Influence of ammonium salts and temperature on the yield, morphology and chemical structure of hydrothermally carbonized saccharides

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Abstract

In this work, the influence of $(\text{NH}_4)_2\text{SO}_4$ and $(\text{NH}_4)_2\text{HPO}_4$ as well as temperature is examined on the hydrothermal carbonization of glucose, fructose and sucrose. Increasing the temperature from 160 to 220 °C increased the yield of hydrothermal carbon for each saccharide for the $(\text{NH}_4)_2\text{SO}_4$ solution, whereas $(\text{NH}_4)_2\text{HPO}_4$ produced a yield that was independent of temperature. The addition of $(\text{NH}_4)_2\text{SO}_4$ increased the yield obtained at 220 °C by 4.27, 7.03 and 2.01 wt% for glucose, fructose and sucrose over the baseline salt free solution, respectively. $(\text{NH}_4)_2\text{SO}_4$ also increased the quantity of acid produced and the average size of the hydrothermal carbon spheres. Conversely, $(\text{NH}_4)_2\text{HPO}_4$ produced carbon structures consisting of interlocked spherical shapes and produced almost no acidic products. XPS analysis revealed that $(\text{NH}_4)_2\text{SO}_4$ incorporated nitrogen and sulfur into the hydrothermal structure, while $(\text{NH}_4)_2\text{HPO}_4$ only allowed nitrogen to be incorporated. It was assessed that NH_4^+ enhances the production of hydrothermal carbon, except in the presence of PO_4^{3-} , which prevents the reaction from effectively forming hydrothermal carbon and organic acids.

Graphical abstract

Keywords Ammonium phosphate · Ammonium sulfate · Glucose · Fructose · Sucrose · FTIR · XPS

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1 Introduction

Hydrothermal carbonization has gained significant interest over the last 10 years for its ability to synthesize functionalized carbon materials at low temperatures (150–350 °C) from a wide variety of carbon precursors [1–5]. The resultant materials include micro and mesoporous carbons [6–9], hollow carbon spheres [10], non-metal doped carbons [1, 11–14], carbon gels [15, 16] and cabbage or flower-like carbon materials [5, 8, 17]. This has resulted in hydrothermal carbons (HTC) being utilized in wide range of applications such as catalysts [10], adsorbents [2], CO₂ capture [12], fuels [3], batteries and electrochemical capacitors [4, 6–8, 13–17].

The wide range of carbonaceous structures from hydrothermal carbonization is due to the versatility and tunable nature of the hydrothermal reaction. This process consists of heating carbon containing precursors under water and self-generated pressures below the critical point of water (374 °C). Through changing the reaction conditions, such as temperature, reaction time and pH, the properties of hydrothermal carbons are easily modified. For example, raising the reaction temperature increases both the yield and hydrothermal carbon sphere size [18], while adding Na₂SO₄ has been shown to enhance the yield of HTC at the same temperature [19]. Changes to the spherical nature of HTC can also be achieved through adding various precursors [i.e., Co(acac)₂] into the solution prior to carbonization [5]. Nevertheless, some additions to the hydrothermal solution are detrimental to hydrothermal carbon production. For example, previous work has shown that the addition of NaOH reduces the yield of HTC considerably [11], while NaCl seems to have limited effect on enhancing the yield of HTC [19]. Furthermore, the addition of dopants into the carbon structure (i.e., nitrogen, phosphorus and sulfur) have been shown to enhance the properties of hydrothermal carbons in electrochemical capacitors [13, 14] and oxygen reduction catalysts [20]. It is for this reason that examining the effects of various dopants and additives is important to understanding their influence on hydrothermal carbonization and the resultant carbonaceous product.

In terms of the sheer number of investigations, nitrogen is one of the most examined dopants for hydrothermal carbonization, due to its natural abundance in hydrothermal precursor materials (i.e., chitosan [12], tannin [21]) as well as having a wide variety of soluble nitrogen containing compounds (i.e., urea [22], (NH₄)₂SO₄) [11]. However, research examining dopants for nitrogen doped hydrothermal carbonization tends to have been focused on single precursor. The lack of studies

examining multiple nitrogen precursors makes it difficult to effectively compare the effects of these precursors on hydrothermal carbonization, as hydrothermal carbonization conditions are not standard. Thus, in this work we examine the effects of (NH₄)₂SO₄, (NH₄)₂HPO₄ and Na₂SO₄ on the hydrothermal carbonization of glucose, fructose and sucrose.

2 Materials and methods

2.1 Hydrothermal precursor solutions

Four non-nitrogenated saccharide solutions were prepared by dissolving solid sucrose (34.23 g, Sigma Aldrich, ≥ 99.0%), glucose (18.02 g, Sigma Aldrich, ≥ 99.0%), fructose (18.02 g, Sigma Aldrich, ≥ 99.0%), or a combination of glucose (9.01 g) and fructose (9.01 g) in of 1 L of Milli-Q ultrapure water (resistivity > 18.2 MΩ cm) to give a final concentration of 0.1 M. The non-nitrogenated hydrothermal carbons are referred to as F, G, S, G + F, for fructose, glucose, sucrose and glucose + fructose with their respective hydrothermal carbonization temperatures (i.e., F200 is fructose at 200 °C).

Nitrogenated solutions were prepared by dissolving solid (NH₄)₂SO₄ (26.43 g, Sigma Aldrich, ≥ 98.0%) or (NH₄)₂HPO₄ (26.412 g, Sigma Aldrich, ≥ 98.0%) into each of the four saccharide solutions to produce a solution containing of 0.1 M saccharide and of 0.2 M ammonium salt. The nitrogenated hydrothermal carbons are denoted with AS or AP for (NH₄)₂SO₄ or (NH₄)₂HPO₄ (i.e., FAS200 is fructose with (NH₄)₂SO₄ at 200 °C).

2.2 Hydrothermal synthesis

15 mL aliquots of the hydrothermal precursor solutions were placed in a Teflon-lined steel bomb reactor with an internal volume of 23 cm³. The bomb reactor was sealed and heated in an oven at temperatures between 160 and 220 °C for 4 h. After this period, the oven was opened and allowed to cool quickly to ambient temperature. Quenching the reactors quicker would have resulted in the release of the hydrothermal contents. The insoluble product (denoted as hydrothermal carbon) was collected by filtration and washed thoroughly with Milli-Q ultra pure water and acetone, to remove any salts and organic compounds that have precipitated on the carbon surface, before being dried at 110 °C overnight. The final solid product was weighed after drying to obtain yield. Each hydrothermal carbon sample was synthesized three times and the average of their yields is reported. The liquid phase, pre- and post-hydrothermal treatment, was pH tested to

determine the overall acid contribution from the hydrothermal process.

2.3 pH measurements

The pH data was obtained using a pH box and probe, and calibrated using pH standard solutions of pH 4.0 and pH 7.0, at ambient temperature. The pH of the starting solutions and post hydrothermal solutions was measured. Solutions were stirred before measurements taken to ensure homogeneity.

2.4 GCMS

A 1 μL sample of the liquid phase from G180, G220, F180, F220, S180 or S220 was injected into a Shimadzu GC–MS QF2010 EI/NCI system fitted with a ZB-5MS column (30 m $\times$ 0.25 mm) with a 5% phenylarylene stationary phase. A temperature program was set to rest at 50 $^{\circ}\text{C}$ for 2 min before increasing in temperature at 25 $^{\circ}\text{C}/\text{min}$ until 200 $^{\circ}\text{C}$ was reached, where it was held constant for 7 min. The solvent cutoff was set to 2 min, with the mass spectroscopy detector set to record after this time. Qualitative compound determination was performed by comparing the resulting m/z spectra to the NIST 09 database. Quantitative analysis was performed on 5-hydroxymethylfurfural (Sigma Aldrich $\geq 99.0\%$) and levulinic acid (Sigma Aldrich $\geq 98.0\%$) using calibration standards ranging in concentrations from 0.1 to 250 mMol L^{-1} , prepared from pure samples.

2.5 FTIR spectroscopy

FTIR spectra of the hydrothermal carbons were recorded on a Perkin Elmer Spectrum Two IR Spectrometer equipped with a diamond ATR crystal. The sample was placed on the diamond crystal of the detector where force was applied until a spectrum was adequately resolved. The sample was scanned 8 times between 4000 and 450 cm^{-1} and ATR and background corrected using Perkin Elmer Spectrum 10 software.

2.6 X-ray photoelectron spectroscopy

The X-ray Photoelectron Spectroscopy (XPS) measurements were performed using a Thermo ESCALAB250i X-ray photoelectron spectrometer in an ultrahigh vacuum (1×10^{-9} Pa) system equipped with a hemispherical analyzer. Three hydrothermal carbon samples, S200, AS200 and AP200, were mounted on indium then degassed and transferred into the analysis chamber. An unmonochromated Mg K α X-ray source of incident energy 1253.7 eV was applied to generate core excitation. The spectrometer

was calibrated assuming the binding energy (BE) of the $\text{Au}4f_{7/2}$ line at 84.0 eV with respect to the Fermi level. The standard deviation for the BE values was 0.1 eV. Survey scans (1 eV/step) were obtained in the 0–750 eV range and used to determine the surface composition. Detailed scans (0.25 eV/step) were recorded for the O1s, C1s and N1s regions. Spectra were analyzed and processed using CasaXPS 2.3.16 software with full width half maximum (FWHM) for synthetic peaks in O1s, C1s and N1s identified using calibration standards. The background was approximated by a Shirley algorithm and the detailed spectra were fitted with Gaussian–Lorentzian functions. Peak assignments were based previous XPS work on hydrothermal carbon [1, 11].

2.7 Morphological analysis

The morphology and size were examined with a Philips XL30 scanning electron microscope (SEM) at different magnifications. Hydrothermal carbon samples were mounted on aluminum stubs with double sided carbon tape and gold coated at four different angles to ensure complete coverage of gold around the microspheres.

Sizing of the hydrothermal carbons was performed using Image J software on the 10,000 $\times$ magnification images of each hydrothermal carbon. The software inserts ellipses around each hydrothermal carbon microsphere and measures the pixels across the major and minor axes, comparing these to the number of pixels in the scale bar. A total of ~ 250 individual microspheres were chosen at random for sizing measurements.

3 Results and discussion

3.1 Yield of hydrothermal carbons and acid production

Figure 1 displays the hydrothermal carbon yield (wt%) at increasing temperatures obtained with (a) no nitrogen, (b) $(\text{NH}_4)_2\text{SO}_4$ and (c) $(\text{NH}_4)_2\text{HPO}_4$. For the non-nitrogenated environment (Fig. 1a) HTC yield for all saccharides other than glucose, increased with increasing temperature. The HTC yield for glucose remained below 6 wt% until the temperature was raised 220 $^{\circ}\text{C}$, in which the yield rose to 21 wt%.

To understand the difference in yields and the influence of ammonia salts the overall mechanism of hydrothermal carbon formation will be discussed. The formation of hydrothermal carbon can be broken into two main stages, decomposition/fragmentation of the precursor into intermediates (e.g., hydroxymethylfurfural (HMF)) and polymerization of intermediates into solid

Fig. 1 Average yields in wt% of each of the selected precursors hydrothermally carbonized in the presence of **a** no nitrogen, **b** $(\text{NH}_4)_2\text{SO}_4$, and **c** $(\text{NH}_4)_2\text{HPO}_4$

carbon particles (Fig. 2). For mono, di and polysaccharides, the most important intermediate is the formation of hydroxymethylfurfural (HMF). HMF undergoes a series of polymerization, condensation and aromatization steps to form the furanic structural backbone of hydrothermal carbon [1, 23]. A detailed explanation of the breakdown steps can be found in studies by [24–26] and formation steps in studies by [27–29]. As a result, any factor that impedes or enhances the formation of HMF can have a negative impact on HTC formation. However, this is not the only char formation pathway, with aldehydes, ketones and phenols also forming that can participate in polymerization/condensation reactions. In addition to these products, several organic acids are produced that are not incorporated into the char structure and are seen as by-products to char formation.

Fig. 2 Simplified reaction mechanism for hydrothermal carbon from glucose or fructose displaying the main compounds formed and reaction pathways

Although the overall mechanism is similar for each of the precursors in this study, the initial breakdown step is different, leading to slightly different reaction rates. For sucrose, the glycosidic linkage between the glucose and fructose subunits is broken first, leaving a fructofuranosyl cation and glucose molecule. The cation is highly reactive and increasing the rate of HMF formation and decomposition of sucrose [30, 31]. For glucose, epimerization into fructose is the first step before it forms HMF, while fructose forms HMF directly (Fig. 2) [32, 33]. The reduction in char formation in glucose at lower temperatures is attributed to the epimerization step, which is rate limiting below 210, and is the reason for the decrease in yield relative to fructose at 160 °C, 180 °C and 200 °C. However, to assess whether this is occurring here, glucose was hydrothermally carbonized from 160 to 220 at 10 °C intervals. It can be seen in Fig. 3 that the yield of the glucose sample increases

Fig. 3 Yield of glucose HTC at 10 °C temperature intervals clearly showing the increase in yield at 210 °C

considerably at 210 °C, suggesting that the lack of HTC produced from glucose at low temperatures is attributed this additional epimerization step.

Regarding sucrose under non-nitrogenated conditions (Fig. 1a), the yield was observed to be lower than fructose at 160 °C and 180 °C, while producing slightly higher yields to both the monosaccharides at 200 °C and 220 °C. The lower yields are attributed to the additional energy required to cleave the glycosidic bond in sucrose [30], followed by the epimerization of glucose to fructose. The effect of this additional step for sucrose is evident in the G + F series (Fig. 1a), where the yield is higher for G + F in comparison to sucrose. Interestingly, the G + F series also produces higher yields than all other saccharides at 200 °C and 220 °C. This suggests that the byproducts from the decomposition of fructose, which would occur before glucose decomposition, may assist with the decomposition of glucose. This is likely to occur via the organic acids produced from fructose decomposition as the production of important intermediates, such as 5-hydroxymethylfurfural, are acid catalyzed and increases with decreasing pH [26, 34, 35].

To examine the effect of organic acids produced in situ, pH readings were taken prior to and after hydrothermal carbonization and converted into H^+ produced. As the acids formed under hydrothermal carbonization are weak acids (i.e., formic acid, acetic acid, propanoic acid, levulinic acid), their pKa and the final pH of the solution must also be considered. The pKa of the main organic acids identified in hydrothermal carbonization is displayed in Table 1.

Considering the final pH of each of the final hydrothermal solutions is below the pKa, the equilibrium between the protonated and deprotonated forms is shifted towards the protonated form. Thus, to decrease the pH of the solution below the pKa of the acids produced in hydrothermal carbonization requires an increasingly larger quantity of acid. To validate this, hydrothermal solutions for G180, F180, S180 G220, F220 and S220 were quantitatively analysed by GCMS for levulinic acid and HMF (Table 2). The rationale behind quantifying the amount of HMF and levulinic acid

Table 2 Concentration of hydroxymethylfurfural (HMF) and levulinic acid found in hydrothermal solutions after carbonization for various saccharides carbonized at 180 and 220 °C

Sample	HMF (mM)	Levulinic acid (mM)	Initial pH	Final pH	[H ⁺]* produced (mmol)
G180	52.75	1.49	4.83	2.99	1.01
G220	7.02	24.55	4.80	2.63	2.33
F180	9.54	33.14	4.01	2.59	2.47
F220	5.14	30.94	4.74	2.65	2.22
S180	48.26	46.79	4.62	2.40	3.96
S220	5.14	95.23	4.28	2.23	5.84

*Calculated from the [H⁺] difference between the initial [H⁺] from pH and final [H⁺] in solution from pH

remaining in the solution is that HMF has been shown to produce HTC, and levulinic acid is a competing process from the decomposition of HMF [42–44]. It can be seen from Table 2, that the lower the final pH, the higher the level of levulinic acid in solution. This relationship is exponential, confirming the previous conclusion that as pH decreases, the level of organic acids in the solution increases exponentially.

Comparing the H^+ produced for the non-nitrogenated solutions (Fig. 4), H^+ production increases with temperature, except for fructose, which remains almost constant after 180 °C. This would suggest that the reaction pathways towards acid production from fructose have gone to completion at 180 °C. For the G + F sample, it can be seen that the H^+ produced is higher than both glucose and fructose, indicating that fructose is assisting in the decomposition of glucose. If fructose was not assisting, the level of acid production would be expected to be approximately the same as the fructose sample at 160 °C, as glucose had not begun to degraded at this point.

The addition of $(NH_4)_2SO_4$ was found to increase the yield of HTC across all saccharides, particularly at lower temperatures (Fig. 1b), for example SAS160 produced 10.84 wt% whereas S160 only produced 2.01 wt%. In addition to increased yields, the temperature restriction highlighted earlier for glucose to form HTC only appears at 160 °C.

The increase in yield here is likely from the presence of NH_4^+ and subsequently NH_3 . These compounds have been shown to produce cascading Maillard reactions under hydrothermal conditions, providing additional reaction paths for char formation [1, 45]. Additionally, NH_3 is known to participate in ring opening reactions on glucose (Amadori rearrangement), which may remove the need for glucose to be epimerized to fructose before forming hydrothermal carbon and explain the increased yield for glucose at lower temperatures. In

Table 1 List of common organic acids with their pKa found in solution after hydrothermal carbonization

Organic acid	pKa	References
Formic acid	3.75	[29, 33, 36, 37]
Lactic acid	3.86	[29, 36, 38–40]
Acetic acid	4.76	[29, 33, 36, 37, 39, 41]
Propanoic acid	4.87	[29, 40]
Levulinic acid	4.78	[29, 36, 37, 41]
Acrylic acid	4.25	[29, 40]

Fig. 4 $[H^+]$ produced in each hydrothermal carbonization calculated from the pH reading prior to heating and after heating for **a** no nitrogen, **b** $(NH_4)_2SO_4$, and **c** $(NH_4)_2HPO_4$

regard to organic acid formation (Fig. 4b), the presence of $(NH_4)_2SO_4$ also increased the degree of H^+ in solution.

Interestingly, the addition of NH_4^+ from $(NH_4)_2HPO_4$ produced an entirely different effect on the yield of HTC across all saccharides. The yield at 160 °C was greater than the other series, but was almost constant regardless of temperature. There were slight differences between saccharides, with sucrose producing higher yields than both fructose and glucose. Considering that NH_4^+ has been shown to have an enhancing effect on the production of HTC, the lack of yield in the presence of $(NH_4)_2HPO_4$ clearly indicates the impact of the PO_4^{3-} anion on hydrothermal carbonization.

Further insight can be gained by examining the H^+ produced for $(NH_4)_2HPO_4$ (Fig. 4c), where almost no H^+ is formed in solution. The $(NH_4)_2HPO_4$ solutions were the only solutions to start with an alkaline pH in between 7.5 to 8.0 and had a final pH between pH 6 to 6.4 for glucose and fructose, and pH 4.0 to 4.5 for sucrose. As the final pH is above or close to pK_a of the common organic acids (Table 1), these acids are likely to be in their deprotonated form and produce a larger impact on the pH. The lack of H^+ production suggests that PO_4^{3-} inhibits on the hydrothermal carbonization mechanism prior to the formation of organic acids or significantly hinders their production.

The effect of the anion on the yield was also found by Ming et al., when examining the effects of $NaSO_4$, $NaCl$ and $NaNO_3$ on the hydrothermal carbonization of glucose [19]. The yield varied depending on the sodium salt used, however the pH fell considerably for all salts, indicating the production of organic acids was not impacted by these anions. This indicates that an entirely different mechanism is occurring under PO_4^{3-} . The reaction rate is initially faster than the neutral or $(NH_4)_2SO_4$ solutions (high yield at 160 °C), before being stopped when the yield of HTC reaches 10–15 wt%. Unfortunately, yield and pH data are not enough to fully understand how PO_4^{3-} influences HTC and this is best suited for a subsequent study examining multiple PO_4^{3-} salts using NMR to fully understand the structural differences and hydrothermal liquid changes.

3.2 SEM images and sizing

The formation of HTC is a complex series of hydrophobic ripening [28], dies alder [29], aldol addition [25], dehydration [18, 29] and polymerization reactions [24, 46]. These reactions, and the HTC material resulting from them have been shown to be influenced by the feedstock type [18, 47], temperature [18], residence time [18], pH [11] and dopants [1, 11, 29]. This allows the morphology of HTC materials to be tailored towards specific sizes and shapes and is reflected in the morphology of the different HTC series produced at 220 °C (Fig. 5).

The hydrothermal carbonization of saccharides formed predominately spherical particles, however differences between HTC's can be noted in both the size of the spheres and their interconnectivity. The most significant difference is seen in the $(NH_4)_2HPO_4$ series, where fully formed spherical particles are not apparent. Instead, a series of interconnected spherical shapes form a bulk macro structure. To further examine the differences in morphology, the spherical size distribution was calculated from measuring 250 spheres across multiple SEM images of each sample (Fig. 5). For the non-nitrogenated HTC, a broad distribution of sizes between 1 and 10 μm can be observed for each saccharide. However, the glucose, sucrose and fructose

Fig. 5 SEM images of each HTC produced at 220 °C, the scale bar is 5 μm

HTC tend to have a larger distribution between 0 and 2 μm with their mean between 1.6 and 2.8 μm (Table 3), while the mean of G + F HTC was significantly higher.

The addition of nitrogen into the hydrothermal solution allows mullard reactions to occur [29, 45], which will also affect the growth of HTC materials. The effect with $(\text{NH}_4)_2\text{SO}_4$ on HTC size and growth can be seen in Fig. 6b. The overall size of the HTC microspheres is

larger, except for GFAS220, while the range of sizes has decreased. This indicates that the addition of $(\text{NH}_4)_2\text{SO}_4$ enhances HTC formation, allowing for the formation of larger microspheres. Conversely, $(\text{NH}_4)_2\text{HPO}_4$ produced smaller spherical sizes than $(\text{NH}_4)_2\text{SO}_4$, indicating that PO_4^{3-} significantly impacts the formation of HTC materials. It should be noted that the sizing for $(\text{NH}_4)_2\text{HPO}_4$ was measured from the spherical ends of each joined chain.

Table 3 List of minimum size, mean and maximum HTC sphere size for all HTC produced at 220 °C

Sample	Minimum size (μm)	Mean (μm)	Maximum size (μm)
G220	0.7	2.8	8.6
F220	1.0	2.5	5.5
S220	0.9	1.6	9.7
GF220	1.4	5.2	9.3
GAS220	1.2	2.7	5.97
FAS220	1.3	3.2	7.1
SAS220	1.6	3.7	6.0
GFAS220	1.1	3.9	7.5
GAP220	0.6	1.7	2.8
FAP220	1.1	2.4	6.6
SAP220	1.9	4.2	6.46

3.3 XPS analysis

XPS analysis of the non-doped and nitrogen doped HTC from sucrose at 200 °C is displayed in Table 4. There are subtle differences between each of the HTC materials, for instance carbon content decreased in the order of S200 (81.42 at.%), SAP200 (80.11 at.%) and SAS200 (78.75 at.%). This would suggest that S200 is the most carbonized sample, however deconvolution of the C1s peak revealed that the nitrogen doped samples have considerably more C=C linkages (S200 29.05 at.%, SAS200 31.92 at.%, SAP200 36.16 at.%). Oxygen content was also seen to decrease with nitrogen doping from 18.58 at.% in S200 to 14.48 at.% and 14.17 at.% for SAS200 and SAP200, respectively. These findings correlate with previous studies [1, 29] that indicated that the addition of nitrogen increases the aromaticity of HTC materials.

Examining the nitrogen content, SAP200 had a higher degree of nitrogen incorporation (7.05 at.%) than SAS200 (4.2 at.%). However, the same types of functional groups were found when deconvoluting the N1s spectra with in higher concentrations being observed in SAP200. Regarding the ammonium anion, sulfur was observed in the SAS200 sample at low concentrations, indicating that it is incorporated into the carbon structure. A possible peak for phosphorus was observed at 135 eV in the SAP200 sample, however its signal to noise ratio was considerably poor (1.4:1, sulfur in SAS200 was 6.2:1) and thus considered to be below the detection limit of the XPS. This suggests that if phosphorus is incorporated into HTC, it is at very low concentrations (> 0.1 at.%).

To further examine the impact of temperature on hydrothermal carbon, XPS was used to examine the (NH₄)₂SO₄ doped HTC series (Fig. 7). As the temperature was increased from 160 to 220 °C, carbon content

Fig. 6 Histograms of HTC microsphere size for **a** no nitrogen, **b** (NH₄)₂SO₄, and **c** (NH₄)₂HPO₄. Due to the interconnected nature of **c** (NH₄)₂HPO₄, only the end spheres of each joined chain were sized

increased (79.9–81.62 at.%) while oxygen content decreased (15.31–11.32 at.%). This result correlates with previous results from the literature, which found that as HTC temperature increased, carbon content increased while oxygen content decreased [18]. Additionally, nitrogen and sulfur content also increased with increasing temperature, indicating that their concentrations can be tuned with temperature.

3.4 FTIR

3.4.1 Analysis of HTC nitrogen bands in FTIR

The XPS indicated that the surface of the nitrogen doped samples contain a mixture of pyrrolic, pyrrole and amine

Table 4 XPS analysis of S200, SAS200 and SAP200 for the C1s, O1s and N1s peak regions

	Functionality (BE; eV)	S200	SAS200	SAP200
Carbon	C=C (284.1)	29.05	31.92	36.16
	C–C, C–H _x (284.4)	35.17	28.47	22.81
	C–O– (286.2–288.0)	21.73	12.09	15.10
	C=O (287.2–288.1)	9.09	4.86	3.15
	COO [−] (288.0–289.2)	3.22	2.24	1.10
	CO ₃ (289.0–291.6)	1.74	1.23	0.46
	Total	81.42	80.11	78.75
Oxygen	O=C (531.2)	10.08	8.06	7.93
	–O–C (532.9)	8.50	5.40	6.24
	Total	18.58	14.48	14.17
Nitrogen	Quaternary nitrogen (401.6)	N/A	0.41	0.28
	Pyrrolic, pyridonic and lactam (400.2)	N/A	1.14	1.39
	Amine, amide and nitrile (399.3)	N/A	1.54	3.19
	Pyridinic and imines (398.4)	N/A	1.12	2.19
	Total	N/A	4.2	7.05
Sulfur		N/A	1.55	N/A

Fig. 7 XPS analysis of the carbon, oxygen and nitrogen content of the $(\text{NH}_4)_2\text{SO}_4$ doped hydrothermal carbons with temperature. Carbon at.% is plotted on the left axis and oxygen, nitrogen and sulfur at.% on the right axis

functionalities. Thus, comparing their FTIR spectra to that of pyrrolic, pyrrole and ethylamine can assist in the identification of regions in the FTIR spectra related to nitrogen functionalities in HTC (Fig. 8). It should be noted however, that the position of ring stretching vibrations on nitrogen rings shift depending on the position and type of substituents attached to the ring [51–53]. For instance, pyrrole displays ring stretching vibrations at 1561, 1530 and 1464 cm^{-1} , while 3,4-dimethylpyrrole has peaks at 1580, 1500 and 1439 cm^{-1} and 2,5-dimethylpyrrole has peaks at 1593, 1515 and 1464 cm^{-1} for the same ring stretching vibrations [51, 52]. As pyrrole and pyridine have been shown to be attached in multiple configurations on the surface of nitrogen doped HTC [1], this will create broader

peaks in the FTIR spectra of nitrogen doped HTC. Evidence of this can be observed when comparing the strong and distinct C–N ring stretching vibrations of pyridine at 1580 and 1440 cm^{-1} to SAS200 and SAP200. The peaks from these stretches are observed in the FTIR, but are broader and weaker than the pure sample.

Despite these limitations, two major C–N regions can be assigned relating to ring stretching vibrations (1400–1660 cm^{-1}) and C–N stretching vibrations (1100–1300 cm^{-1}) [51–53]. Comparing SAS200 and SAP200, the same peak locations can be observed in both samples, although there are slight differences between the two samples. These variances are probably the result of different concentrations of nitrogen functional groups found in both samples. For instance, SAP200 contains a higher degree of amine and pyridinic functionalities (from XPS) compared to SAS200, which is reflected in the C–N/C=N ring stretching vibrations between 1300 and 1500 cm^{-1} . Overall, despite $(\text{NH}_4)_2\text{HPO}_4$ impeding the formation of HTC, the product is chemically similar to the HTC formed with $(\text{NH}_4)_2\text{SO}_4$.

A comparison between S200 and SAS200 to examine the difference that nitrogen makes on oxygen functionalities is presented in Fig. 7. Firstly, it is important to highlight the main peaks related to furan, as furans make up the main structural motif of HTC. These are located at 1700 (C=O stretch), 1600 (C=C, stretch), 1510 (C=C, stretch), 1305 (C–O–C, asymmetric stretch), 1165 (C–O–C, asymmetric stretch), 950 (C–H, in/out-of-plane bending), 850 (C–H, in/out-of-plane bending) and 750 (C–H, in/out-of-plane bending) cm^{-1} [54, 55]. It can be seen in Fig. 9 that upon the addition of nitrogen, all identified furan peaks have their intensity reduced significantly.

Fig. 8 FTIR spectra of SAS200, SAP200, pyrrole, pyridine and ethylamine with region assignments. The FTIR spectra of pyrrole, pyridine and ethylamine are from NIST references [48–50]

Fig. 9 Comparison of S200 with SAS200 with location of stretch's and deformations related to oxygen functionalities and ring structures. Peaks related to furan rings are marked with * [54, 55]

Additionally, there is an increase in C–H in/out plane ring deformations that are associated with aromatic ring structures. This correlates with previous findings [1, 29, 45] that the incorporation of nitrogen into the HTC structure reduces the degree of furan and increases its aromaticity.

3.4.2 FTIR comparison of feedstock on HTC produced at 220 °C

The FTIR of each HTC sample produced at 200 °C is displayed in Fig. 10. Each spectra displays a number of

Fig. 10 FTIR spectra of each HTC sample produced at 200 °C under **a** no nitrogen, **b** $(\text{NH}_4)_2\text{SO}_4$, and **c** $(\text{NH}_4)_2\text{HPO}_4$. A split in the wavenumber is included to highlight the bands below 2000 cm^{-1}

common features independent of saccharide or treatment type, these are; (i) O–H stretch between 3200 and 3400 cm^{-1} , (ii) C=O stretch at 1690 cm^{-1} , (iii) C=C aromatic stretch at 1590 cm^{-1} (iv) C–H/O–H stretch at 1370 cm^{-1} , (v) C–O stretch at 1275 cm^{-1} , (vi) C–O–C stretch at 1020 cm^{-1} , (vii) C=C aromatic stretch at 985 cm^{-1} , and (viii) C–H aromatic stretch at 770 cm^{-1} .

Interestingly, there is almost no difference between the spectra of each saccharide in each series, indicating that each HTC is chemically similar regardless of precursor. However, there are differences between each treatment method in the intensity of the stretches, with minor shifting of peaks also occurring. For example, the C=O stretch at 1690 cm^{-1} is a prominent peak in the neutral and Na_2SO_4 series, while it is a shoulder in the $(\text{NH}_4)_2\text{SO}_4$ and $(\text{NH}_4)_2\text{HPO}_4$ series. Additionally, the C=C aromatic stretch shifts its position and is located at 1602 and 1600 for the neutral and Na_2SO_4 series, while it is located at 1588 and 1589 in the $(\text{NH}_4)_2\text{SO}_4$ and $(\text{NH}_4)_2\text{HPO}_4$ series. This suggest there is a change in the local chemical environment upon the incorporation of nitrogen into these samples, as the peak heights and locations tend to correlate between the neutral and Na_2SO_4 series, while a similar correlation can be found between the $(\text{NH}_4)_2\text{SO}_4$ and $(\text{NH}_4)_2\text{HPO}_4$ series.

4 Conclusion

The hydrothermal carbonization of glucose, fructose and sucrose under different temperatures and ammonium salts produced a wide range of yields, sizes and chemical morphologies depending on the temperature and ammonium salt added. In general, the yield of HTC increased with increasing temperature, with a maximum yield of $45.0\text{ wt}\%$ achieved using an equimolar mixture of glucose and fructose. Adding $(\text{NH}_4)_2\text{SO}_4$, $(\text{NH}_4)_2\text{HPO}_4$ or Na_2SO_4 increased the yield of HTC at lower temperatures, although, the yield of $(\text{NH}_4)_2\text{HPO}_4$ was stagnant at $\sim 8\text{ wt}\%$ for glucose and fructose and $\sim 13\text{ wt}\%$ for sucrose, regardless of temperature. The SEM results displayed a range of spherical sizes for the HTC, while $(\text{NH}_4)_2\text{HPO}_4$ produced several interconnected shapes.

The XPS analysis revealed that carbon content increased, while oxygen content decreased upon the addition of ammonium salts. The nitrogen doped HTC materials had similar nitrogenated functionalities, however the nitrogen content increased significantly in the $(\text{NH}_4)_2\text{HPO}_4$ doped HTC material from $4.2\text{ at.}\%$ in $(\text{NH}_4)_2\text{SO}_4$ HTC to $7.05\text{ at.}\%$. This indicated that the nitrogen content in HTC materials can be altered by changing the anion. Additionally, the $(\text{NH}_4)_2\text{SO}_4$ HTC contained sulfur groups, while the $(\text{NH}_4)_2\text{HPO}_4$ HTC did not have phosphate incorporated into the structure.

The FTIR analysis indicated that there was very little difference between saccharides in each series, while significant differences were found between the normal solution, $(\text{NH}_4)_2\text{SO}_4$ and $(\text{NH}_4)_2\text{HPO}_4$. Using reference spectra, two major C–N regions were assigned at $1400\text{--}1660\text{ cm}^{-1}$ for C–N ring stretching vibrations and at $1100\text{--}1300\text{ cm}^{-1}$ for C–N stretching vibrations. Additionally, the FTIR indicated that the addition of nitrogen was shown to decrease the degree of peaks related to the furan structure of HTC. Several peaks were also found to be common between samples that represented, –OH, C=O, C=C aromatic, C–O, C–O–C functionalities, although these peaks tended to be slightly shifted in the $(\text{NH}_4)_2\text{SO}_4$ and $(\text{NH}_4)_2\text{HPO}_4$ added HTC. This suggested that there is a change in the local chemical environment upon the incorporation of nitrogen into these samples. Overall, the temperature and saccharide used had more impact on the yield, while the incorporation of $(\text{NH}_4)_2\text{SO}_4$ and $(\text{NH}_4)_2\text{HPO}_4$ lowered the activation energy required to produce HTC and modified the overall chemical structure.

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Compliance with ethical standards

Conflict of interest The authors express that there are no conflicts of interest with the work contained in this manuscript.

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