Simultaneous Fe$_3$O$_4$ Nanoparticle Formation and Catalyst-Driven Hydrothermal Cellulose Degradation

Alexander Wotton,* Tracey Yeung, Sreenu Jennepalli, Zhi Li Teh, Russell Pickford, Shujuan Huang, Gavin Conibeer, John A. Stride, and Robert John Patterson

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ABSTRACT: Breakdown and utilization of cellulose are critical for the bioenergy sector; however, current cellulose-to-energy conversion schemes often consume large quantities of unrecoverable chemicals, or are expensive, due to the need for enzymes or high temperatures. In this paper, we demonstrate a new method for converting cellulose into soluble compounds using a mixture of Fe$^{2+}$ and Fe$^{3+}$ as catalytic centers for the breakdown, yielding Fe$_3$O$_4$ nanoparticles during the hydrothermal process. Iron precursors transformed more than 61% of microcrystalline cellulose into solutes, with the composition of the solute changing with the initial Fe$^{3+}$ concentration. The primary products of the breakdown of cellulose were a range of aldaric acids with different molecular weights. The nanoparticles have concentration-dependent tuneable sizes between 6.7 and 15.8 nm in diameter. The production of value-added nanomaterials at low temperatures improves upon the economics of traditional cellulose-to-energy conversion schemes with the precursor value increasing rather than deteriorating over time.

1. INTRODUCTION

Increasing fossil fuel prices and lower emission targets have driven the development of carbon-neutral biofuels. Biofuels cover a wide gamut of fuel types and uses, including bioethanol, biodiesel, biogas, and syngas. However, all are derived from the processing and conversion of recently captured carbon from sources such as agricultural crops or marine algae. Much work has been done on the optimization of bioenergy feedstocks to maximize energy production. Researchers have aimed to increase the yield of easily processed carbohydrates and lipids while limiting the relative production of the less energetically valuable, difficult to process cellulosic material. However, due to the role of cellulose in the structure of plant cell walls, it will always represent a highly significant portion of all plant and algal biomass. The transformation of cellulose polymers into energetically valuable compounds is thus critical for the bioenergy sector.

Cellulose is the most abundant polymer on earth, representing approximately 70% of all woody matter and up to 33% of the dry weight of microalgae. Chemical and biological cellulose processing methods are the two dominant industrial-scale cellulose-to-energy conversion schemes. During chemical energy extraction, cellulose is often exposed to strong acids and high temperatures, creating glucose monomers after cleaving glycosidic bonds. Alternatively, biological cellulose processing involves the hydrolytic extraction of sugars by a combination of enzymes and microbes. However, neither chemical nor biological cellulose-to-energy conversion schemes have achieved wide-scale adoption, largely due to high energetic and economic costs, limiting net energy production and potential value.

Recently, to reduce energy expenditure and maximize net energy yields, lower-temperature pyrolytic and hydrothermal schemes using catalysts have been demonstrated. These catalytic conversions have demonstrated promise with high conversion rates and additional product selectivity. Unfortunately, many of these catalysts show diminishing returns, with even highly robust silica/carbon nanocomposite catalysts optimized for reusability, showing approximately 10% loss after two reuses. Catalytic pyrolysis is impacted by the composition and size of the catalyst, with smaller nanoparticle catalysts performing better than larger, micron-sized structures.

Nanoparticles and ions are typically much more reactive than equivalent larger bulk phase particles. The greater catalytic activity of nanoparticles is due to the high surface area to volume ratios and undercoordinated surface atoms, which impact charge
transfer, strain, and quantum size effects. Undercoordinated atoms increase molecular adsorption by increasing localized charge across the surface of a particle, which selectively attracts oppositely charged molecular regions. A range of industries uses the high adsorption and molecular selectivity of these undercoordinated surface regions to control redox reactions.

Cellulose degradation approaches often aim to optimize the production of specific cellulose breakdown products by modifying the catalysts, buffers, enzymes, and temperatures utilized. Typical cellulose-energy schemes aim to maximize production of specific energetically valuable compounds like monosaccharides, sugar alcohols, and aldaric acids. Aldaric acids are oxidized sugar molecules with carboxylic acid groups on the first and terminal carbon atoms; they are currently primarily used in the production of bioplastics and bio-nylon. The US Department of Energy has labeled aldaric acids as one of the twelve most promising platform molecules. Typical aldaric acid production schemes involve the oxidation of monosaccharides, often using enzymes, high-value metal catalysts, or nitric acid.

The use of iron catalysts has been extensively demonstrated to act upon a wide variety of organics. The impact of nanomaterials and iron ions has been examined as catalysts for cellulose and cellulose-based organic degradation, with a variety of different approaches taken. The use of magnetic nanoparticles attached to cellulase demonstrated greatly improved cellulase reusability and a maximum efficiency of 61.94% during the decomposition of corn cobs. Magnetic biochar organic anaerobic digestion pretreatments were found to improve methane yields by 11.69%. High concentrations of water-soluble iron chloride were found to quickly hydrolyze cellulose, yielding 52% gluconic acid at 110 °C. Magnetite nanoparticle-catalyzed thermochemical cellulose decomposition processes demonstrated conversion rates of ~97.5% at 400 °C at pressures approaching 40 MPa. Subsequently, the different approaches, iron species, morphologies, and feedstocks impact the reaction scheme and the products yielded during the degradation. Researchers have even hybridized the cellulose and iron nanoparticles to bio-nanocomposite materials that are capable of acting as highly recyclable catalysts with minimal leaching.

This paper aims to demonstrate an effective novel methodology for the low-temperature conversion of cellulose to smaller, valuable aldaric acids while simultaneously creating value-added nanoparticles. Small quantities of iron nanoparticle precursors greatly assisted the breakdown of cellulose while forming magnetite nanoparticles that may further participate in the breakdown process. The bulk of the catalysis is likely performed by the Fe(II) ions, with the catalytic activity decreasing during the formation and growth of the nanoparticles as per ref 38. As such, the catalytic mechanisms and reaction products differ depending on the nucleation rate of iron within the solution (S4). Having magnetite as a product of degradation has some attractive features such as magnetism, nontoxicity, and high industrial demand. The scheme produces energetically valuable aldaric acids, tunable nanoparticle sizes, and high conversion rates of cellulose to soluble derivatives.

2. RESULTS AND DISCUSSION

The process of breaking down cellulose and forming magnetite nanoparticles is complementary. Fe(OH) acts as a catalyst for the hydrothermal breakdown of cellulose while simultaneously forming Fe₃O₄ nanoparticles of varying sizes. Through the catalytic action of iron, cellulose is modified into a variety of solutes and to create a nanoparticle coating as well as acting as a reducing agent for Fe³⁺, allowing for the formation of Fe₃O₄ instead of Fe₂O₃.

2.1. Particle Characterization. Solids formed post synthesis were characterized to determine features such as size, shape, and compound composition. The crystalline material present within the solid is composed of Fe₃O₄ and crystalline cellulose remnants throughout all initial iron concentrations. The size of the synthesized Fe₃O₄ nanoparticles decreased, with decreasing initial iron concentrations.

All examined samples have consistent crystalline structures, with all XRD peaks maintaining constant locations at various initial iron concentrations (Figure 1). The difference in amplitude between cellulose and Fe₃O₄ peaks increased with...
decreasing initial iron concentrations. The shifting peak amplitudes suggest that increased initial iron concentrations lead to increased crystalline cellulose breakdown, that increased initial iron contents lead to increased magnetite production, and that lower initial concentrations of iron lead to smaller production magnetite crystals. Crystaline cellulose peaks
broadened and decreased in amplitude with increasing initial iron content. As all samples had the same initial cellulose concentration, the increasing peak width and decreased amplitudes suggest decreased cellulose crystallinity with increasing initial iron content, indicative of breakdown.

When further examined, peak widths of magnetite signals increased with decreasing iron concentrations, indicating a shift toward smaller particle sizes at lower initial iron concentrations, as per the Scherrer equation (Figure 1ii). Particle size was estimated to increase linearly between 0.90 and 6.79 g/L iron concentration, suggesting that, in these conditions, the ratio of organic material to initial iron content plays a significant role in determining the sizes of the nanoparticles produced. TEM images show decreasing particle size with decreasing initial iron content (Figure 2). Particles ranged in size from approximately 14 nm at 6.79 g/L Fe to under 7 nm at 0.90 g/L, which is consistent with the Scherrer estimation. All particles were found within a coating of a variable thickness, suggesting that the breakdown of cellulosic material forms a protective organic coating, limiting particle growth.

The magnetic activity of the nanoparticles increased with decreasing initial iron concentrations (Figure 3). All nanoparticles exhibited superparamagnetism at room temperature with minimal hysteresis, coercivity, and remanence, indicating that the nanoparticles are likely all superparamagnetic regardless of the initial iron concentration. The saturation magnetization increases with decreasing initial iron concentrations, likely due to increased organic surface passivation. At 6.79 g/L, saturation occurs at 9.2 emu g$^{-1}$, while at 4.07 g/L, saturation increases to 17.3 emu g$^{-1}$. Finally, a maximum saturation magnetization value of 23.1 emu g$^{-1}$ is achieved by the 1.36 g/L sample.

Figure 3. VSM curves showing particles synthesized with initial iron concentrations of 6.79, 4.07, and 1.36 g/L. All samples exhibit minimal hysteresis, coercivity, and remanence, indicating that the nanoparticles are likely all superparamagnetic regardless of the initial iron concentration. The saturation magnetization increases with decreasing initial iron concentrations, likely due to increased organic surface passivation. At 6.79 g/L, saturation occurs at 9.2 emu g$^{-1}$, while at 4.07 g/L, saturation increases to 17.3 emu g$^{-1}$. Finally, a maximum saturation magnetization value of 23.1 emu g$^{-1}$ is achieved by the 1.36 g/L sample.

Particle samples exhibited superparamagnetism at room temperature with minimal hysteresis, coercivity, and remanence observed in VSM, as expected, given their single domain and small size <15 nm. Saturation maxima increased with decreasing iron concentrations from a low maximum of 9.15 emu g$^{-1}$ at 6.79 g/L iron to a high maximum of 23.1 emu g$^{-1}$ at 1.36 g/L iron. The results are significantly lower than bulk phase magnetite, which saturates at 92 emu g$^{-1}$. The lower maxima are typical of coated nanoparticles, with pure magnetite nanoparticles exhibiting maxima between 55 and 75 emu g$^{-1}$ without organic coatings and decreasing to as low as 3.7 emu g$^{-1}$ with coatings. Typically, saturation maxima increase with decreasing particle size. However, in this case, maxima get larger as particles become smaller, likely due to increased particle surface passivation with increased nanoparticle size. Higher-iron-content samples nucleate more rapidly than lower-iron-content samples, allowing for greater passivation rates, altering the cellulose conversion to soluble organics, as observed in Figure 11.

During the synthesis of the Fe$_3$O$_4$ nanoparticles, cellulose is broken down and modified into a coating agent. Fourier transform infrared (FTIR) spectroscopy results indicate a greater presence of double-bonded oxygen groups within the processed solid organic matter (Figure 4). Each strand of cellulose terminates into two end groups, a nonreducing end and a reducing end, with an aldehyde group. Subsequently, the increased abundance of double-bonded oxygen atoms suggests a shortening of the mean cellulose chain length, increasing the abundance of aldehyde or carboxylic acid end groups. The organics’ polar functional groups have likely oriented around the Fe$_3$O$_4$ nanoparticles, which could potentially disrupt the hydrogen bonding between cellulose strands, decreasing the tensile strength and resulting in more amorphous content. The shortening and reorientation of cellulose strands are further evidenced in Figure 2, which shows organics situated around the nanoparticles rather than in the linear formation possessed by cellulose bundles.

During this synthesis, the cellulose appears to act as a bifunctional agent by providing a reducing functional group to assist the formation of Fe$_3$O$_4$ instead of Fe$_2$O$_3$ as well as providing the coating and steric hindrance required to impact the particle size during the breakdown. This process appears possible through the breakdown of cellulose to reducing intermediaries, which is likely assisted by the catalytic activity of Fe$^{3+}$ ions at the beginning of the synthesis.

2.2. Supernatant Characterization. Solutes were characterized to determine the value of the supernatant post hydrothermal treatment. In every examined sample, the pH of
the supernatant produced post synthesis had decreased from the constant presynthesis pH value of 10, indicating the production of acidic molecules or the breakdown of the ammonia across all initial iron concentrations (Figure 5).

![Figure 5. pH measurements post hydrothermal processing. The fit line is a sigmoidal curve. The pH increased exponentially between 0.33 and 2.72 g/L iron before reaching a plateau at 9.5 ± 0.05 at 4.07 g/L, slightly lower than the original presynthesis pH of 10 ± 0.05. The decrease in pH across all samples is indicative of the production of acids from the cellulose.](image)

The FTIR spectrum of the supernatant possessed consistent peaks across all examined iron concentrations (Figure 6). However, the relative transmission of some peaks changed. In samples produced with higher iron concentrations, the C=H bending at 1457 cm$^{-1}$ possessed a substantially larger peak than the C=O stretching at 1583 cm$^{-1}$, while samples with lower initial iron contents had larger peaks corresponding to the C=O stretch than the C−H bend, indicating a change in molecular population at different initial iron contents. The change in peak ratios suggests that the mean carbon chain at higher concentrations of iron is likely to be longer than that at lower concentrations. The C=O stretch at 1114 cm$^{-1}$ decreases in relative amplitude with decreasing iron concentration. The change in peak ratios coincides with the previously mentioned decrease in pH (Figure 5) and is likely due to the carboxylic acid groups’ deprotonation at high pH values.

![Figure 6. FTIR spectra of supernatants of processed samples after subtracting the background spectrum of water. Iron concentrations are 6.79, 4.07, 2.04, 0.90, 0.68, and 0.00 g/L. Paired peaks at 1583 and 1457 cm$^{-1}$ indicate the presence of conjugated carboxylic acids, further evidenced by an O−H stretch between 3300 and 2500 cm$^{-1}$. The peak at 1114 cm$^{-1}$ is consistent with the presence of C−O bonds, while peaks at 2928 and 2854 cm$^{-1}$ suggest the presence of C−H$_{3}$ and C−H$_{2}$ group vibrations, respectively. The peak present at 3404 cm$^{-1}$ likely represents NH$_{3}$, and the decrease in transmission with decreasing iron concentrations is due to the lower NH$_{3}$ concentrations required to achieve a pH of 10 before synthesis. The FTIR spectra showed no evidence for the production of amines.](image)

![Figure 7. LC−MS results’ plotting peak areas obtained from compounds of various molecular weights at differing initial iron concentrations; data points normalized to the highest found area are marked, and a linear interpolation is performed. The molecular weights plotted in this figure are 180,150, 148, 134, 132, 120, and 118 Da, with the analytes at 180 and 150 possessing the greatest overall abundance/peak area (Figure 7). The data revealed shifts in the observed abundance of solutes depending on the solute’s molecular weight and the initial iron concentration. Low-molecular-weight compounds appeared more abundant at lower initial iron concentrations. High-molecular-weight compounds were more abundant at greater initial iron concentrations, confirming our observations from the FTIR analysis (Figure 6). As such, cellulose derivatives appear to undergo further breakdown at lower iron concentrations. Interestingly, the hydrolysis of cellulose did not produce significant concentrations of monosaccharides. At a molecular weight of 180 Da, retention times of glucose, fructose, galactose, and mannose, run at calibration standards, occurred at between 3.6 and 5.3 min. In contrast, the discovered compound at a molecular weight of 180 Da from the samples had its peak at 1.6 min, suggesting that it is a different compound. The $^{13}$C glucose internal standard had a retention time of approximately 5.1 min, which corresponded to a separately run glucose standard, indicating that the discovered compounds were likely not monosaccharides. Given the substantially shorter retention time, it is likely that the compounds discovered are more polar than monosaccharides. This conclusion, combined with the
previously mentioned FTIR results, suggests the presence of carboxylic acids at this molecular weight rather than cyclic structures. Similar polar solutes were also likely produced at lower molecular weights with discovered compounds at a molecular weight of 150 Da possessing a retention time of 1.6 min, while external xylose, arabinose, and ribose standards had retention times between 3.1 and 3.9 min.

The production of carboxylic acids likely explains the shift toward lower pH values at lower iron concentrations. It appears likely that the initial product of the cellulose breakdown is a six-carbon sugar, which then undergoes additional reactions, forming shorter chain carboxylic acid groups (Figure 8).

Figure 8. Comparison of FTIR spectra between a sample with an initial iron concentration of 2.04 g/L of iron and tartaric acid prepared in water buffered with ammonia to a pH of 9. Post sampling, both samples had a background spectrum of water subtracted. The green lines show the peak positions common to both samples, suggesting that the compounds produced in the synthesis have a similar structure to tartaric acid.

Subsequently, the increased presence of smaller carboxylic acids creates proportionally more carboxylic acid groups in the supernatant, resulting in the large pH decrease at low initial iron concentrations and explaining the change in the C=O and C–H peak ratios observed in the FTIR spectra.

Results of pH, FTIR, and LC–MS would indicate the presence of molecules with carboxylic acid groups and molecular weights of 180, 150, 134, and 120 Da, suggesting the formation of α-dalaric acids (Figure 8). The most likely molecular candidates at each discovered molecular weight are pentaric acid at a molecular weight of 180 Da, tartaric acid at a molecular weight of 150 Da, malic acid at 134 Da, and tartronic acid at 120 Da. The Spectral Database for Organic Compounds revealed that these molecules, when paired with a conjugate base, possess similar peaks to those observed.

The low-cost precursors and minimal hazards associated with this synthesis improve upon the safety and economics of typical catalytic α-dalaric acid production schemes that use high-value metal catalysts and nitric acid.29,30 The maximum concentrations for different molecular weights occurred at different iron concentrations, suggesting that there is potential to increase the selectivity of solute production through fine-tuning the initial iron concentration.

2.3. Cellulose Breakdown Efficiency and Soluble Product Yield. Maximum conversions of soluble iron into solid magnetite nanoparticles and maximum conversion of cellulose into soluble carbohydrates occurred at different initial soluble iron concentrations. Thus, the ideal initial iron concentration is dependent on the desired outcome.

A sigmoidal relationship exists between the conversion percentages of soluble iron into iron nanoparticles across initial iron concentrations between 0.33 and 6.79 g/L (Figure 9).

Figure 9. Conversion of soluble iron into an insoluble form. Conversion of soluble iron increased rapidly from 71 to 86% between 0.33 and 0.90 g/L before reaching a plateau at 1.36 g/L, where more than 99% of iron became insoluble.

Soluble iron conversion increased exponentially between 0.33 and 0.9 g/L before reaching a plateau at 1.36 g/L, where more than 99% of iron precursors became solid magnetite nanoparticles. The lower conversion at lower initial iron concentrations is likely due to steric hindrance from the cellulose precursor and cellulose derivative surfactants.30 The steric effects of the organics promote slow particle growth, resulting in the desirable smaller nanoparticle sizes. At concentrations less than 0.9 g/L, iron was unable to nucleate completely.

The decreased Fe3+ conversion at lower initial iron concentrations likely explains the observed shift toward lower-molecular-weight compounds. Increased Fe3+ retention times in samples with low iron contents allow for lengthier catalytic interactions between the soluble iron and cellulose breakdown products. As the particles begin to grow (Figure 1), their catalytic activity becomes increasingly limited as the particles start to take on the properties of the more inert bulk phase. As ICP measurements were taken several weeks after synthesis, leaching is likely not a significant concern at iron concentrations greater than 1 g/L; however, at very low iron concentrations, leaching could be an issue, caused by the greater strain induced during small nanoparticle formation.

Across all initial iron concentrations, TGA analysis revealed the familiar two-stage cellulose volatilization31 (Figure 10). The initial mass loss at 300 °C represents the hydrolysis of hydroxyl groups, followed by a second hydrolysis stage where residual carbon and Fe₃O₄ undergo oxidation to CO₂ and Fe₂O₃, respectively. Slight differences within the temperatures and inflection of the two large mass loss events are likely due to different quantities of amorphous organic material and different carbon to oxygen to hydrogen ratios present within the solid. Minor differences in the completion of the two mass loss phases of all samples containing iron occurred between 465 and 485 °C, which was substantially lower than that of pure microcrystalline cellulose, which completed both phases at 542 °C. The lower
temperature of degradation is likely due to the shortening of the cellulose chains (Figure 4) and creation of a shift toward a more amorphous and less crystalline structure.

DSC analysis of the thermal decomposition showed two exothermic reactions during the mass loss events. The temperature span of the first reaction was variable across all groups examined, ranging from approximately 40 °C at an iron concentration of 6.79 g/L to up to approximately 70 °C at an iron concentration of 0.90 g/L, with the first microcrystalline cellulose-related mass loss event occurring at the smallest temperature range of approximately 30 °C. The increased temperature span of the first reaction is further evidence of a shift toward more amorphous, less uniform shorter chained cellulose structures (Figure 4) as materials with greater crystallinity and uniformity promote more stable, higher-temperature melting points and sharper DSC peaks. Subsequently, it would appear that the sample with 0.90 g/L iron possessed the shortest cellulose chains with chain length increasing sequentially in samples with both higher and lower iron contents. The changing initial temperature further evidences the shift toward shorter chained amorphous cellulose at the start of the first reaction. The initial temperature of mass loss occurred earliest at 0.90 g/L iron. It exhibited a similar trend to the previously mentioned changes in peak width, with the reaction beginning to occur at increasing temperatures with increasing deviation from the 0.90 g/L sample.

After both large mass loss events, the mass of samples with iron present oscillates slightly as the remaining iron changes oxidation states between Fe₃O₄, Fe₂O₃, and FeO. Under 570 °C, Fe₂O₃ and Fe₃O₄ are the only two stable phases of iron, with Fe₂O₃ being the energetically favorable configuration at −163.7 kg mol⁻¹.⁵² However, above 570 °C, FeO becomes the most stable oxide.⁵³ The oxidation of Fe₃O₄ to Fe₂O₃ likely occurs after the initial cellulosic mass loss, as the protective organic layer is volatilized. This phenomenon can be observed by the apparent appearance of an additional DSC peak between the two cellulosic mass loss events. The oscillations observed in the DSC at higher temperatures are likely due to a phase change between Fe₂O₃ and FeO, which results in a minimal mass loss (Figure 10).

The efficiency of cellulose conversion into soluble compounds across iron concentrations appears to be a two-stage process (Figure 11). The initial stage occurs between 0.33 and 0.90 g/L iron, where conversion rates increase sequentially from 25.51 to 61.67%. At these concentrations, the nucleation of nanoparticles was incomplete (Figure 9), suggesting that the sharp linear increase is caused by a limited number of catalytic centers to perform the breakdown. The greatest TON and TOF values were 52.67 mol soluble product/mol Fe catalyst and 26.33 day⁻¹, respectively, achieved at an initial iron concentration of 0.9 g/L. However, given the value-added proposition of the magnetite nanoparticles, catalyst consumption presents itself as an opportunity, rather than a hindrance.

Figure 10. (i) Thermogravimetric analysis (TGA) of samples with different initial iron concentrations between 25 and 1000 °C, heating at 5 °C per minute. Initial iron concentrations are 6.79, 4.07, 2.04, 0.90, and 0.34 g/L Fe, along with unprocessed microcrystalline cellulose. All samples exhibited two-stage organic volatilization with a rapid initial mass loss at approximately 300 °C followed by a secondary mass loss between 325 and 525 °C, leaving a final mass comprised of iron oxides. (ii) Differential scanning calorimetry (DSC) analysis of the same samples present in (i). All samples exhibited two exothermic reactions corresponding with the two stages of mass loss. Widening of the temperature span of reactions at various concentrations of iron indicates a shift toward a more amorphous structure with shorter length carbon chains.

Figure 11. Conversion of cellulose into soluble compounds plotted against the sample concentration of iron. The maximum conversion of cellulose to soluble material of 61.67% occurs at 0.90 g/L iron. At concentrations greater than 0.90 g/L, conversion rates appeared to decrease exponentially with increasing concentrations of iron. At concentrations of iron lower than 0.90 g/L, the conversion efficiency appeared to dramatically decrease to 44.00% at 0.68 g/L and 25.51% at 0.33 g/L iron. Experimental errors for all measurements were less than 0.01%.
The second stage occurs between 0.90 and 6.79 g/L iron, where conversion rates decrease exponentially from 61.67 to 30.16%. The exponential decay is likely indicative of a two-stage process. Initially, the increased presence of Fe\(^{3+}\) allows for a proportionally increased catalytic activity; however, with increased iron concentration, it is likely that the rate of particle nucleation and rate of particle growth is higher. As such, in high-iron-content samples, cellulosic breakdown likely occurs very rapidly until particles reach a size where they have a limited capacity to function as catalytic centers. The second stage of breakdown occurs as particles increase in size past that required to be direct catalysts, and the surface area to volume ratio begins to decrease as particles continue to grow. During this growth, the cellulosic coatings orientated around the particles are likely placed under additional strain, creating additional solutes. As initial iron concentrations increase, so do the concentration of chloride ions and the required amount of ammonia to reach a pH of 10. The maximum conversion was achieved at relatively low concentrations of FeCl\(_3\) and NH\(_3\), indicating that the dominant mechanism of cellulose degradation is the formation of small magnetite nanoparticles rather than the presence of chloride ions or ammonia concentrations. If ammonia or chloride ions were the primary sources of cellulose degradation, conversion efficiency would likely increase with increasing iron/chloride/ammonia content.

The highest conversion efficiencies occurred before the majority of iron became insoluble (Figure 9), suggesting that catalytic activity is either greatly reduced by the formation of nanoparticles or that only the smallest possible particles and ions can act as direct catalysts for the breakdown of cellulose. Based on this insight, it would appear that there is potential to improve efficiency through a further, more detailed examination of concentrations between 0.67 and 1.35 g/L. Furthermore, greater efficiency is likely to be achieved by slowing down the formation of nanoparticles, increasing the length of time during which the iron is acting as a functional catalyst.

3. CONCLUSIONS

Cellulose is the most abundant polymer on earth, and as such, its energetic utilization is essential within the bioenergy space. In this paper, we have introduced and demonstrated an energy scheme that reduces the economic burden of cellulose degradation through the simultaneous production of magnetic nanoparticles. More than 60% of cellulose was converted into microcrystalline cellulose and stirred in 50 mL of deionized (DI) water. The pH of the solution was increased to 10.0 via the dropwise addition of ammonia (30%). Fifteen milliliters of the sample was then extracted, placed within a Par 25 mL Teflon-lined hydrothermal reactor, and heated in an oven at 180 °C for 48 h. Post processing, 10 mL of DI water was added to assist the removal of all remaining particles from the Teflon liner.

The products were separated to perform characterization of the supernatant and the solids produced during the synthesis. The 25 mL mixture was centrifuged, and the supernatant was poured off and filtered through 33 μm filters to remove any particle agglomerations before being stored in a fridge at 3 °C. Three-quarters of the remaining particles were washed with and stored in ethanol at room temperature, while the remaining quarter was dried in a vacuum oven at 60 °C before particle characterization.

4. EXPERIMENTAL METHODS

4.1. Cellulose Degradation Procedure. Various quantities, ranging between 0.08 and 1.64 g of iron chloride hexahydrate (FeCl\(_3\)-6H\(_2\)O), were mixed with 3.33 g of microcrystalline cellulose and stirred in 50 mL of deionized (DI) water. The pH of the solution was increased to 10.0 via the dropwise addition of ammonia (30%). Fifteen milliliters of the sample was then extracted, placed within a Par 25 mL Teflon-lined hydrothermal reactor, and heated in an oven at 180 °C for 48 h. Post processing, 10 mL of DI water was added to assist the removal of all remaining particles from the Teflon liner.

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4.2. Particle Characterization. Characterization of the insoluble particle remnants was used to determine the particle size and composition using a combination of transmission electron microscopy (TEM), X-ray powder diffraction (XRD), and Fourier transform infrared (FTIR) spectroscopy. To determine the particle size, TEM was performed on a Philips CM200. Before TEM imaging, samples were placed in ethanol and ultrasonicated to assist in resuspension and to limit agglomeration, before being drop-cast onto Formvar-coated copper TEM grids. To determine the composition of crystalline forms post synthesis, XRD was performed with an Empyrean instrument, with scans running between 10° ≤ 2θ ≤ and 80°. Crystalline structure identification of organics and iron oxides was performed using the Dataviewer Highscore Plus software package, and the Fe\(_3\)O\(_4\) particle size was estimated using the Scherrer equation. FTIR was used to determine the structural changes within the dried solid organic cellulosic remnants. The dried organic cellulosic remnants were scanned on a PerkinElmer spotlight between 4000 and 650 cm\(^{-1}\); the results were compared to those of the initial microcrystalline cellulose.

The products’ magnetic properties were examined through vibrating sample magnetometry using a quantum design, physical property measurement system at room temperature with an applied field between +20 and −20 kOe.

4.3. Supernatant Characterization. Functional groups and concentrations of specific compounds present within the supernatant were characterized via a combination of pH testing with a handheld pH meter, FTIR, and liquid chromatography–mass spectroscopy (LC–MS). A drop of the filtered sample supernatant was placed on a PerkinElmer spotlight 400 FTIR attenuated total reflectance (ATR) crystal, and absorption was measured between 4000 and 650 cm\(^{-1}\). To better display absorption characteristics of the mixed products, DI water was measured, and its spectrum was subtracted from those of the supernatants.

LC–MS was performed on a Q-Exact HF mass spectrometer with a U3000 chromatography system (Thermo Fisher Scientific); samples were prepared at 20 μg/mL in 1:1 acetonitrile/water and run for 30 min at 35 °C through a Waters BEH Amide UHPLC column (2.1 × 100 mm). Mobile phase A was composed of 80:20 MeCN/H\(_2\)O with 0.1% NH\(_4\)OH, and mobile phase B was identical except for a 70:30 ratio of MeCN/H\(_2\)O. Commercially available standards for glucose, fructose, galactose, mannose, xylose, ribose, arabinose, deoxyglucose, deoxyribose, and glutaric acid were analyzed as external standards, and a 13C-labeled glucose compound was run across all samples as an internal standard.
4.4. Cellulose Conversion Efficiency. The conversion of soluble iron to nanoparticles and cellulose to soluble carbohydrates was determined using a combination of inductively coupled plasma-mass spectrometry (ICP-MS) and thermogravimetric analysis (TGA).

To determine the elemental conversion efficiency of iron, post-synthesis ICP-MS was utilized. Filtered samples of the supernatants were analyzed, and conversion efficiencies of iron were calculated by dividing the concentration found within the supernatant by the sample’s known initial concentration. Total insoluble iron was calculated by subtracting the concentration of iron found in the supernatant from the known initial iron concentration.

A Mettler Toledo TGA/DSC 1 STAR system was used in conjunction with information from ICP, and XRD analysis was used to determine the overall conversion of cellulose material into soluble carbohydrates. Dry samples were initially weighed on a high-precision 100 μg analytical balance and inserted into the TGA instrument. The TGA instrument was run between 25 and 1000 °C, with an air flow rate of 20 mL/min. TGA showed the removal of all cellulosic/insoluble heating represented a mixed phase of iron oxides comprising FeO and Fe3O4. The mass of iron from Fe2O3 formed during the TGA was assumed to be the mass of pure Fe2O3.

Fe3O4 → Fe2O3 + FeO

(1)

The mass of iron from Fe2O3 formed during the TGA was compared to the volatilized cellulose mass to calculate the posthydrothermal treatment ratio of iron to solid organic material. The total insoluble iron ratio to the pretreatment cellulose concentration was then compared to the post-treatment ratio, uncovering the overall conversion of cellulose into soluble derivatives from the hydrothermal treatment.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c00393.

EDS images of the crystalline material obtained post synthesis of a sample containing 5.43 g/L iron (S1), percentage of chlorine found within supernatant (S2), XRD patterns showing cellulosic remnants and FeO nanoparticles at 4.07 g/L initial iron concentration between 25 and 65° (S3), and proposed reaction schematic (S4) (PDF)

AUTHOR INFORMATION

Corresponding Author

Alexander Wotton — School of Photovoltaic and Renewable Engineering, University of New South Wales, Kensington, NSW 2052, Australia; orcid.org/0000-0002-1584-9854; Email: a.wotton@unsw.edu.au

Authors

Tracey Yeung — School of Photovoltaic and Renewable Engineering, University of New South Wales, Kensington, NSW 2052, Australia; orcid.org/0000-0001-6402-7585
Sreenu Jenneppali — School of Chemistry, University of New South Wales, Kensington, NSW 2052, Australia
Zhi Li Teh — School of Photovoltaic and Renewable Engineering, University of New South Wales, Kensington, NSW 2052, Australia
Russell Pickford — School of Chemistry, University of New South Wales, Kensington, NSW 2052, Australia
Shujuan Huang — School of Photovoltaic and Renewable Engineering, University of New South Wales, Kensington, NSW 2052, Australia
Gavin Conibeer — School of Photovoltaic and Renewable Engineering, University of New South Wales, Kensington, NSW 2052, Australia
John A. Stride — School of Chemistry, University of New South Wales, Kensington, NSW 2052, Australia
Robert John Patterson — School of Photovoltaic and Renewable Engineering, University of New South Wales, Kensington, NSW 2052, Australia

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c00393

Notes

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