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## 5 Hydrothermal carbon from biomass: a comparison of the local structure from poly- to monosaccharides and pentoses/hexoses

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Carbon particles are synthesized under hydrothermal conditions using different biomass (glucose, xylose, maltose, sucrose, amylopectin, starch) and biomass derivatives (5-hydroxymethyl-furfural-1-aldehyde – HMF – and furfural) as carbon sources. Carbons obtained from mono and polysaccharides, hexose and pentose sugars, and from the biomass derivatives, HMF and furfural, 15 are compared from the particle morphology, chemical composition and structural point of view. A clear structural and morphological difference can be observed in carbons from pentoses and hexoses but in the last case, no matter the nature of the hexose sugar, all carbon materials showed astonishing similarities opening the way to the use of renewable biomass in the synthesis of such carbon materials.

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### Introduction

Research on materials usually gives the priority to increase the performance-to-cost ratio, disregarding the sustainability of the methods, techniques and processes involved in the 25 conception and synthesis of the material itself. In the field of carbon-based materials activated charcoals are usually made under high-energy conditions. Recently developed routes to obtain a periodic porous carbon network<sup>1,2,3,4</sup> were successful but again did not take into account any criteria of 30 sustainability. In this case, it involves: indirect impregnation techniques (mesoporous silica is generally used as template), hydrogen fluoride etching<sup>1,2</sup>, and finally high carbonization temperatures<sup>1</sup>. Even direct templating of resins (phenol/formaldehyde)<sup>4</sup> are still far from following 35 sustainable principles such as energy and atom economy, low toxicological impact of materials and processes and use of renewable resources.

The problem of carbon synthesis under sustainable conditions was recently revisited and implemented by several 40 research teams<sup>5,6,7,8</sup>, where hydrothermal treatment of biomass in water under relatively mild conditions provided bulk, mesoporous, or nanostructured carbon materials. This technique was already known for longer times<sup>9</sup>, but the need of exploring cheap and sustainable ways to obtain chemicals<sup>10</sup> 45 and carbons from raw materials other than crude oil or natural gas (for soot generation) lead to a re-exploration of this field. In addition, the implementation of a low-cost pathway to recycle byproducts of farmed biomass would additionally

represent a way to sequester significant amounts of CO<sub>2</sub><sup>5</sup>, 50 creating a materials benefit at the same time.

The use of hydrothermal synthesis between 180°C and 220°C allowed to obtain carbon-based powders, nanofibers<sup>11,12</sup>, or sponge-like mesoporous carbons being potentially useful as soil conditioner, ion exchange resins or 55 sorption coals<sup>7</sup>. The synthesis proved to be feasible when glucose<sup>6</sup> is used or even when side products from raw biomass materials like oak leaves and orange peels are taken<sup>7</sup>. In the first case, surface chemistry could also be modified by mean of hydrophilic or hydrophobic coupling agents<sup>13</sup>. Along 60 similar lines, the group of Clark showed that a slightly different approach using expanded starch treated with sulfuric acid instead of pure hydrothermal conditions could provide functional materials with disordered mesoporosity which proved to be satisfactory as catalysts in the esterification of 65 succinic acid<sup>14,15</sup>. In spite of the undoubted usefulness of the recent re-discovery of the hydrothermal process to obtain carbonaceous material, some basic work is still lacking as far as process of formation and final structure are concerned.

Some groups tried to investigate, directly or indirectly, the 70 reaction mechanisms which transforms glucose first into 5-hydroxymethyl-furfural-1-aldehyde (HMF), the dehydrated intermediate<sup>16,17</sup>, and then from here to the carbonaceous structure<sup>18,19</sup>, but a clear reaction path is still missing and chemistry of furans and furan-derived compounds is far too 75 large to easily forecast any possible result<sup>20</sup>. Even less is known about the final material structure mainly because of its intrinsic complexity and lack of technique allowing discrimination among all carbon sites with satisfactory

resolution. In general, FT-IR, and in some cases FT-Raman, is the main, easily accessible technique used to discriminate between various functional groups (C=O, C=C, aliphatic carbons)<sup>7,18,19</sup>. XPS was also used to identify the main carbon sites but resolution here is worse than in vibrational-based spectroscopies. <sup>13</sup>C solid state NMR has also been already tempted<sup>18,8</sup> but its use was a complement to other techniques. Even if exploitation of solid state NMR data on these materials was in its very beginnings, the authors have found that hydrothermal carbon materials hand out very nicely resolved <sup>13</sup>C spectra which have deserved recent deeper investigations<sup>21</sup>. So far, several studies<sup>7,8,22,23</sup> have proved that different types of biomass could be used to obtain carbon under hydrothermal conditions but in no case a clear comparison analyzing the local structure has been made.

In this study we will attribute the chemical and structural fingerprint of hydrothermal carbons obtained from hexose and pentose sugars as well as from their corresponding main dehydration intermediates, HMF and furfural reactions<sup>24,25</sup>. The aim of this work is to lead a comparative structural study of hydrothermally synthesized carbon materials obtained from different saccharides classified according to their number of carbons (pentoses vs. hexoses) and growing complexity (mono- vs. di- vs. polysaccharides).

We will show that all materials obtained from hexoses-based mono (glucose, HMF), di- (maltose, sucrose) and polysaccharides (amylopectin, starch) have the same chemical nature in terms of atom percentage and functional groups, as verified by <sup>13</sup>C solid-state Cross Polarization (CP) NMR analysis and Scanning Electron Microscopy (SEM) images. On the other hand, pentose-based (xylose, furfural) carbonaceous materials clearly showed interesting morphological and chemical differences with respect to hexose-based ones.

This work also clearly underlines that no substantial difference exist between monosaccharide- and polysaccharide-derived carbons, suggesting that the complexity of sugar-constraining biomass hardly has any influence on the material-forming mechanisms. This is important as it indicates that basic studies performed on simple test molecules, like glucose<sup>21</sup>, have broader validity and that no matter the complexity of the saccharide source, the final material have very similar local functionalities and connection patterns.

## Experimental

### Materials

For all samples, about 15 ml of a deionized water solution containing 10 wt% in mass of carbohydrate biomass was used. D(+)-glucose, D(+)-xylose, D(+)-maltose monohydrate, sucrose, amylopectin from potato starch, starch from potatoes or carbohydrate-dehydrated derivatives, HMF and furfural, were used as received (Sigma Aldrich). In order to prevent any contamination from multiple experiments, the mixture was sealed into a glass vial inside a typical PTFE-lined autoclave system and hydrothermally reacted in a pre-heated oven at 180°C for 24h. After reaction, the autoclave is cooled down in a water bath at room temperature. The obtained black

solid powder is then separated from the remaining aqueous solution by centrifugation (7000 rpm for 20 minutes) and put into an oven at 80°C under vacuum overnight for drying.

Sample notation for carbon material introduces an italic-styled capital “C” before each carbonized material; e.g., if glucose is the starting product, then *C*-glucose is its corresponding carbon sample obtained from hydrothermal treatment. In some cases, the terms *C*-hexose or *C*-pentose are used referring to all carbons from hexose and pentose sugars.

### Characterization

Gas Chromatography (GC) coupled to Mass Spectroscopy (MS) was used to separate and identify the main molecular species by mean of the NIST database included in the spectrometer software package. The instrument used is an Agilent Technologies (GC= 6890N; MS= 5975) apparatus.

*Solid-state NMR*: <sup>1</sup>H and <sup>13</sup>C solid-state Magic Angle Spinning (MAS) NMR experiments have been acquired on Bruker Avance 300 MHz (7 T) spectrometer using the 4 mm zirconia rotors as sample holders spinning at MAS rate  $\nu_{MAS}$ = 14 kHz. The chemical shift reference was tetramethylsilane (TMS;  $\delta$ = 0 ppm). Proton-to-carbon CP MAS was used to enhance carbon sensitivity: recycle delay for all CP experiments is 3 s and TPPM decoupling is applied during signal acquisition. Cross-polarization transfers were performed under adiabatic tangential ramps<sup>26,27</sup> to enhance the signal with respect to other known methods<sup>28</sup> and CP time  $t_{CP}$ = 3 ms was found to be a good compromise in order to have a good overview on all carbon species. Number of transients is 1840 (*C*-glucose, *C*-xylose) and 1200 for all other carbon samples. Peak attribution was done after references 29, 30, 31, 32 and 33.

Elemental chemical analysis was performed on a (C, N, O, S, H) Elementar Vario Micro Cube. SEM images were acquired on a LEO 1550/LEO GmbH Oberkochen provided with a Everhard Thornley secondary electron and In-lens detectors. N<sub>2</sub> adsorption and desorption isotherms were performed at 77 K with a Quadachrome Adsorption Instrument and BET method was used for specific surface area determination.

## Results and discussion

### Monosaccharide-derived carbons

Particle dispersions of carbonaceous materials were prepared from biomass at 180°C in water in a closed autoclave.

Figure 1 and Figure 2 show, respectively, SEM pictures and solid state <sup>13</sup>C CP-MAS NMR spectra of *C*-glucose and *C*-xylose (highlighted in gray for convenience) carbon materials. Despite the similar chemical nature of the employed sugars, the first being a hexose and the second a pentose, the final materials have remarkably different shapes. The decomposition of xylose leads to separated carbon spheres with diameter between 100 and 500 nm (Table 1) while glucose-based carbon is characterized by a mixture of spheres whose size varies between 500 nm and 1  $\mu$ m, randomly dispersed inside an interconnected matrix of smaller particles

(< 200 nm).

<sup>13</sup>C NMR spectra present some common peaks at 208 ppm (though a difference in 4 ppm at higher fields is observed for C-xylose), 175 ppm, 150 ppm and 40 ppm. On the other side, significant differences occur in the regions between 130 and 110 ppm, at 75 ppm and between 40 and 20 ppm. These observations show that similarities can be related to a comparable amount of carbonyl groups (aldehydes, ketones and carboxylic acids at chemical shifts between 210 and 170 ppm) as well as to the presence of oxygen-substituted protonated and non-protonated C=C bonds resonating at 150 ppm.

On the contrary, the peak at 129 ppm, which is generally attributed to aromatic carbons, as it is typical for graphitic structures or long-range conjugated double bonds, indicates the higher aromatic character of C-xylose carbon with respect to C-glucose. The peak at 75 ppm is indicative for the presence of hydroxylated methylene groups, which constitute an important part of C-glucose, while almost no hint of such groups is observed in C-xylose. Finally, at low chemical shifts, C-xylose seems to be dominated by ether groups resonating in the 40-50 ppm region while C-glucose shows an additional contribution of methylene groups, as it has been already discussed.

Overall, it seems that carbon material obtained from xylose has a higher aromatic character than C-glucose, and its higher carbon content (68.5%) supports this view (Table 2). Nonetheless, the oxygen level keeps quite high even in C-xylose (27.3%) meaning that the conjugated C=C network is always accompanied by larger quantities of functional groups (CHO, CC=CO, COOH), furan rings and ethers.

To reveal further details of this difference, we also tried to carbonize the known intermediates of dehydration, HMF and furfural under the same carbonization conditions. SEM images and <sup>13</sup>C NMR spectra of carbons obtained from HMF and furfural are also presented in Figure 1 and Figure 2. The C-HMF microstructure is composed of small particles (< 200 nm) which forms an interconnected network, and the similarities to C-glucose are obvious. Interestingly, furfural produces larger polydispersed spherical carbon particles whose size ranges between 500 nm and 3 μm (Table 1). The analysis of local chemical environments around carbon atoms probed by <sup>13</sup>C NMR also reveals some astonishing similarities between C-glucose and C-HMF and between C-xylose and C-furfural, respectively. The characteristic aromatic peak at 129 ppm is clearly prominent only in the pentose-derived carbon samples. Elemental analysis (Table 2) reveals, first of all, a high oxygen content, which undoubtedly makes these materials different from coal; secondly, carbon content in C-HMF (65.6%) is lower than in C-furfural (68.6%), and those values are coherent with values detected for C-glucose and C-xylose, discussed above. Mechanistic implications will be discussed later. Isothermal nitrogen adsorption/desorption experiments (results not shown) indicate them as non-porous materials (BET specific surface areas <10 m<sup>2</sup>·g<sup>-1</sup>).

Figure 1 SEM images of samples C-glucose, C-HMF, C-xylose and C-furfural

Figure 2 <sup>13</sup>C solid-state CP-MAS NMR spectra (t<sub>CP</sub>= 3 ms) of C-starch, C-amylopectin, C-sucrose and C-maltose, C-HMF, C-glucose, C-xylose and C-furfural.

Table 1 Morphological and dimensional aspect of carbon powders, as observed from SEM images.

Sample	Morphology	Size (nm)
Hexoses		
C-Glucose	Interconnected particles	<200
	Spheres	500-1000
C-HMF	Interconnected particles	<200
	Interconnected particles	200-500
C-Maltose	Agglomerated particles	200-500
	Spheres	2000
C-Sucrose	Interconnected spheres	700-2000
C-Amylopectin	Interconnected spheres	1000-2000
C-Starch	Interconnected spheres	300-1000
Pentoses		
C-Furfural	Dispersed spheres	500-3000
C-Xylose	Dispersed spheres	100-1000

### Polysaccharide-derived carbons

SEM micrographs of carbon materials from disaccharides (maltose, sucrose) and polysaccharides (amylopectin, starch) are depicted in Figure 3. C-maltose and C-sucrose are composed of interconnected particles, in coexistence with domains (larger in C-maltose) where aggregation occurs. Differences in morphology and size are summarized in Table 1: C-maltose is composed of a larger number of small (200-500 nm) particles in coexistence with larger spheres (2 μm). On the contrary, C-sucrose is composed of spherical particles whose size vary between 700 nm and 2 μm. Strong similarities are found for C-maltose and C-glucose materials, both characterized by isolated large spherical particles within a large matrix of interconnected small particles with ill-defined shape. Polysaccharides including amylopectin and starch, whose SEM images (Figure 1) show interconnected spherical particles ranging from 700 nm to 2 μm, provide very similar dispersion patterns despite their low solubility in water at room temperature.

When one compares SEM structures of final carbons to original saccharides (examples from pure glucose, xylose, amylopectin and starch powders are provided in Figure 4), it is self-evident the destructuring process which took place during carbonization and transformed the original disordered bulky materials into micrometer-sized particles and/or spheres. Chemical composition largely changed during hydrothermal process, as well: saccharides turn into dark brown or black powders with a carbon content increasing from original 40w% to 64-70w% (Table 2); meanwhile, oxygen presence is reduced from 53w%, as found in, e.g., glucose, to 27-30w% for carbon powders.

<sup>13</sup>C solid-state NMR (Figure 2) spectra from *C*-maltose, *C*-sucrose, *C*-amylopectin and *C*-starch show exactly the same characteristics already observed for *C*-glucose and *C*-HMF. The materials can be considered as chemically equivalent, in good agreement with the elemental analysis shown in Table 2, where the carbon content for all hexose-based carbons is 64% ± 1%.

Figure 3 SEM images of samples *C*-sucrose, *C*-maltose, *C*-starch and *C*-amylopectin

Figure 4 SEM images of pure glucose, xylose, amylopectin and starch solid powders

Table 2 Elemental analysis of carbon materials

Sample	Elemental analysis		
	C w%	H w%	O w%*
Hexoses			
<i>C</i> -Glucose	64.47	4.69	30.85
<i>C</i> -HMF	65.63	4.15	30.22
<i>C</i> -Maltose	64.70	4.54	30.76
<i>C</i> -Sucrose	64.15	4.77	31.09
<i>C</i> -Amylopectin	65.76	4.56	29.69
<i>C</i> -Starch	64.47	4.57	30.97
Pentoses			
<i>C</i> -Xylose	68.58	4.11	27.31
<i>C</i> -Furfural	68.60	3.90	27.50

### Mechanistic considerations

As we pointed out earlier in the discussion, it is generally assumed that dehydration of pentoses and hexoses leads to the formation of furfural and HMF as a first and main dehydration product. Our experiments strongly suggest that these furans are also the reacting species for carbon material. In fact, the morphologies and chemical structures of carbons obtained from saccharides are directly related to those of carbons obtained from pure furans according to the following parallelism: *C*-hexoses ~ *C*-HMF and *C*-pentoses ~ *C*-furfural. Additionally, intermediate molecules derived from saccharide dehydration (levulinic acid, dihydroxyacetone, formic acid, acetic acid, formaldehyde, pyruvaldehyde, etc...) coexist with furans they can be probably be responsible for particle size, powder texture and aggregation discrepancies. The striking similarities of NMR fingerprint spectra between all hexose-based carbons and *C*-HMF, or between *C*-xylose and *C*-furfural clearly prove that chemical complexity, the usual problem of raw biomass as an educt for materials chemistry, is indeed essentially resolved throughout hydrothermal carbonization by driving all saccharides only through two main reaction pathways: from sugar to furan-based (furfural or HMF) intermediate and from the furan to carbon. This is supported by GC-MS analysis (figure 1, supplementary

material information) of the side products in the remaining product waters, where in all cases the nature and amount of the unreacted by-products is very similar for the hexoses, e.g. *C*-glucose and *C*-HMF, and pentoses, *C*-xylose and *C*-furfural. These side-product molecules mainly come either from the dehydration of carbohydrates or from the rehydration of the furans, plus the hydrolytic splitting of those intermediates. Table 3 shows the normalized integrated intensity of HMF, furfural and 4-oxo-pentanoic acid detected by GC in the final liquors of the indicated final materials as well as for pure furfural and HMF solutions at three different concentrations, used as reference for quantification. Errors are estimated to 10% of the indicated values and account for possible discrepancies in manual simulation of each GC peak. When only monosaccharides and furans values are compared, one observes that: 1) carbonization process from glucose seems slightly more efficient if compared to xylose one, since HMF concentration in solution for *C*-glucose after reaction is less than half with respect to remaining furfural concentration from *C*-xylose; additionally, the amount of final carbon powder from glucose is about 1.5 times higher than carbon obtained from xylose. This is probably not a big surprise as it is known from furan chemistry that furfural, the dehydration product of xylose, is a low reactive compound due to the joint stabilizing effects of furan aromatic ring and carbonyl function<sup>20</sup> with respect to polycondensation. On the other hand, even if general knowledge about the reactivity of HMF itself is smaller, its molecular similarity to furfuryl alcohol, a widely studied and highly reactive modified furan<sup>20</sup>, may justify its higher reactivity. 2) The reaction seems to be less efficient when starting from pure furans rather than from carbohydrates, especially when pure furfural is employed (concentration in solution after reaction is around 5 w%). As pointed out earlier, reactivity of furfural is low and extremely condition dependent. In general, addition of proper co-monomers, like furfuryl alcohol, increase its reactivity<sup>20</sup>. Consequently, the heterogeneous medium composed of furans and dehydrated forms of saccharides (when sugars are used instead of pure HMF and furfural) may be highly favourable to the overall efficiency of the carbon-formation process. Reaction between HMF and de-hydrated glucose was recently used to obtain liquid alkanes<sup>34</sup>. 3) The higher the HMF content, the lower the 4-oxo-pentanoic acid content (also known as levulinic acid, it is a common side product of hexose dehydration, and it is expected to increase with decreasing hexose concentration<sup>25</sup>), indicating the competition of monomolecular decomposition reactions and the (at least) bimolecular carbonization reaction which is obviously promoted at higher concentrations.

Chemical reactions in the presence of a di- or polysaccharide do follow the same path, that is, dehydration of hexose units and formation of HMF, which then turns into hydrothermal carbon. As shown in Table 3, HMF residues do not exceed the 0.4 w%, and the actual values for *C*-maltose (0.14 w%) and *C*-sucrose (0.19 w%) are almost as low as those registered for glucose (0.12 w%). In the case of *C*-amylopectin and *C*-starch, residual HMF increases, respectively, to 0.26 w% and 0.37 w%. The slightly higher values are attributed to a

delayed dehydration kinetics due to the required hydrolysis of the macromolecular structure towards the monosaccharides.

An additional aspect which constitutes a difference between hexoses and pentoses is the colloidal structure of the carbon powders: nicely dispersed, separated spherical particles are always found for *C*-xylose and *C*-furfural. Explanation for this may probably come from the limited water solubility of furfural (< 8.5 m/v%), which tends to emulsify in solution, and carbonization may only take place inside droplets. The intense peak at 129 ppm observed for these materials, typical for aromatic C=C sites, is most presumably indicative for a higher degree of self reaction between furfural molecules within the droplets via the unprotected, highly reactive, 5-position<sup>20</sup>.

Table 3 Relative integrated peak areas from GC-MS experiments and w% concentration for residual HMF and furfural compounds.<sup>1</sup>

Sample (solution)	<sup>13</sup> Oxopentanoic acid	HMF	HMF w%	Furfural	Furfural w%
Hexoses					
Pure HMF solution		0.20	0.50		
		0.50	1.00		
		1.00	2.00		
<i>C</i> -Glucose	0.12	0.01	0.12		
<i>C</i> -HMF	0.05	0.43	0.91		
<i>C</i> -Maltose	0.11	0.02	0.14		
<i>C</i> -Sucrose	1.00	0.05	0.19		
<i>C</i> -Amylopectin	0.66	0.09	0.26		
<i>C</i> -Starch	0.54	0.15	0.37		
Pentoses					
Pure furfural solution				0.31	0.50
				0.52	1.00
				1.00	2.00
<i>C</i> -Furfural				2.42	5.08
<i>C</i> -Xylose				0.21	0.29

On the contrary, <sup>13</sup>C solid state NMR spectra and elemental analysis data for *C*-hexoses and *C*-HMF are remarkably similar, thus indicating that the system most presumably has to pass the same reaction pathway via the hydroxymethylfurfural stage and before carbonization can take place. In addition, interconnected spherical particle networks are generally observed, especially for low-weight sugars-derived carbons. These results may appear in contrast with previous experiments, where relatively well separated particles from mono- and polysaccharides (glucose, starch or rice) under similar conditions were obtained<sup>35,36</sup>. Nevertheless, those experiments were lead in presence of metal salts (Fe(II), Co(II), Cu(II), etc..) or metal nanoparticles

<sup>1</sup> Experiments were performed on remaining liquor solutions of indicated samples after 24h of hydrothermal treatment synthesis of indicated carbon materials. On the contrary, pure HMF and furfural solution were freshly prepared for comparison purposes. Residual solution w% values for HMF and furfural are calculated after a linear fit of recorded values for pure solutions. Errors, coming from integration procedure, are estimated to be ± 10% of indicated concentration values.

(Fe<sub>2</sub>O<sub>3</sub>), which can act as external nucleators and stabilizers<sup>37</sup>. Since our experiments used pure sugar solutions, emulsion polymerization occurs in absence of a stabilizer; hence, the dispersed spherical particles formed from pentoses should depend only on the hydrophobic character of furfural.

An important question may arise. Is hydrothermal carbon just a polymerization product of HMF and furfural? At the moment, a clear-cut answer cannot be provided but an insight on polyfurans generally reveal the existence of cross-linked polymers which may appear as black and glassy materials<sup>20</sup> according to the polymerization mechanism and type of added co-monomers. Unfortunately, the number of examples provided in ref. 20 and references therein show that the chemistry of furans is very large and many possible reaction ways can simultaneously occur especially in an heterogenous system like the one where hydrothermal carbon is obtained. Hydrothermal carbon is on the contrary a rather low-dense, dark brown powder which is not soluble in common solvents. So, even if during hydrothermal carbonization furfural and HMF are most likely the main reactive species, we cannot depict neither the exact reaction mechanisms nor the clear final structure, yet. This last point will be dealt with in a further communication by mean of highly advanced solid state NMR techniques<sup>21</sup>.

Finally, the fact that no substantial difference exist between all hydrothermal hexose carbons also shows that glucose can be safely used as a model molecule for the understanding of the formation of these materials<sup>21</sup>. Scheme 5 makes a summary of the main results of this communication, indicating that all hexoses (including their dehydration product, HMF) lead to the same type of material, called for convenience carbon- $\alpha$ , while pentoses lead to a different type of carbon, called arbitrarily carbon- $\beta$ .

Figure 5 – Reaction pathways encountered in the formation of hydrothermal carbons from hexose and pentose sources and leading to the differently structured and shaped materials.

## Conclusions

In this work, we compared hydrothermal carbons synthesized from diverse biomass (glucose, xylose, maltose, sucrose, amylopectin, starch) and biomass derivatives (HMF and furfural) under hydrothermal conditions at 180°C with respect to their chemical and morphological structures. SEM, <sup>13</sup>C solid state NMR and elemental analysis on final powders combined to GC-MS experiments on residual liquor solutions were the main tools which allowed us demonstrate that all sugars in their hexose form, no matter their complexity, degradate into hydroxymethyl furfural, which finally condenses to a carbon-like material having morphological similarities and the same chemical and structural composition. On the contrary, all sugars in their pentose form dehydrate into furfural, which in turn react to provide very similar carbon materials as obtained from pure furfural. <sup>13</sup>C solid state NMR show that the local structure of these two families

of carbons, from hexoses and pentoses, are relatively different.

Contrary to simple expectations, starting from more complex biomass instead of clean sugars does not harm the outcome of the hydrothermal carbonization reaction, and remarkable similarities between the products of homologous series do occur, both with respect to morphology and local structural connectivity. This is a positive outcome concerning the green chemistry aspects of this process, as even complex waste biomass can be used without too much influence on the final carbonized structure: biological diversity is simply reduced by the elemental steps of the carbonization reaction. This study paves the way to the use of complex biomass as renewable source for carbon materials.

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## Notes and References

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† Electronic Supplementary Information (ESI) available: Figure 1. GC experiments of residual liquors from C-glucose, C-HMF, C-xylose and C-furfural. See DOI: 10.1039/b000000x/

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