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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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All reactions were performed in an Ace Pressure Tube purchased from Sigma-Aldrich[®]. All reagents were purchased from Sigma-Aldrich[®] and were used without further purification. Tap water was used.

¹H NMR and spectra were recorded on a Bruker ALS 300 MHz spectrometer with a QNP probe in D_2O containing acetonitrile as standard or in CDCl₃. ¹³C and ¹⁵N 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, and 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 adamantane (δ 38.0 ppm) in the case of ¹³C CP MAS NMR and glycine (δ 34.0 ppm) in the case of ¹⁵N CP MAS NMR.

Elemental analyses were carried out by Welience – Pôle Chimie Moléculaire Dijon, and Oxygen percentages were deduced by difference with the other atoms.

Infra-Red spectra were recorded on a Nicolet[™] iS[™] 10 FT-IR spectrometer of Thermo Fisher Scientific.

Gas phase was analyzed on 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 to reach 250°C.

I. Protocol of the treatment of the reaction mixture

In all cases, the reaction mixtures after cooling to room temperature using an ice bath, were treated following the same protocol, as described in Figure S1.



Pressure Tube, were placed D-glucose (4.00 g, 22.2 mmoles), ammonium sulfate (0.70 g, 5.2 mmoles) or ammonium acetate (0.40 g, 5.2 mmoles) or sulfuric acid 95-97% (0.53 g, 5.2 mmoles), and water (4.70 / 4.40 / 4.53 g, respectively, affording a solid content of 50%). After a few minutes of heating, a homogeneous solution was

obtained, and the pH was measured (pH = 4.5 / 6.1 / 1.0, respectively). Next, the mixture was heated at 150° C for 80 minutes. After cooling to room temperature using an ice bath, the reaction mixture was treated as described in the Figure S1.

II-1. Analysis of the humins

After drying at 40°C for 24 hours, the humins were analyzed by elemental analysis.

Table S1 Masses and elemental analyses of the humins obtained during the hydrothermal decomposition of D-glucose at 150°C for 80 minutes in the presence of 5.2 mmoles of promotor.

	_	Humins		Elemen	tal anal	ysis (%)		Formula		
Entry	Promotor	[mg]	С	Н	Ν	O ^a	S	$C_{6.0}H_xN_yO_t$	O/C	H/C
1	(NH ₄) ₂ SO ₄	1470	59.02	4.70	4.08	32.20	0.00	$C_{6.0}H_{5.7}N_{0.4}O_{2.}$	0.41	0.95
								5		
2	NH₄OAc	650	55.59	4.99	4.35	35.07	/	$C_{6.0}H_{6.4}N_{0.4}O_{2.}$	0.47	1.08
								8		
3	H_2SO_4	1020	62.97	4.44	/	32.59	0.00	$C_{6.0}H_{5.0}O_{2.3}$	0.39	0.85

^a By difference with the other atoms.



Fig. S2 IR spectra.

II-2. Analysis of the water soluble compounds

After lyophilisation, the water soluble compounds were analyzed by ¹H NMR. The organic compounds were determined by ¹H NMR using acetonitrile as standard. During the lyophilization step, the majority of FA was eliminated, and only traces were observed on the ¹H NMR spectra.

Table S2 Composition of the lyophilized water soluble compounds obtained during the hydrothermal decomposition of D-glucoseat 150°C for 80 minutes in the presence of 5.2 mmoles of promotor.

				Water s	oluble compour	ids ^b	
Entry	Promotor	pH ª	Mass [mg]	D-glucose [mg]	WSO [mg]	HMF [mg]	LA [mg]
1	(NH ₄) ₂ SO ₄	1.4	2030	837	262	254	102
2	NH₄OAc	4.3	3310	1688	920	234	0
3	H_2SO_4	1.5	2420	275	420	0	1065

^a pH of the first water phase (see Fig. S1). ^b Water soluble compounds obtained after lyophilization.

III. Kinetic study of the hydrothermal decomposition of D-glucose at 150°C in the presence of NH_4OAc

In an Ace Pressure Tube, were placed D-glucose (4.00 g, 22.2 mmoles), ammonium acetate (0.40 g, 5.2 mmoles) and water (4.40 g, affording a solid content of 50%). After a few minutes of heating, a homogeneous solution was obtained, and the pH was measured (pH = 6.1). Next, the mixture was heated at 150°C during the indicated time. After cooling to room temperature using an ice bath, the reaction mixture was treated as described in the Figure S1. After lyophilisation, the WSC were analyzed by ¹H NMR. The organic compounds were determined by ¹H NMR using acetonitrile as standard. During the lyophilization step, the majority of FA was eliminated, and only traces were observed on the ¹H NMR spectra.

Fata	Time	والع		Water solu	ble compound	S ^b		Humins
Entry	[min.]	рп	Mass [mg]	D-Glucose [mg]	WSO [mg]	HMF [mg]	LA [mg]	[mg]
1	20	4.4	4320	2660	1420	106	0	10
2	40	4.3	4180	2300	1460	170	0	130
3	80	4.3	3310	1688	920	234	0	650

Table S3 Hydrothermal decomposition of D-glucose at 150°C in the presence of NH₄OAc (mmoles).

^a pH of the first water phase (see Fig. S1). ^b Water soluble compounds obtained after lyophilization.

IV. Kinetic study of the hydrothermal decomposition of D-glucose at 150°C in the presence of $(NH_4)_2SO_4$

In an Ace Pressure Tube, were placed D-glucose (4.00 g, 22.2 mmoles), 15 N enriched or not ammonium sulfate (0.70 g, 5.2 mmoles) and water (4.70 g, affording a solid content of 50%). After a few minutes of heating, a homogeneous solution was obtained, and the pH was measured (pH = 4.5). Next, the mixture was heated at 150°C during the indicated time. After cooling to room temperature using an ice bath, the reaction mixture was treated as described in the Figure S1.

IV-1. Analysis of the humins

After drying at 40°C for 24 hours, the humins were analyzed by elemental analysis.

Table S4 Masses and elemental analyses of the humins obtained during the hydrothermal decomposition of D-glucose at 150°Cin the presence of ammonium sulfate.

	Time	Humins		Elemen	ital anal	ysis (%)		Formula	- 1-	
Entry	[min.]	[mg]	С	н	Ν	O ^a	S	$C_{6.0}H_xN_yO_t$	0/C	H/C
1	20	348	55.56	5.03	4.26	35.15	0.00	$C_{6.0}H_{6.5}N_{0.4}O_{2.8}$	0.47	1.08
2	40	1070	56.83	4.65	4.09	34.43	0.00	$C_{6.0}H_{5.9}N_{0.4}O_{2.7}$	0.45	0.98
3	60	1301	58.60	4.72	4.13	32.55	0.00	$C_{6.0}H_{5.8}N_{0.4}O_{2.5}$	0.42	0.96
4	80	1470	59.02	4.70	4.08	32.20	0.00	$C_{6.0}H_{5.7}N_{0.4}O_{2.5}$	0.41	0.95

^a By difference with the other atoms.



Fig. S3 van Krevelen diagram.

IV-2. Analysis of the water soluble compounds

After lyophilization of the aqueous phases, the water soluble compounds were analyzed by ¹H NMR and by elemental analysis. The Table S5 summarizes the pH of the aqueous phase before lyophilization, the amount of the water soluble compounds obtained after lyophilization with the corresponding elemental analysis. And the Table S6 describes the quantity of D-glucose, WSO, HMF, LA and ammonium salts $(NH_4)_2SO_4$ and NH_4HSO_4 present in the water soluble compounds. During the lyophilization step, the majority of FA was eliminated, and only traces were observed on the ¹H NMR spectra in the case of longer time.

Based on the pKa values of the 2 acidities H_2SO_4 / HSO_4^- (-3.0) and HSO_4^- / SO_4^{2-} (1.9) and on the pH of the aqueous phases (see Table S5), we concluded that HSO_4^- ion was much more abundant than H_2SO_4 which was not considered. From the numbers of mmole of sulfur and nitrogen atoms of water soluble compounds, we established 2 equations to determine the numbers of mmole of the 2 ammonium salts $(NH_4)_2SO_4$ and NH_4HSO_4 :

Number of mmoles of S = t mmoles of $(NH_4)_2SO_4 + y$ mmoles of NH_4HSO_4

Number of mmoles of N = 2 t mmoles of $(NH_4)_2SO_4 + y$ mmoles of NH_4HSO_4

The amounts of D-glucose, HMF and LA were determined by ¹H NMR using acetonitrile as standard. And the amount of WSO was calculated with the elemental analyses by estimating that the residual amount of carbon, hydrogen and oxygen atoms obtained after subtracting the amount of monomeric organic compounds (D-glucose, HMF and LA) and inorganic compounds (ammonium sulfate and ammonium bisulfate) corresponds to the WSO.

Entry	Time [min.]	pH ª	Mass ^b [mg]	С	Elemer H	ntal ana N	lysis (%) O ^c	S
1	20	1.8	3830	36.71	6.17	3.62	49.13	4.37
2	40	1.5	2900	35.99	5.80	4.17	47.94	6.10
3	60	1.4	2560	32.98	5.69	4.43	50.03	6.87
4	80	1.4	2030	31.41	5.95	4.81	50.48	7.35

Table S5 Masses and elemental analyses of the water soluble compounds obtained during the hydrothermal decomposition of D-glucose at 150°C in the presence of ammonium sulfate.

^a pH of the first water phase (see Fig. S1). ^b Mass of water soluble compounds obtained after lyophilization. ^c By difference with the other atoms.

 Table S6
 Composition of the water soluble compounds obtained during the hydrothermal decomposition of D-glucose at 150°C in the presence of ammonium sulfate.

[ntm/	Time			Time Water soluble compounds [mg] ^a										
Entry	[min.]	Mass	D-Glucose ^b	WSO ^c	HMF ^b	LA ^b	(NH ₄) ₂ SO ₄ ^d	NH ₄ HSO ₄ ^d	[mg]					
1	20	3830	1931	706	512	0	618	62	+1					
2	40	2900	1037	669	472	34	412	276	0					
3	60	2560	941	571	314	58	345	331	0					
4	80	2030	837	262	254	102	306	269	0					

^a Water soluble compounds obtained after lyophilization. ^b Based on ¹H NMR. ^c Based by mixing ¹H NMR and elemental analysis. ^d Based on elemental analysis. ^e The difference was determined by subtracting the total amount of organic and inorganic compounds to the mass of water soluble compounds obtained after lyophilization.

The hydrothermal decomposition of D-glucose is done with the formation of water. Comparing the numbers of mmole of C, H, N, O and S atoms determined from elemental analyses of the humins and the WSC with those coming of the D-glucose and ammonium sulfate introduced in the sealed tube at the starting, we observed that some H and O atoms were missed with a H/O ratio close to 2. We postulated that these H and O missed atoms corresponded to the formed water which was eliminated during the lyophilization step. The amount of formed water is given in the Table S7.

								Ator	ns ^a								
Entry	Time [min.]		лн	ins			Water so	luble con	spunodu			Δ	ifference	٩		°0/H	H ₂ O ^d [mg]
		U	т	z	0	U	т	z	0	S	U	т	z	0	S		
1	20	16.1	17.4	1.1	7.6	117.1	234.5	9.9	117.6	5.2	+ 0.1	+ 57.0	-0.4	+29.2	+0.1	2.0	513
7	40	50.6	49.4	3.1	23.0	86.9	166.9	8.6	86.9	5.5	- 4.3	+ 92.6	-1.2	+44.5	-0.2	2.1	834
m	60	63.5	60.9	3.8	26.5	70.3	144.5	8.1	80.1	5.5	- 0.5	+103.4	-1.3	+47.9	-0.2	2.2	931
4	80	72.2	68.5	4.3	29.6	53.1	119.8	7.0	64.1	4.7	+ 7.9	+120.4	-0.7	+60.8	+0.6	2.0	1085
^a Numbe soluble o of H anc	er of mmc compoun I O missec	oles of eac ds to the n d atoms (d	h atom de umbers of ifference c	termined mmole of olumn). ^d	from elem atoms of t Based on F	ental analy the startin _i 1 missed an	/ses. ^b Diffe 3 material (:oms (diffe	rrence ob D-glucos rence col	tained by s e and amm umn).	ubtracting onium sul	g the addi fate introc	tion of nun Juced in th	nbers mm e sealed t	ioles of ato ube). ^c Base	ms of the ed on the r	humins ar numbers o	id water f mmole

Table S7 Water formation during the hydrothermal decomposition of D-glucose at 150°C in the presence of ammonium sulfate.

IV-3. Analysis of the gas phase in the case of the hydrothermal decomposition of D-glucose at 150°C during 80 minutes

To analyze the observed gas phase, in an Ace Pressure Tube with septum, D-glucose (4.00 g, 22.2 mmoles), ammonium sulfate (0.70 g, 5.2 mmoles), and water (4.70 g, affording a solid content of 50%) were introduced. After a few minutes of heating, a homogeneous solution was obtained. Next, the mixture was heated at 150°C during 80 minutes. After cooling to room temperature using an ice bath, the gas was collected with a sealed Hamilton[®] syringe, and was analyzed by gas chromatography (Figure S4).



Fig. S4 Qualitative chromatogram of gas phase collected during the hydrothermal decomposition of D-glucose at 150°C during 80 minutes.

IV-4. Study summary

The Figure S5 and the Table S8 summarize this study on the hydrothermal decomposition of D-glucose at 150°C in the presence of ammonium sulfate.

Error ^d [%]	/	0.2	2.5	2.4	1.6
Σ ° [mg]	4700	4691	4817	4815	4625
H ₂ O ^b [mg]	0	513	834	931	1085
NH ₄ HSO ₄ [mg]	0	62	276	331	269
(NH ₄) ₂ SO ₄ [mg]	002	618	412	345	306
FA ^a [mg]	0	0	13	23	40
LA [mg	0	0	34	58	102
HMF [mg]	0	512	472	314	254
WSO [mg]	0	706	699	571	262
D-Glucose [mg]	4000	1931	1037	941	837
Humins [mg]	0	348	1070	1301	1470
Hd	4.5	1.8	1.5	1.4	1.4
Time [min.]	0	20	40	60	80
Entry	1	2	3	4	5

Table S8 Summary of the hydrothermaldecomposition of D-glucose at 150°C in the

presence of ammonium sulfate.

^a Based on equimolar formation of LA and FA. ^b Water formed during the decomposition.^c Addition of all compounds which were present at the considered time..^d Error in percentage based on the starting material (D-glucose + ammonium sulfate).



Fig. S5 Graphical resume of the hydrothermal decomposition of D-glucose at 150° C in the presence of ammonium sulfate.

V. ¹H NMR spectra

1H NMR D-Glucose







V-1. Analysis of the water soluble compounds obtained in the presence of H_2SO_4

Fig. S7 1 H NMR (300 MHz, 298 K, D₂O with CH₃CN as standard centered at δ 2.06 ppm) spectra of water soluble compounds.

V-2. Analysis of the water soluble compounds obtained in the presence of NH_4OAc



Fig. S8 ¹H NMR (300 MHz, 298 K, D_2O with CH_3CN as standard centered at δ 2.06 ppm) spectra of water soluble compounds obtained after 20 minutes.

1H NMR of WSC (23 mg) obtained from NH4OAc 5.2 mmoles / 40 min.



Fig. S9 ¹H NMR (300 MHz, 298 K, D_2O with CH_3CN as standard centered at δ 2.06 ppm) spectra of water soluble compounds obtained after 40 minutes.





Fig. S10 1 H NMR (300 MHz, 298 K, D₂O with CH₃CN as standard centered at δ 2.06 ppm) spectra of water soluble compounds obtained after 80 minutes.



V-3. Analysis of the water soluble compounds obtained in the presence of $(NH_4)_2SO_4$

Fig. S11 ¹H NMR (300 MHz, 298 K, D_2O with CH_3CN as standard centered at δ 2.06 ppm) spectra of water soluble compounds obtained after 20 minutes.



Fig. S12 ¹H NMR (300 MHz, 298 K, D_2O with CH_3CN as standard centered at δ 2.06 ppm) spectra of water soluble compounds obtained after 40 minutes.



Fig. S13 ¹H NMR (300 MHz, 298 K, D_2O with CH_3CN as standard centered at δ 2.06 ppm) spectra of water soluble compounds obtained after 60 minutes.



Fig.S14 ¹H NMR (300 MHz, 298 K, D_2O with CH_3CN as standard centered at δ 2.06 ppm) spectra of water soluble compounds obtained after 80 minutes.