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## ARTICLE

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## Influence of the ammonium salts used in the Brønsted acid catalyzed hydrothermal decomposition of D-glucose towards 5-HMF<sup>+</sup>

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In this work, we compare the effect of two ammonium salts (ammonium sulfate and ammonium acetate) used as promotors in the hydrothermal decomposition of D-glucose with the results obtained in the presence of sulfuric acid. For the first time, we demonstrate that the ammonium acetate is not a good promotor due to the low conversion of D-glucose. Conversely, the ammonium sulfate appears as a much more promising promotor. Indeed, even if a large amount of humins is observed, 5-HMF is obtained in good yield with a fast conversion of D-glucose. After isolation and characterization of the liquid and solid phases, the role of the ammonium sulfate was thoroughly investigated. A structural characterization of the humins obtained from D-glucose and ammonium salts is also proposed. In addition, we demonstrated that with an ammoniumcontaining promotor, part of the nitrogen atoms is inserted in the humins structure as pyrrole derivatives.

### Introduction

It is well established that one of the most promising solution to replace fossil resources involves the use of biomass.<sup>1-2</sup> Being abundant and renewable, the lignocellulosic biomass offers a great potential for providing green chemicals.<sup>3</sup> Indeed, the biomass raw material can be converted by hydrolysis into oligomers and mono-carbohydrates. Next, by dehydration and hydration processes, the latter can afford bio-based building blocks such as 5-hydroxymethylfurfural (5-HMF) which then leads to levulinic acid (LA) and formic acid (FA).4-8 Among the top list of bio-based building blocks listed by the US Department of Energy,<sup>9</sup> 5-HMF and LA are of prime interest. For example, LA is easily transformed into  $\gamma\text{-valerolactone}^{10\text{-}12}$  or in the presence of FA and amine into N-substituted-5methylpyrrolidinnones.13-15 With three functional groups, 5-HMF is the key intermediate towards high value derivatives <sup>16</sup> by oxidation, hydrogenation or hydrogenolysis, amination, esterification, etherification, or carboligation reactions.

Compared to the synthesis of LA, access to 5-HMF from bioresources remains a challenge because of its high reactivity.<sup>17-18</sup> Indeed, as 5-HMF is not stable in water under acidic conditions, during the dehydration and hydration processes of the biomass raw material, LA and FA are generally obtained along with a black solid considered as a byproduct and called the humins. The char obtained during the acidic treatment has received more attention to determine its intrinsic structure and envision a valorization. The generally accepted structure consists of a network of furan rings linked with ether or acetal aliphatic linkers.<sup>19</sup> In addition to 5-HMF, 2,5-dioxo-6-hydroxyhexanal (DHH) has been proposed as a key intermediate in the formation of the humins. This compound has been identified for the first time by Horvat *et al.*<sup>20</sup> in 1985, and is

obtained by rehydration of HMF. However, to the best of our knowledge, DHH has never been isolated, but Infra-Red study carried out by Lund et al.<sup>21-22</sup> and by Vlachos et al.<sup>23</sup> has revealed that DHH can react with the carbonyl group of 5-HMF by aldol condensation. <sup>13</sup>C MAS NMR analyses proposed by Weckhuysen et al.<sup>24</sup> and Seshan et al.<sup>25</sup> confirmed this structure. A revised molecular structure of the humins obtained from D-glucose has shown that no keto group is directly connected to a furanic ring,<sup>26</sup> and water soluble oligomers (WSO), which are D-glucose oligomers with a maximum of 9 units, are also inserted in the structure of the humins by reaction with the aldol condensation intermediates.<sup>27</sup> Recently, Vlachos et al.28 have screened different classes of organic solvents (polar protic or aprotic and nonpolar) to solubilize part of the humins obtained after acid catalyzed dehydration of fructose. The amount of the extracted humins is dependent of the electron-donor-acceptor type interactions with the solvents used, suggesting that part of the humins are agglomerated oligomeric species linked together by weak interactions. The identified species are in agreement with the mechanism of condensation of furanic ring as proposed in the literature. Scheme 1 resumes the hydrothermal decomposition of Dglucose into LA and FA and the humins.



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59 60 Scheme 1 Hydrothermal decomposition of D-glucose.

Up to now, one of the most accomplished process to obtain 5-HMF is the biphasic system catalyzed with a mineral acid, as reported by Dumesic et al.29-30 Generally, the reactions are carried out in the presence of polar organic solvents with high boiling points such as dimethylsulfoxide. From the report of Moreau et al. on the use of 1H-3-methyl imidazolium chloride as solvent and catalyst for the conversion of fructose to 5-HMF,<sup>31</sup> various ionic liquids such as tetraalkylammonium salts can be used to replace these solvents.<sup>32-33</sup> By mixing choline chloride with glucose or fructose, deep eutectic solvent (DES) can be prepared and be used in the aqueous Lewis acidcatalyzed formation of 5-HMF as proposed by Jérôme et al.34 It was also shown that the addition of carbon dioxide to the DES system, decreased the pH with the formation of carboxylic acid, and 5-HMF was obtained in similar yield (70%) from fructose with lower temperature (120°C instead of 165°C).35

To the best of our knowledge, there is no recent study using ammonium salts as acidic promotors in the hydrothermal decomposition of oses. In 1982, Brown et al. have disclosed the dehydration reaction of fructose in non-aqueous media, and in the presence of ammonium chloride or bisulfate as catalyst.<sup>36</sup> In order to optimize the synthesis of 5-HMF and to have a better understanding of its formation in the presence of ammonium salts used as mild promotors (5-HMF being highly sensitive), we decided to elucidate the formation of the by-products detected during the hydrothermal decomposition of D-glucose. To this end, we have investigated the acid catalyzed hydrothermal dehydration of D-glucose using ammonium sulfate or acetate as Brønsted acid promotors. Firstly, we have compared the results obtained from ammonium acetate and ammonium sulfate with those obtained from sulfuric acid. Secondly, we studied the kinetics of the hydrothermal decomposition of D-glucose using ammonium sulfate as promotor.

## Experimental

The reactions were performed in an Ace Pressure Tube® purchased from Sigma-Aldrich®. All compounds were purchased from Sigma-Aldrich® and were used without further purification. Tap water was used. <sup>1</sup>H NMR spectra were recorded on a Bruker ALS 300 MHz spectrometer with a QNP probe in D<sub>2</sub>O containing acetonitrile as internal standard. <sup>13</sup>C and <sup>15</sup>N CP MAS NMR spectra were recorded on a Bruker Avance III 500 WB using a 4 mm MAS Bruker probe and zirconia rotors with Kel-F drive caps using a recycling delay of 5 s, a contact time of 2 and 3 ms, and a spinning rate of 13 and 10 KHz, respectively. The chemical shifts are given relative to adamantine ( $\delta$  38 ppm) in the case of <sup>13</sup>C CP MAS NMR and glycine ( $\delta$  34 ppm) in the case of <sup>15</sup>N CP MAS NMR. Elemental analyses were carried out by Welience - Pôle Chimie Moléculaire Dijon, and oxygen percentages were calculated by difference with the other atoms. Infra-Red spectra were recorded on a Nicolet<sup>™</sup> iS<sup>™</sup> 10 FT-IR spectrometer of Thermo Fisher Scientific. The gas phase was analysed by a gas phase chromatography 6890 Agilent with a CP-Molsieve 5Å column Varian. 200 µL of gas were injected. The program of temperature was 40°C during 2 minutes, then 60°C per minute up to 250°C. DOI: 10.1039/DONJ00155D A mixture of D-glucose (4.00 g, 22.2 mmoles), ammonium sulfate, ammonium acetate or sulfuric acid (5.2 mmoles) and water (affording a solid content of 50%) was heated at 150°C for the indicated time. After cooling to room temperature using an ice bath, the reaction mixture was treated as described in the ESI (Figure S1<sup>+</sup>) to isolate the water soluble compounds on the one hand and the humins on the other hand.

## **Results and discussion**

After treatment of the reaction mixture obtained by heating at 150°C for 80 minutes a mixture of D-glucose (22.2 mmoles), ammonium sulfate, ammonium acetate or sulfuric acid (5.2 mmoles) as promotor and water in quantity to afford a solid content of 50%, the liquid phase gave the water soluble compounds after lyophilisation, and the solid gave the humins after drying for 24 hours at 40°C. The Figure 1 discloses the proportion of the humins and the organic species contained in the water phase (D-glucose, 5-HMF, LA and WSO) determined during the hydrothermal decomposition of D-glucose in the presence of one of the three Brønsted acids. FA was not considered because during the lyophilisation step, the majority of FA was evaporated, and only traces were detected. However, it is well-established that during the hydrothermal decomposition of 5-HMF, <sup>10, 37</sup> equimolar amounts of LA and FA are produced.



**Fig. 1** Evolution of the humins, D-glucose, WSO, 5-HMF and LA in the hydrothermal decomposition of D-glucose heated at 150°C during 80 min. in the presence of 5.2 mmoles of  $(NH_4)_2SO_4$ ,  $NH_4OAc$  or  $H_2SO_4$ . The conversion of D-glucose and the yields of 5-HMF and LA were based on the starting amount in mole of D-glucose. The yields of WSO and the humins were based on the starting amount in mass of D-glucose.

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The activity of the three promotors was proven totally different. In the case of sulfuric acid, 93% of conversion of D-glucose was measured. Conversely, with ammonium sulfate or ammonium acetate, the conversions were lower, reaching 79 or 58%, respectively. In addition, these different acids did not afford the formation of the same species. Indeed, in the case of sulfuric acid, a large quantity of LA was obtained (41.1 mole % based on starting Dglucose), whereas in the case of the ammonium salts, no LA was formed in the case of NH<sub>4</sub>OAc or only in small amount in the case of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (4.0 mole % based on the starting D-glucose). No 5-HMF was detected in the case of sulfuric acid, whereas in the case ammonium promotors, low similar yields based on starting D-glucose were determined with 9.0 mole % in the case of  $(NH_4)_2SO_4$  and 8.3 mole % in the case of NH<sub>4</sub>OAc. The maximum amount of WSO was obtained when NH<sub>4</sub>OAc was used (23.0 weight % based on starting D-glucose). In the case of sulfuric acid, the yield was divided by 2 (10.5 weight % based on starting D-glucose), and divided by 4 in the case of ammonium sulfate (6.5 weight % based on starting Dglucose). Regarding the formation of the humins, a maximum amount (36.8 weight % based on starting D-glucose) was observed when ammonium sulfate was used. For the two other Brønsted acids, the humins yields were lower, with 16.3 weight % (based on starting D-glucose) in the case of NH<sub>4</sub>OAc and 25.5 weight % (based on starting D-glucose) when H<sub>2</sub>SO<sub>4</sub> was used.

These preliminary results confirmed the low stability of 5-HMF during the hydrothermal treatment of oses in the presence of sulfuric acid. Instead, in the presence of ammonium salts, 5-HMF was not decomposed into LA. The difference in quantities of organic species and the humins depending on the Brønsted acid promotor used, can possibly be explained by the pH of the water phase. It is known that the formation of 5-HMF is pH dependent, with an optimal pH area between 1.5 and 2.38 In the case of NH<sub>4</sub>OAc, the pH of the water phase from 6.1 to 4.3 was out of the ideal zone of the 5-HMF formation, the key intermediate in the synthesis of LA and the humins. The drop in pH value was explained by the formation of acetic acid (pKa CH<sub>3</sub>CO<sub>2</sub>H / CH<sub>3</sub>CO<sub>2<sup>-</sup></sub> 4.4). In the case of sulfuric acid, the initial pH was too acid (from 1.0 to 1.5), and the 5-HMF was transformed into LA in large amount. Hence, in the case of ammonium sulfate, the water phase offered the most appropriate acidity (from 4.5 to 1.4) to transform D-glucose into 5-HMF. Using the latter promotor, 5-HMF was converted mainly into the humins, and only some traces of LA were observed, while the pH of the aqueous solution (1.4) was close to the one measured from sulfuric acid (1.5). This observation suggests that the cationic ammonium ions prevent the formation of LA from 5-HMF. In the presence of water, the NH<sub>4</sub><sup>+</sup> cations are in equilibrium with NH<sub>3</sub> and H<sub>3</sub>O<sup>+</sup>. In the case of ammonium acetate, the CH<sub>3</sub>CO<sub>2</sub>- anions are protonated affording acetic acid that buffers the medium around pH 4.3. As for ammonium sulfate, the SO42- anions are mono-protonated to give the  $HSO_4$  anions hence, explaining the low pH to 1.4.

A kinetic study was considered for the two ammonium salts. In the case of the ammonium acetate promotor (Table 1), the conversion of D-glucose increased with the time from 33 to 58%. The 5-HMF

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yield increased slightly (from 3.5 to 8.3 mole % based on starting Deglucose) with the reaction time. For shore: reaction times, D-glucose was mainly converted into WSO. Then, for longer reaction time (80 minutes), the D-glucose conversion was in favor of the formation of the humins (16.3 weight % based on starting D-glucose), and not of the formation of 5-HMF. Meanwhile, the amount of WSO decreased over time (from 35.5 to 23.0 weight % based on starting D-glucose). Hence, the use of ammonium acetate as promotor is probably not a good candidate for the production of 5-HMF, even if no LA was obtained during the hydrothermal decomposition of D-glucose.

A second and more detailed study was carried out using ammonium sulfate as the promotor for several durations. The main compounds detected in the water soluble compounds were D-glucose, 5-HMF, LA, WSO, ammonium salts (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and NH<sub>4</sub>HSO<sub>4</sub>. As previously discussed, FA was not considered because during the lyophilisation step, the majority of FA was eliminated, and only traces were detected. The Table 2 gathers the yields of each species depending on the reaction time. As reported in the ESI, the amounts of Dglucose, 5-HMF and LA were determined by <sup>1</sup>H NMR using acetonitrile as standard, and the amount of WSO was calculated from the elemental analyses. WSO were isolated and characterized as already reported in the case of sulfuric acid as promotor.<sup>27</sup> The WSO presented a similar structure of D-glucose oligomers with a maximum of 9 units. To determine the ratio of ammonium sulfate and ammonium bisulfate, we compared the pKa values of the 2 acidities  $HSO_4^{-}/SO_4^{2-}$  (1.9) and  $H_2SO_4$  /  $HSO_4^{-}$  (-3.0) with the pH of the aqueous phase before treatment. The pH range (1.4 – 1.8) evidenced that the amount of H<sub>2</sub>SO<sub>4</sub> was negligible compared to that of HSO<sub>4</sub>. Thanks to the amount of the water soluble compounds and the corresponding elemental analyses, we were able to determine the amount of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and NH<sub>4</sub>HSO<sub>4</sub> (see ESI). While all the total amount of sulfur was found (within the experimental errors), the quantity of nitrogen was in default, suggesting an incorporation of nitrogen in the structure of the humins. The loss in nitrogen atoms gradually increased with the reaction time, and explained the release of HSO<sub>4</sub><sup>-</sup> ions responsible for the decrease of the pH. The amounts of the water soluble compounds obtained after lyophilization were compared to the total amounts of the different organic (residual Dglucose, 5-HMF, LA and WSO) and inorganic (ammonium sulfate and ammonium bisulfate). The values appeared very similar (Table S6<sup>+</sup>), suggesting a total identification of the compounds.

 Table 1
 Hydrothermal decomposition of D-glucose in the presence of ammonium acetate as promotor.

Time	۴ Ha	Conv. <sup>b</sup>	5-HMF <sup>c</sup>	LA <sup>c</sup>	WSO <sup>d</sup>	Humins <sup>d</sup>	
[min.]	•	[mol%]	[mol%]	[mol%]	[wt%]	[wt%]	
20	4.4	33.5	3.5	0.0	35.5	0.2	
40	4.3	42.5	5.9	0.0	36.5	3.2	
80	4.3	57.8	8.3	0.0	23.0	16.3	

<sup>a</sup> pH of aqueous phase before treatment (initial pH 6.1). <sup>b</sup> Conversion of Dglucose. <sup>c</sup> Based on the starting amount in mole of D-glucose. <sup>d</sup> Based on the starting amount in mass of D-glucose. ARTICLE

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**Table 2** Composition of the water soluble compounds obtained during the hydrothermal decomposition of D-glucose in the presence of ammonium sulfate as promotor.

Time [min.]	pH ª	Conv. <sup>b</sup> [mol%]	5-HMF <sup>c</sup> [mol%]	LA <sup>c</sup> [mol%]	WSO <sup>d</sup> [wt%]	(NH4)2SO4 <sup>e</sup> [mmol]	NH4HSO4 <sup>e</sup> [mmol]	Loss of N <sup>f</sup> [mmol]
20	1.8	51.7	18.3	0.0	17.7	4.7	0.5	0.5
40	1.5	74.1	16.9	1.3	16.7	3.1	2.4	1.8
60	1.4	76.5	11.2	2.2	14.3	2.6	2.9	2.3
80	1.4	79.1	9.1	4.0	6.6	2.3	2.3	3.5

<sup>a</sup> pH of aqueous phase before treatment (initial pH 4.5). <sup>b</sup> Conversion of D-glucose. <sup>c</sup> Based on the starting amount in mole of D-glucose. <sup>d</sup> Based on the starting amount in mass of D-glucose. <sup>e</sup> Amount determined from the elemental analyses of the water soluble compounds (see ESI).<sup>f</sup> Loss determined by comparison between the number of mole of nitrogen introduced and the quantity found by the elemental analyses of the water soluble compounds.

While the amount of 5-HMF was low in the hydrothermal decomposition of D-glucose in the presence of ammonium acetate, in the presence of ammonium sulfate in the same experimental conditions, the amounts of 5-HMF was six times larger after 20 minutes (Table 2, entry 1), and close after 80 minutes (Table 2, entry 4). The consumption of 5-HMF was not related to the formation of LA. Indeed, the amount of LA did not exceed 4.0 mole % based on starting D-glucose.

Regarding the formation of the WSO, their quantity decreased gradually until 20 minutes, from 17.7 to 6.6 weight % based on starting D-glucose (Table 2). This is reminiscent with the fact that the WSO are a "D-glucose reservoir" or can also react directly with aldol condensation intermediates resulting in their insertion in the structure of the humins.<sup>27</sup>

In order to confirm the insertion of some nitrogen atoms into the structure of the humins, the latter were characterized by elemental analyses, <sup>13</sup>C and <sup>15</sup>N CP MAS NMR and Infra-Red. The elemental analyses of the humins (Table 3) shown clearly the insertion of nitrogen atoms in the structure of the solids when ammonium salts were used as promotor. In agreement with a different activity between the promotors, the humins obtained after 80 minutes from NH<sub>4</sub>OAc were more hydrated with a formula of C<sub>6.0</sub>H<sub>6.4</sub>N<sub>0.4</sub>O<sub>2.8</sub> than the humins obtained after the same reaction time in the presence of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub> with a formula of C<sub>6.0</sub>H<sub>5.7</sub>N<sub>0.4</sub>O<sub>2.5</sub> and C<sub>6.0</sub>H<sub>5.0</sub>O<sub>2.3</sub>, respectively. The yields of the humins obtained in the presence of ammonium sulfate as promotor increased with the reaction time reaching 36.8 weight % (based on starting D-glucose) after 80 minutes of reaction.

 Table 3
 Elemental analyses of the humins obtained during the hydrothermal decomposition of D-glucose.

Promotor	Time [min.]	Yield <sup>a</sup> [wt%]	Formula	O/C	H/C
(NH4)2SO4	20	8.7	$C_{6.0}H_{6.5}N_{0.4}O_{2.8}$	0.47	1.08
	40	26.8	$C_{6.0}H_{5.9}N_{0.4}O_{2.7}$	0.45	0.98
	60	32.5	$C_{6.0}H_{5.8}N_{0.4}O_{2.5}$	0.42	0.96
	80	36.8	$C_{6.0}H_{5.7}N_{0.4}O_{2.5}$	0.41	0.95
NH₄OAc	80	16.3	$C_{6.0}H_{6.4}N_{0.4}O_{2.8}$	0.47	1.08
$H_2SO_4$	80	25.5	$C_{6.0}H_{5.0}O_{2.3}$	0.39	0.85

<sup>a</sup> Based on starting amount in mass of D-glucose.

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The ratio O/C and H/C of the humins obtained after 80 minutes of reaction, were compared to those of D-glucose, WSO, HMF and LA in a van Krevelen diagram (Figures S3<sup>+</sup>). The plots corresponding to the humins match nicely with the dehydration line of D-glucose, even if the plots are slightly below the line. This observation can be easily explained by the incorporation of the nitrogen atoms at the expense of oxygen atoms in the structure of the humins. The more dehydrated solids obtained in the case of sulfuric acid was confirmed by the IR spectra of the humins (Figure S2<sup>+</sup>).

The comparison of the <sup>13</sup>C CP MAS NMR spectra (Figure 2) of the humins were similar to those reported in the literature <sup>24-27</sup> with the observation of saturated aliphatic groups (region of  $\delta$  0 to 55 ppm), alcohol or ether groups (region from  $\delta$  60 to 90 ppm), aromatic groups such as furan rings (region from  $\delta$  100 to 160 ppm), ester or carboxylic groups (region from  $\delta$  165 to 180 ppm) and ketone or aldehyde groups (region from  $\delta$  195 to 210 ppm). Even if the <sup>13</sup>C CP MAS NMR sequence is not quantitative, as the spectra were recorded using the same experimental conditions, the main difference was found in the area of alcohol or ether groups (region from  $\delta$  60 to 90 ppm). The spectra recorded for the humins obtained from ammonium salts were similar, suggesting very close structures with a high intensity for the signals in this area. On the contrary, the spectrum recorded for the humins obtained from sulfuric acid revealed low intensity for the signal in this area, suggesting also a more dehydrated structure.

A hydrothermal decomposition of D-glucose using <sup>15</sup>N enriched ammonium sulfate was carried out to enable a <sup>15</sup>N CP MAS NMR spectrum of the humins obtained in similar conditions of temperature and concentration and after a reaction time of 80 minutes. On the <sup>15</sup>N CP MAS NMR spectrum (Figure 3), 2 signals are mainly present, centered at  $\delta$  130 and 155 ppm. These chemical shifts are in good agreement with the formation of pyrrole derivatives. To explain the formation of pyrrole derivatives, knowing that NH<sub>4</sub><sup>+</sup> and NH<sub>3</sub> are in equilibrium and based on the DHH intermediate in the humins formation as proposed by Lund *et al.*,<sup>22</sup> we postulated a Paal-Knorr reaction between NH<sub>3</sub> and DHH (Scheme 2), as already described by Amarnath *et al.* <sup>39</sup> between 4oxoaldehyde derivatives and primary amines.

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Scheme 2 Synthesis of pyrrole derivative from DHH.

During the hydrothermal decomposition of D-glucose, the process occurs with the formation of water. In the case of ammonium sulfate as promotor, by comparing the number of mole of all atoms (C, H, N, O, and S) initially introduced with those determined from elemental analyses of the water soluble compounds and the humins, the amount of formed water during the reaction was estimated (Table S7†).

This study allowed us to determine all the species present during the hydrothermal decomposition of D-glucose using ammonium sulfate as promotor (Table S8<sup>+</sup> and Figure S5<sup>+</sup>) with a total mass balance very close to the initial amount introduced in the sealed tube (Dglucose and ammonium sulfate). The mass difference is less than 2.5 wt %, which is expected within the experimental errors. In addition, in the case of the reaction ran for 80 minutes, when the sealed tubed was opened after cooling down to room temperature, a little over pressure was detected, even if the mass difference was only about 1.6%. A gualitative head-space GC analysis of the gas phase did not evidence the formation of SO<sub>x</sub>. CO<sub>2</sub> and CO were main gases detected in the gas phase in 97.5 and 2.5 molar %, respectively (Figure S4<sup>+</sup>). As for NH<sub>3</sub>, it was only detected at the level of traces. The (quasi)absence of NH<sub>3</sub> in the gas phase is easily explained by the fact that DHH reacts with it to give pyrrole derivatives in a Paal-Knorr reaction, as already stated.

### Conclusions

The acidic hydrothermal decomposition of D-glucose using ammonium sulfate or ammonium acetate as promotor was studied. With ammonium sulfate as the promotor, the first steps of the decomposition of D-glucose are very similar to those observed with sulfuric acid. The dehydration of D-glucose to 5-HMF competes with the oligomerization to WSO. We proposed that in these two Brønsted acidic conditions, the WSO played the role of a "D-glucose reservoir", but we cannot exclude the direct incorporation in the humins by aldol condensations. The formation of 5-HMF from Dglucose is limited by 2 hydration routes known to be in competition. On the one hand, 5-HMF can be transformed into LA and FA, and on the other hand it can it can incorporate into the humins structure *via* aldol condensation with the DHH. These two routes were observed when sulfuric acid was used. However, in the case of ammonium sulfate, a very little amount of LA was observed. The pH of the aqueous phases after 80 minutes of reaction at 190°C 96 Phases of sulfuric acid and ammonium sulfate as promotor, were very close, suggesting that the ammonium part inhibits the LA formation in favor of the humins. The analyses the humins showed that a part of nitrogen atoms was inserted into the solid when ammonium salts were used as promotor. In our conditions, we never observed the DHH intermediate due to its high reactivity, but it may play a key role, reacting with NH<sub>3</sub> to give pyrrole derivatives, which can be incorporated in the structure of the humins. In the presence of ammonium acetate, LA was not formed even after a reaction time of 80 minutes. However, the absence of LA can also be explained by the low conversion of D-glucose, probably related to the buffered medium at pH 4.3. Conversely, the use of ammonium sulfate as the promotor offers a double benefit: the NH<sub>4</sub><sup>+</sup> ions prevent the formation of LA and the equilibrium between NH4<sup>+</sup> and NH3 allowed the slow release of HSO<sub>4</sub>- ions, decreasing the pH to the optimal 1.5-2 range for osidic cleavage of the WSO and for 5-HMF formation, even if the humins formation could not be avoided.







Fig. 3  $^{15}N$  CP MAS NMR spectra of the humins obtained after 80 minutes in the presence of  $^{15}N$  enriched (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>.

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**Conflicts of interest** 

There are no conflicts to declare.

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# Influence of the ammonium salts used in the Brønsted acid catalyzed hydrothermal decomposition of D-glucose towards 5-HMF

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Graphical resume of the hydrothermal decomposition of D-glucose at 150°C in the presence of ammonium sulfate

