated pressures when used in HTC (as high as 134 bar at 220 °C for high concentrations). Catalytic HTC. Proportionate quantities of wet corn fiber and FeCl₃ solution were measured out so that the mass ratio of dry biomass to FeCl₃ would be as desired, with 82.4 g of wet biomass (30 g dry) used per trial. Dry biomass-to-FeCl₃ mass ratios of 1:0, 10:1, 5:1, 2:1, 1:1, and 1:2 were tested. In all tests, deionized water was added to the mixture to bring the total solution volume to 200 mL before the biomass was added to keep a biomass-to-water ratio of approximately 8.4. The mixture was then poured into a Hastelloy 300 mL autoclave (Parker Autoclave Engineers, Erie PA) with temperature control and a magnetic stirring unit. Hastelloy was used to resist the corrosive nature of FeCl₃, which also restricted the testing of higher temperatures as the risk of corrosion increases with temperature. The unit was sealed and pressurized with nitrogen up to approximately 9.3 bar (135 psi) to ensure that the internal pressure would stay above the water saturation pressure, so steam would not form during the experiment. The magnetic stirrer was set to 150 rpm. The internal pressure, temperature, and stirrer speed were monitored and recorded in 1 s intervals throughout the experiment. The reactor was heated, and the temperature was maintained at 220 ± 5 °C for 60 min. The reactor was then quickly cooled using an internal water-cooling loop. The solid products were separated by filtration and washed. The washing procedure involved washing the solid sample with several liters of hot deionized water, followed by washing with 100 mL of 0.1 N HCl and again washing with hot deionized water for several hours. This washing procedure was adapted from Oliveira et al. (2009) which confirmed the removal of iron species from the solid product after FeCl₃ activation.¹⁹ The washed solid samples were then dried at 105 °C for a minimum of 12 h and stored in airtight bags. The samples were named with respect to their dry biomass-to-FeCl₃ mass ratio used in the experiment. For example, a trial using 30 g of dry equivalent of biomass mixed with 75 mL of 40% FeCl₃ solution (30 g of FeCl₃ which is equal to 100% the mass of biomass used) would be denoted HTC-100.

Chemical Activation. A total of three samples were chosen for activation, raw corn fiber, HTC-0, and HTC-20. The raw and HTC-0 samples were chosen for baseline comparison, and the HTC-20 sample was chosen as it had the highest carbon content and the lowest ash content of the catalytic hydrochars while maintaining a moderate nitrogen content. The raw corn fiber was first dried at 105 °C and ground into a powder before use. For the KOH activation, we have modified a procedure from Chen et al. (2020).⁴¹ The samples were mixed with KOH in a 2:1 mass ratio (KOH-to-biomass) and inserted into a sealable stainless steel vertical reactor. Nitrogen was passed through the reactor at a rate of approximately 800 mL/min, and the reactor was heated inside a muffle furnace at a rate of 10 °C/min up to the set point of 800 °C. The set point was maintained for 1 h, after which the reactor was allowed to cool before the nitrogen flow was stopped. The activated sample was then washed with deionized water, followed by 100 mL of 0.1 N HCl, and then again washed with a large quantity of deionized water. The products were labelled as AC followed by the precursor, including AC-Raw, AC-HTC-0, and AC-HTC-20.

Characterization Methods. Characterization tests performed include ultimate analysis, ash analysis, moisture analysis, TGA and DTG, FT-IR, SEM, and nitrogen
adsorption/desorption isotherms. Moisture content of the raw sample was determined by taking the weight difference after drying at 105 °C for a minimum of 12 h. Ultimate analysis was performed using a Flash 2000 elemental analyzer (Thermo Fisher Scientific, Waltham, MA, USA). Samples were prepared by mixing approximately 2 mg of the sample with 10 mg of

![Figure 9. Pore size distribution for activated carbon samples. (a) Activated carbon from the raw corn fiber, (b) activated carbon from HTC-0, and (c) activated carbon from HTC-20.](image)

![Figure 10. Possible chemical reaction pathway of KOH activation during pyrolysis of Fe-treated hydrochar.](image)
vanadium pentoxide in a small silver crucible and pinched to seal. BBOT was used as a standard. Each sample was tested three times, and the average value was taken. Oxygen content was taken as the remaining mass after accounting for C, H, N, S, and ash contents, as per eq 13. Ash analysis was performed according to ASTM standard E1755-01 by heating the sample in an open crucible to 250 °C/min, holding for 30 min, and then heating to 575 °C for 3 h. Nitrogen content of the activated carbon samples was determined using a FP-528 Protein/Nitrogen Determinator (LECO Corporation, MI, USA). A small amount of the sample was combusted at approximately 900 °C as outlined in the LECO FP-528 operational manual (Leco, 2001).

\[
O \% = 100\% - C \% - H \% - N \% - S \% - ash \% 
\]

TGA was performed using a TGA machine (SDT-Q600, TA instruments-Waters LLC, New Castle, USA) with a heating rate of 10 °C/min, a maximum temperature of 1000 °C, and a nitrogen flow rate of 50 mL/min. FT-IR absorbance spectra were obtained using a Spotlight 200i FT-IR Microscopy System (PerkinElmer, Massachusetts, USA). A small quantity of the sample was placed onto the crystal surface and secured. A total of 32 scans at a resolution of 4 cm\(^{-1}\) were averaged to give the spectra for analysis with the OriginPro data analysis and graphing software (Version 9, OriginLab Corporation, MA, USA). SEM samples were prepared by spreading a small amount of the sample on a carbon tab and coating it with a thin layer of gold/palladium mixture in an argon atmosphere over 90 s. SEM images were then taken at coating it with a thin layer of gold/palladium mixture in an argon atmosphere over 90 s. SEM images were then taken at various magnifications using an accelerating voltage of 10 kV. SSA, pore size distribution, total pore volume, and average micropore size were determined by a Quantachrome Autosorb iQ nitrogen adsorption/desorption isotherm analyzer at 77.35 K from P/P\(_0\) of 0.1 to 0.9 with a final outgas time and a temperature of 7.5 h and 350 °C. The data were analyzed using Quantachrome ASIQwin Version 5.0 using the N\(_2\) on a carbon slit pore NLDFT equilibrium model.

### ASSOCIATED CONTENT

- **Supporting Information**
  The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c00557.
  Appearance of process water reaction products (PDF)

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