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**Title:** Fast pyrolysis of hot-water-extracted and soda-AQ-delignified okra (*Abelmoschus esculentus*) and miscanthus (*miscanthus x giganteus*) stalks by Py-GC/MS

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### Pyrolytic behavior of lignocellulosics-based polysaccharides

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#### Abstract

The thermochemical behavior of cellulose, glucomannan, and xylan was investigated by pyrolysis-gas chromatography-mass spectrometry (Py-GC/MS). In each case, major GC-amenable condensable products were classified into several compound groups, and the formation of these monomer-related fragments from the model substance samples was determined at 500, 600, and 700 °C with a residence time of 5 s and 20 s. The results revealed that despite some general formation trends, no compound group was selectively formed at certain temperatures. Of the 11 product groups, the primary ones, including lactone, furan, and cyclopentenone derivatives, accounted for 72-85% (from cellulose), 86-90% (from glucomannan), and 76-81% (from xylan) of the total amount of pyrolysis products determined. At 500 °C, about half of the major product groups accounted for lactones, such as 3-hydroxy-2-penteno-1,5-lactone and 5H-furan-2-one. It was also confirmed by thermogravimetric analyses that within the temperature range studied, cellulose was thermally more stable than the heterogeneous hemicelluloses. These kinds of data are of importance, for example, with respect to efforts to develop new biorefinery possibilities for renewable resources.

28 *Keywords:* Cellulose, Glucomannan, Xylan, Pyrolysis-gas chromatography, Condensable products,  
29 Thermogravimetry

30

### 31 **1. Introduction**

32 The biorefinery concept can be defined merely as a process for fractionating and/or converting into energy  
33 carbon dioxide-neutral feedstock (biomass) as well as a great variety of chemicals and other biomaterials in an  
34 ecosystem-friendly way through advanced technologies [1,2]. The pulp industry, as an essential branch of global  
35 industry, is based on vast and multidisciplinary technology. For example, a modern chemical pulp mill that employs  
36 one fibrous feedstock is capable of manufacturing, besides pulp, several pulping by-products, and it can be  
37 considered a rather sophisticated biorefinery. It is also known that the integration of a hot-water-extraction pre-  
38 treatment stage prior to alkaline pulping may offer a feasible possibility, mainly to recover the dissolved  
39 carbohydrates-derived material for further utilization by biochemical and chemical technologies [3]. This concept of  
40 an integrated forest biorefinery has been investigated under a variety of conditions and from several points of view.

41 In our earlier papers, we used pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) for revealing the  
42 thermochemical behavior of silver birch [4] and Norway spruce [5] sawdust, as well as non-wood materials, such as  
43 okra and miscanthus [6]. In all cases, the effects of pyrolysis conditions on the product distribution were studied. All  
44 the materials were investigated as such and after hot-water extraction together with the pulps obtained from these  
45 feedstocks by sulfur-free delignification. In each case, major GC-amenable condensable products were determined  
46 and classified into several compound groups, characteristically originated from the main structural constituents  
47 (cellulose, hemicelluloses, and lignin) of the raw materials. Additionally, the suitability of this analytical pyrolysis  
48 method under varying conditions was investigated as a rapid tool for roughly detecting chemical changes that were  
49 taking place in the feedstocks during the different treatments performed.

50 Thermal analysis can be defined as a set of techniques used to describe the physical or chemical changes  
51 associated with substances as a function of temperature [7]. The thermal behavior of lignocellulosic materials and  
52 their components can be studied in many alternative ways. Py-GC/MS reveals the composition of products and  
53 indicates the mechanisms of degradation reactions; it also provides information about the original structure of the  
54 samples being studied. In general, many studies indicated that during pyrolysis under an inert atmosphere, biomass  
55 converts into low-degree-polymerized products [8-17]. However, there have still been less attention on pyrolysis of

56 glucomannan and xylan as well as their quantification analyses. The dissimilarities in pyrolysis behavior of the main  
57 components in lignocellulosic biomass are due to differences in their molecular structures and chemical natures.  
58 Therefore, the study of pyrolysis behavior of the main biomass substituents is essential to understand the overall  
59 pyrolysis behavior of biomass. In contrast, thermal gravimetric (TG) analysis (i.e., mass change vs. temperature) and  
60 differential scanning calorimetry (DSC) (i.e., heat flux vs. temperature) primarily give information concerning the  
61 mass loss of a sample over the whole process, the rate of mass loss, and the endothermic and exothermic  
62 temperature ranges upon heating. These methods are widely applied techniques, especially for the study of thermal  
63 stability of polymers. In practice, it is useful to record the first derivative of the TG curve (i.e., differential  
64 thermogravimetry (DTG)) for more clearly detecting small features/boulders as peaks on the curve. Particularly,  
65 successful approaches have also been the simultaneous combination of TG methods and spectroscopic techniques. In  
66 general, the mass loss of a sample of the TG curve under a certain heating rate and the peak height of the DTG curve  
67 are directly related to the temperature during the process and the reaction rate at the corresponding temperature,  
68 respectively. Therefore, investigation of samples by TG and DTG is also important due to fluctuations in available  
69 data [18-21].

70 The cellulose content is 40-45 % of the wood dry solids and this carbohydrate is a linear homopolysaccharide  
71 composed of  $\beta$ -D-glucopyranose moieties linked together by (1 $\rightarrow$ 4)-glycosidic bonds (degree of polymerization  
72 (DP) 10,000-15,000) [22]. Many degradation mechanisms with varying reaction kinetics of cellulose pyrolysis have  
73 been proposed under changing conditions [23-32]. In the generally accepted pyrolysis reactions on heating after  
74 gradual depolymerization, mainly by breaking of glycosidic linkages, a great variety of volatile products are  
75 simultaneously formed (the prominent primary example is levoglucosan (LG)). This occurs from the initial  
76 degradation reactions, including dehydration, rearrangement, and ring-opening of glucose units, followed by the  
77 formation of various unsaturated products from which a highly reactive char can be obtained by condensation.

78 Hemicelluloses (30-35 % of the wood dry solids) are linear low-molar-mass heteropolysaccharides with specific  
79 side-groups, and their thermal and chemical stability is generally lower than that of cellulose, presumably due to  
80 their lack of crystallinity and lower DP (100-200) [33,34]. Softwoods and hardwoods (and non-woods) differ not  
81 only in the content of total hemicelluloses but also in the percentages of individual hemicellulose constituents; in  
82 hardwoods and non-woods, primarily xylan (containing xylose units), and in softwoods, mainly glucomannan  
83 (containing mannose and glucose units). In hardwoods, the content of xylan and glucomannan is 20-30 % and <5 %

84 of the wood dry solids, respectively, whereas in softwoods, the corresponding contents are 5-10 % and 15-20 % of  
85 the dry wood solids [33]. The thermal degradation reactions of heteropolymeric hemicelluloses are principally  
86 similar to those of homopolymeric cellulose, although hemicelluloses reacted more readily than cellulose during  
87 heating [13,18,34-36]. The differences observed in the degradation rates of various polysaccharides can be explained  
88 as being primarily due to the different glycosidic bonds between sugar moieties as well as different DP and  
89 crystallinity of cellulose. Of the hemicelluloses, xylan is the least thermally stable because it is more susceptible  
90 than glucomannan to degradation of glycosidic bonds and dehydration reactions [37]. In general, the char formation  
91 from hemicellulose pyrolysis is slightly higher than that from cellulose [13,14,19,38].

92 Lignin is an amorphous polymer with a chemical structure that distinctly differs from the polysaccharide  
93 constituents of wood and non-wood biomass [33,39]. It is generally known that lignin decomposes over a wider  
94 temperature range compared to cellulose and hemicelluloses, which are less resistant to thermal degradation and  
95 rapidly degrade at lower temperatures over narrower temperature ranges [19,37,40]. Thus, the stability of lignin,  
96 cellulose, and hemicelluloses against heating increases in the order: hemicelluloses > cellulose > lignin.

97 A wide range of studies has been made for clarifying the pyrolysis characteristics of varying biomasses by  
98 different analytical and pilot-scale techniques [11,40-46]. Typically, it has been assumed that the pyrolysis behavior  
99 of biomass is almost the integration of its components (cellulose, hemicelluloses, and lignin) [13,23], although the  
100 cellulosic contribution normally predominates due to the larger proportion of cellulose in lignocellulosic materials.  
101 Hence, it can be observed that with the increasing amount of hemicelluloses in the sample mixture of xylan and  
102 microcrystalline cellulose, the maximum decomposition rate of hemicelluloses increases while that for cellulose  
103 declines [13]. Unlike the cellulose, the interaction between hemicelluloses and lignin is strong. The presence of  
104 hemicelluloses decreases the lignin decomposition temperature and the mass-loss rate, whereas the existence of  
105 lignin increases the decomposition rate of hemicelluloses.

106 In our earlier studies, we investigated the thermochemical behavior of differently-treated wood and non-wood  
107 materials [4-6]. In this comparable study with model substances, firstly, the aim was to further clarify the formation  
108 of compound groups under the same pyrolysis conditions as those applied in our previous experiments. Secondly, to  
109 verify the formation of main pyrolysis products with respect to their main carbohydrate constituents as well as the  
110 effect of the interaction of main carbohydrate constituents in hardwood, softwood, and non-wood on the pyrolysis  
111 products. Since carbohydrates are the main components of various biorefinery fractions, we selected for our Py-GC

112 and TG experiments cellulose and hemicelluloses (glucomannan and xylan) and the quantification analyses of GC-  
113 detectable pyrolysis products of these samples were reported. The thermochemical behavior of lignin as well as  
114 lignin-containing black liquors from alkaline delignification of wood and non-wood fibrous feedstocks will be  
115 separately investigated under the analogous conditions in the forthcoming studies.

116

## 117 **2. Experimental**

### 118 *2.1. Thermogravimetric analyses*

119 The slow pyrolysis of the selected biomass components was carried out with a Linseis STA PT1600 instrument.  
120 For each test, a sample size of 10-15 mg was used in an alumina crucible. A nitrogen flow of 200 ml min<sup>-1</sup> was used  
121 to create inert environment and to remove the released volatiles. For drying, the furnace temperature was raised from  
122 room temperature ( $\approx 20$  °C) to 105 °C at 20 °C min<sup>-1</sup> and maintained at that temperature for 30 min to complete the  
123 drying of the sample. Then, the TG run was continued with the same dried samples for pyrolysis. The pyrolysis  
124 temperature was selected as 700 °C. For pyrolysis, the sample temperature was raised from 105 °C to 700 °C at  
125 varied heating rates of 10, 15, and 20 °C min<sup>-1</sup> and maintained at that temperature for 40 min to ensure complete  
126 pyrolysis. The data generated through TG experiments were further processed with Microsoft Excel and Matlab®.

127

### 128 *2.2. Pyrolysis experiments*

129 The model substances were  $\alpha$ -cellulose (Sigma), glucomannan (MB Med. S. r. L.), and oat spelt xylan (Sigma).  
130 In each case, about 0.2 mg of model substances was pyrolyzed in a quartz tube (3.0 cm x 1.0 mm inner diameter)  
131 between quartz wool which was used to keep the solids inside the pyrolysis tube. First, a partly filled quartz tube  
132 with quartz wool was cleaned at 1000 °C to remove all adsorbed gases and vapors on the surface of the quartz tube.  
133 Then, fast pyrolysis of substances was conducted at a temperature of 500, 600, or 700 °C (heating rate 20 °C ms<sup>-1</sup>  
134 and heating times 5 and 20 s) using a CDS Pyroprobe 1000 heated filament pyrolyzer coupled to an HP 5890 II gas  
135 chromatograph (Py-GC, Hewlett Packard Company, Wilmington, NC, USA).

136 The GC conditions were the same as those applied earlier to the similar purpose [4]. The column was a ZB-  
137 35HT (Inferno) capillary GC column (30 m x 0.25 mm with a film thickness of 0.25  $\mu$ m). The GC oven temperature  
138 program in the analyses of pyrolysis products was as follows: 2 min at 40 °C, 4 °C min<sup>-1</sup> to 190 °C, 10 °C min<sup>-1</sup> to  
139 320 °C, and 10 min at 320 °C. Helium was used as the carrier gas with a gas flow rate of 1 ml min<sup>-1</sup> and as an inert

140 atmosphere in the pyrolysis interface. Detection was carried out with an HP 5970 mass spectrometric detector under  
141 electron ionization (70 eV) with 2.92 scan per seconds in the 30-550  $m/z$  interval.

142 Compounds were identified using the National Institute of Standards and Technology (NIST) mass spectral  
143 library. Quantitative analysis was conducted according to our previous study with a set of standard samples of  
144 known concentration based on duplicated injections [4]. To utilize this, standard solutions for the low concentration  
145 range of 0.05-1.0 mg mL<sup>-1</sup> and for the high concentration range of 1.0-8.0 mg mL<sup>-1</sup> were prepared, depending on the  
146 standard's chromatographic response (GC/MS). The conditions of the GC were set to those of the Py-GC/MS. To  
147 obtain the yields of GC-detectable products, a plot of instrument response (i.e., peak area, y-axis) vs. amount of  
148 standard solution ( $\mu$ g, x-axis) was performed. Therefore, the relative mass response of a target compound compared  
149 to the mass of the corresponding external standard was extracted from plot and the corresponding yield  
150 (supplementary S1-3) was calculated based on the initial sample. In addition, the quantification analyses are given in  
151 the supplementary data (S4).

152 Elemental analysis was performed with a CHNOS elemental analyzer GmbH (Vario EL III) to identify the  
153 content of carbon, hydrogen, nitrogen, and oxygen (Table 1). The tests were conducted in duplicates.

154

155 Table 1. Elemental analysis of cellulose, glucomannan, and xylan. Numbers in parentheses are calculated for “pure  
156 substances” without any possible side-groups.

Component	C	H	N	O <sup>a</sup>
Cellulose	43.25(44.45)	6.32(6.21)	- (-)	50.43(49.34)
Glucomannan	39.96(44.45)	6.35(6.21)	0.28(-)	53.41(49.34)
Xylan	41.57(45.46)	6.47(6.11)	- (-)	51.96(48.43)

157 <sup>a</sup> Calculated by difference.

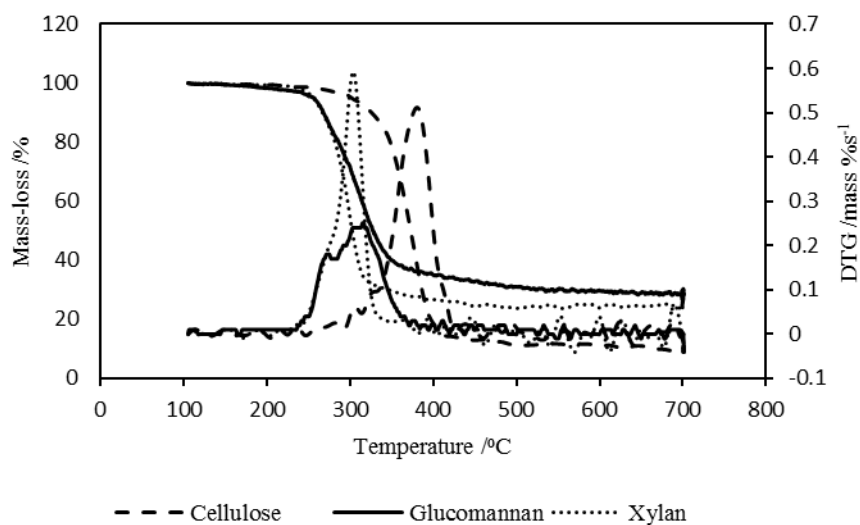
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### 159 3. Results and discussion

#### 160 3.1. Thermogravimetric considerations

161 The temperature at which decomposition reactions of wood occur and the changes in specimen mass associated with  
162 the reactions can be found by thermogravimetric analysis, which exactly recorded the mass loss of the solid sample  
163 versus temperature/time. Traditionally, the chemical kinetic models for the biomass and its components are  
164 proposed from the analysis of the different mass loss stages and validated through the correlation between the  
165 predicted data and the experimental mass loss curve. According to TG the mass loss of cellulose and hemicelluloses  
166 typically starts at about 100 °C (i.e., due to the loss of adsorbed water). At temperatures between 100 °C and 250 °C,  
167 the rate of mass loss is quite slow, but above 250 °C, it increases [19]. For example, cellulose undergoes an

168 extensive endothermic-exothermic sequence immediately above 300 °C [20,47], and it has been reported that for  
 169 xylan, displaying clear exothermic behavior [48], the most intensive thermal degradation takes place in the  
 170 temperature range 200-260 °C [19,49].  
 171 Figure 1 shows TG and DTG curves of cellulose, glucomannan, and xylan. The average active pyrolysis ranges of  
 172 290-410 °C and 230-340 °C were observed for cellulose and hemicelluloses, respectively. The higher thermal  
 173 stability of cellulose (glucan-based polysaccharide), compared to amorphous hemicelluloses with several types of  
 174 glycosidic bonds and side groups, was mainly attributed to its unbranched and ordered (i.e., highly crystalline)  
 175 structure [1,41,19,21,50]. Among the hemicelluloses, xylan had lower thermal stability than glucomannan. The  
 176 pyrolysis char yield determined was 9, 27, and 25 % of the initial mass for cellulose, glucomannan, and xylan,  
 177 respectively. This finding agreed well with the earlier data [19,51] and suggested more multiple reactions of  
 178 heterogeneous hemicelluloses and their monosaccharide moieties. According to [51], the differences in the char  
 179 yield between cellulose and hemicelluloses are clearly due to the somewhat different pyrolysis reaction mechanisms.  
 180 The DTG peak heights ( $\text{wt}\% \text{ s}^{-1}$ ) were as follows: cellulose 0.48 at 382 °C, glucomannan 0.25 at 316 °C, and xylan  
 181 0.57 at 304 °C.



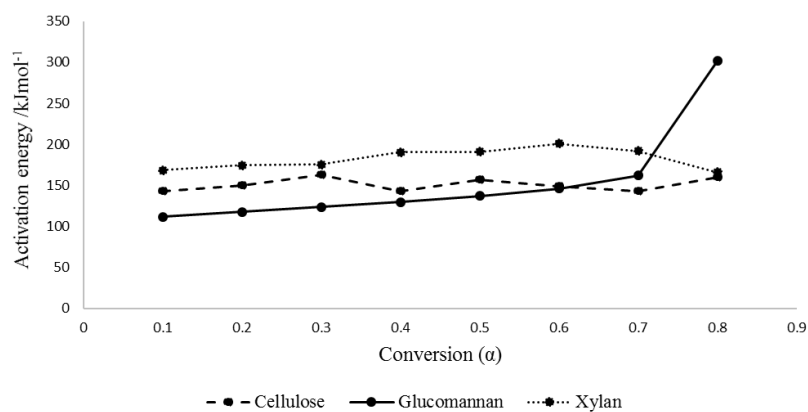
182 --- Cellulose      — Glucomannan      ..... Xylan  
 183 **Fig. 1.** TG and DTG curves of cellulose, glucomannan, and xylan at 20 °Cmin<sup>-1</sup>.

184  
 185 The calculated based on the Flynn-Wall-Ozawa method [52] activation energy ( $E_a$ ) value as a function of fractional  
 186 conversion ( $\alpha$ ) for cellulose, glucomannan, and xylan is presented in Fig. 2. It could be noted that the variation in  $E_a$   
 187 was slightly lower for cellulose ( $142\text{-}162 \text{ KJ mol}^{-1}$ ) than for glucomannan and xylan. In the literature, depending on



188 the sample origin, a variety of  $E_a$  values for cellulose have been given; for example, an average value of 109.4 KJ  
 189  $\text{mol}^{-1}$  [50]. The  $E_a$  value for glucomannan varied between 111 and 301 KJ  $\text{mol}^{-1}$ , and it gradually increased in the  
 190 progress of pyrolysis. However, at the end of pyrolysis ( $\alpha > 0.7$ ), a rapid rise (i.e., from 160 to 300 KJ  $\text{mol}^{-1}$ ) was  
 191 observed. This phenomenon has also been reported earlier by [53]. They also reported the  $E_a$  values between 181  
 192 and 206 KJ  $\text{mol}^{-1}$  for glucomannan in the  $\alpha$  range 0.1-0.75. In the case of xylan, the  $E_a$  value (168-200 KJ  $\text{mol}^{-1}$ )  
 193 increased until  $\alpha = 0.6$ , and, after this point, it started to decrease. In the previous study [54], the  $E_a$  values for xylan  
 194 were between 150 and 250 KJ  $\text{mol}^{-1}$  in the temperature range 185-215 °C.

195



196

197 **Fig. 2.** Activation energy ( $E_a$ ) as a function of fractional conversion ( $\alpha$ ) for cellulose, glucomannan, and xylan.

198

199 It has been reported [55] that the significant variation in the  $E_a$  value with respect to  $\alpha$  indicates a multi-step reaction  
 200 mechanism. Practically, the present data suggested that cellulose degradation during pyrolysis proceeded via  
 201 reasonably simple and straightforward mechanisms without any significant secondary reactions. In contrast, it could  
 202 be concluded that, due to greater variation in the  $E_a$  values for hemicelluloses, their degradation during pyrolysis  
 203 took place by somewhat more complicated reaction mechanisms as already indicated by the high-char yields. The  
 204 thermal degradation of the polysaccharides studied occurred by versatile parallel reaction paths that were not  
 205 characteristically specific for certain temperature ranges. Hence, with this respect, TG, without any definite  
 206 detention possibilities, could not suggest distinct differences in their thermochemical degradation behavior.

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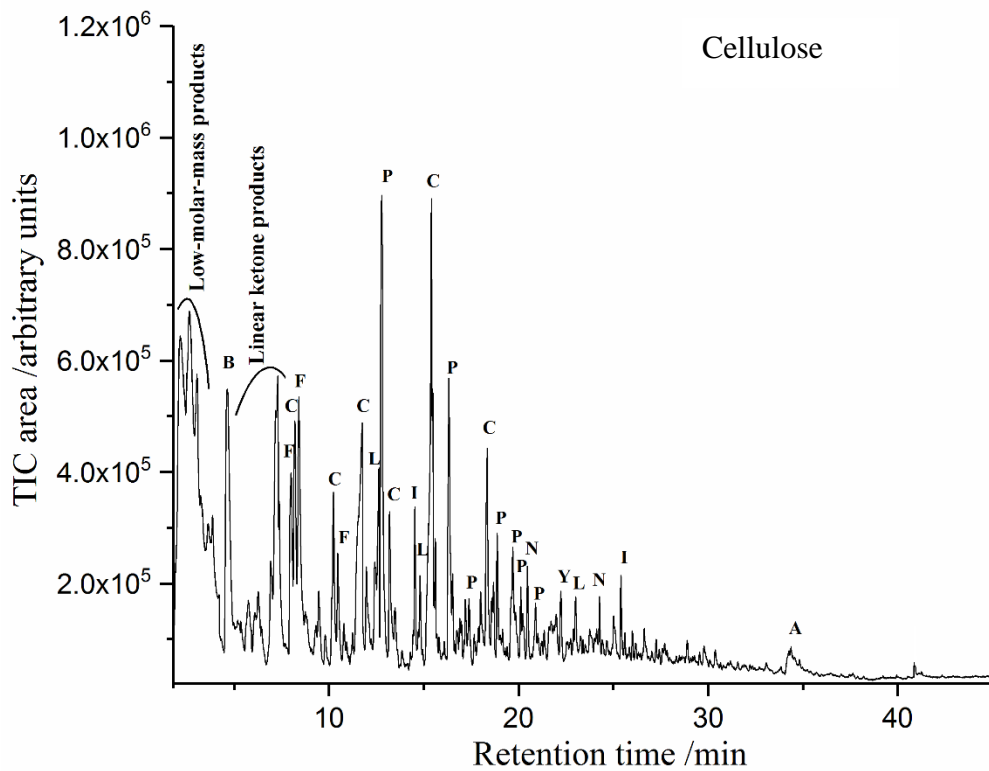
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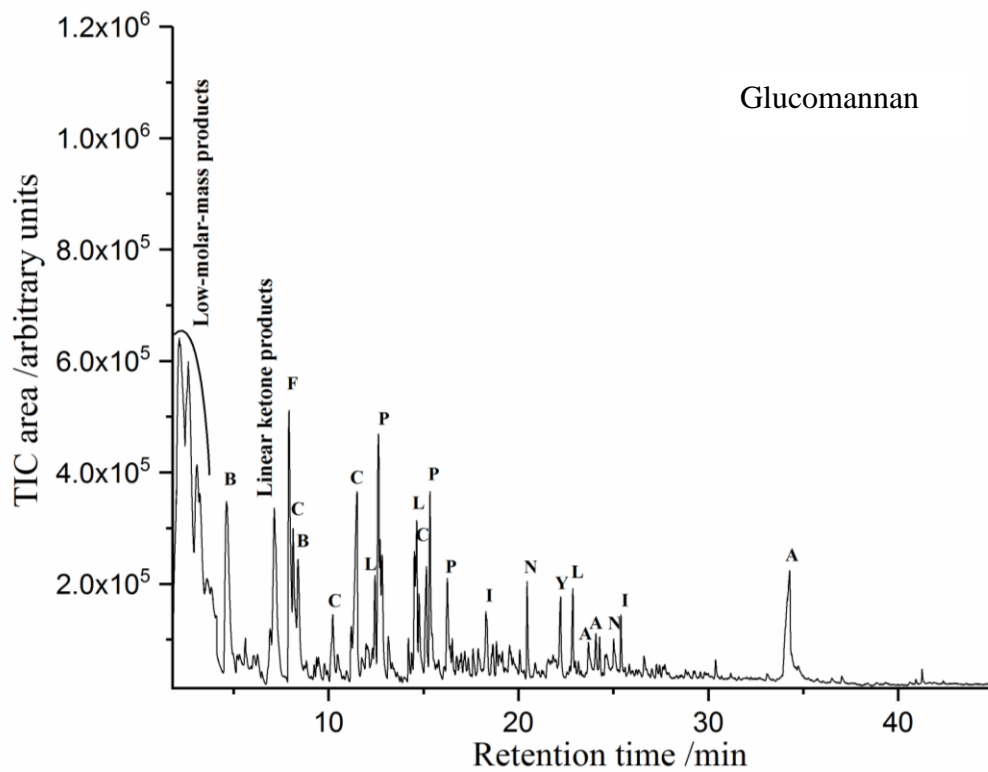
### 210 3.2. Pyrolysis – gas chromatographic analyses

211 The integrated chromatographic system GC/MS applied resolved most of the low-molar-mass compounds  
212 released from the model substances during pyrolysis; altogether, 42 from cellulose, 47 from glucomannan, and 41  
213 from xylan were identified in conformity with pure compounds and MS library. For simplicity, the dominant GC-  
214 amenable pyrolysis products were classified into illustrative compound groups by the same system as that used  
215 earlier for similar purposes [4,5]. It could be roughly concluded that the groups of anhydrosugar (A),  
216 cyclopentenone (C), furan (F), indene (I), lactone (L), and pyrone (Y) derivatives originated from carbohydrates,  
217 and those of guaiacol (G) and phenol (P) derivatives originated from lignin. The characteristic groups of naphthalene  
218 (N) derivatives were obtained from extractives, whereas the groups of other aromatics, benzene (B) and linear  
219 ketones (LK) derivatives, were probably formed from all the model substances; examples of a typical pyrogram  
220 profile at 700 °C and 20 s, for each sample are presented in Fig. 3 and the main compounds identified are listed in  
221 Table 2. Practically, pyrolysis experiments under the same conditions also led to reproducible results with  
222 reasonable accuracy. During the pyrolysis, a wide range of components have been detected and the mechanisms of  
223 the formation of several major products in this study are considered similar to those reported by Wang et al. [13]. It  
224 was assumed that principally, the formation of each compound group occurs via characteristic mechanisms and  
225 pathways. In the case of cellulose pyrolysis [15], ring-opening of glucopyranose units takes place to form open-  
226 chain structures, followed by dehydration and cyclization to generate 5-(hydroxymethyl)furfural (5-HMF), which  
227 further converts through the elimination of the hydroxymethyl group to produce furfural, and LG is produced by the  
228 cleavage of the  $\beta$ -(1  $\rightarrow$  4)-glycosidic linkage in the cellulose macromolecules, followed by an intramolecular  
229 rearrangement. In the case of xylan pyrolysis Shen et al. [36] and Patwardhan et al. [51] have reported that the  
230 depolymerization and ring scission of xylan form ring-opened intermediates, which further produce linear ketone  
231 products, such as hydroxyacetone (via carbon chain fracture), furfural and lactones (by cyclization), and alicyclic  
232 ketones, such as cyclopentenones through the combination of C=C bonds. The degradation of glycosidic linkages  
233 between monomer units of glucomannan results in anhydrosugars and more stable furan rings (such as 5-HMF, 5-  
234 MF, and furfural) [14, 53].

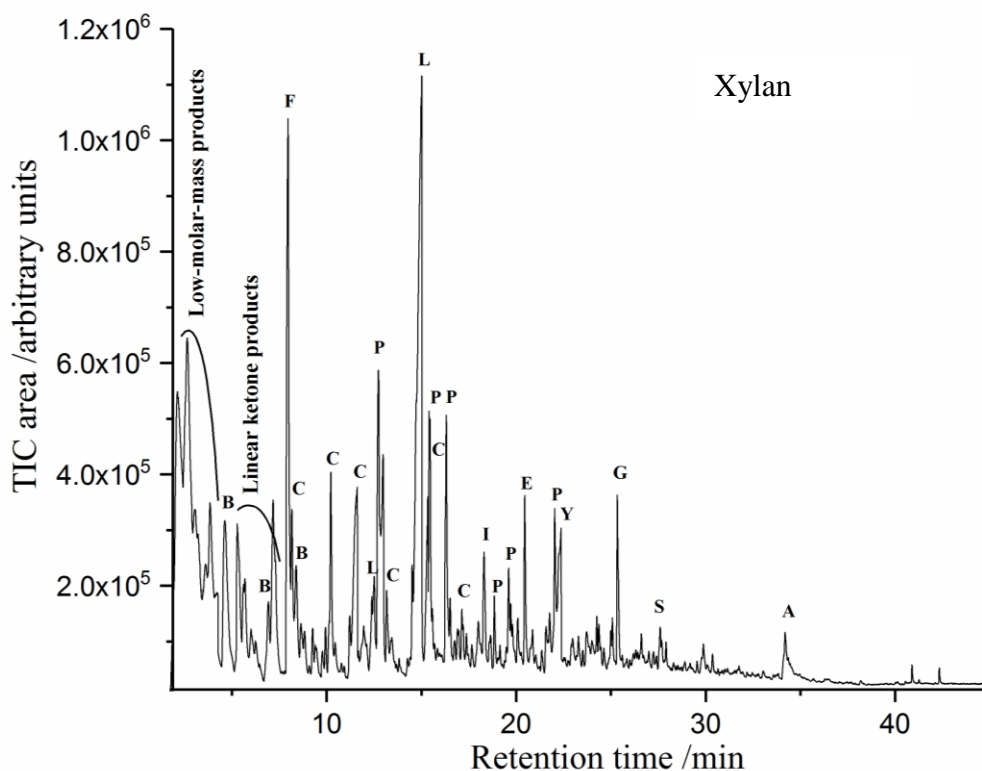
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239 **Fig. 3.** The main products formed in the pyrolysis experiments (700 °C and 20 s) with cellulose, glucomannan, and  
 240 xylan. Letters indicate compound groups to which identified products belong: A (anhydrosugar derivatives), B  
 241 (benzene derivatives), C (cyclopentenone derivatives), E (catechol derivatives), F (furan derivatives), G (guaiacol  
 242 derivatives), I (indene derivatives), L (lactone derivatives), LK (linear ketone derivatives), P (phenol derivatives), S  
 243 (syringyl derivatives), and Y (pyrone derivatives).  
 244

245 Table 2. The main products formed in the pyrolysis experiments with model substances.<sup>a</sup>

Product	RT <sup>b</sup> /min	Cellulose	Glucomannan	Xylan	Group symbol
Anhydrosugars					A
1,4:3,6-Dianhydro- $\alpha$ -D-glucofuranose	24.0	+	-	-	
2,3-Anhydro-D-mannosae	24.2	+	-	-	
1,6-Anhydro- $\beta$ -D-glucofuranose (levoglucosan) <sup>c</sup>	34.5	+	+	+	
Benzene derivatives					B
Toluene <sup>c</sup>	4.6	+	+	+	
Cyclopentenone derivatives					C
Cyclopent-2-en-1-one <sup>c</sup>	8.3	+	+	+	
2-Methylcyclopent-2-en-1-one <sup>c</sup>	10.3	-	+	+	
2-Cyclopentene-1,4-dione	11.2	+	-	+	
2-Hydroxycyclopent-2-en-1-one	11.8	+	+	+	
3-Methylcyclopentane-1,2-dione <sup>c</sup>	15.4	+	+	+	
Catechol derivatives					E
2,3-Dihydroxybenzaldehyde	20.5	+	+	+	
Furan derivatives					F
Furfural (furan-2-carbaldehyde) <sup>c</sup>	8.0	+	+	+	
5-Methylfurfural <sup>c</sup>	12.8	+	+	-	
2,5-Furandicarboxaldehyde <sup>c</sup>	19.1	+	-	-	

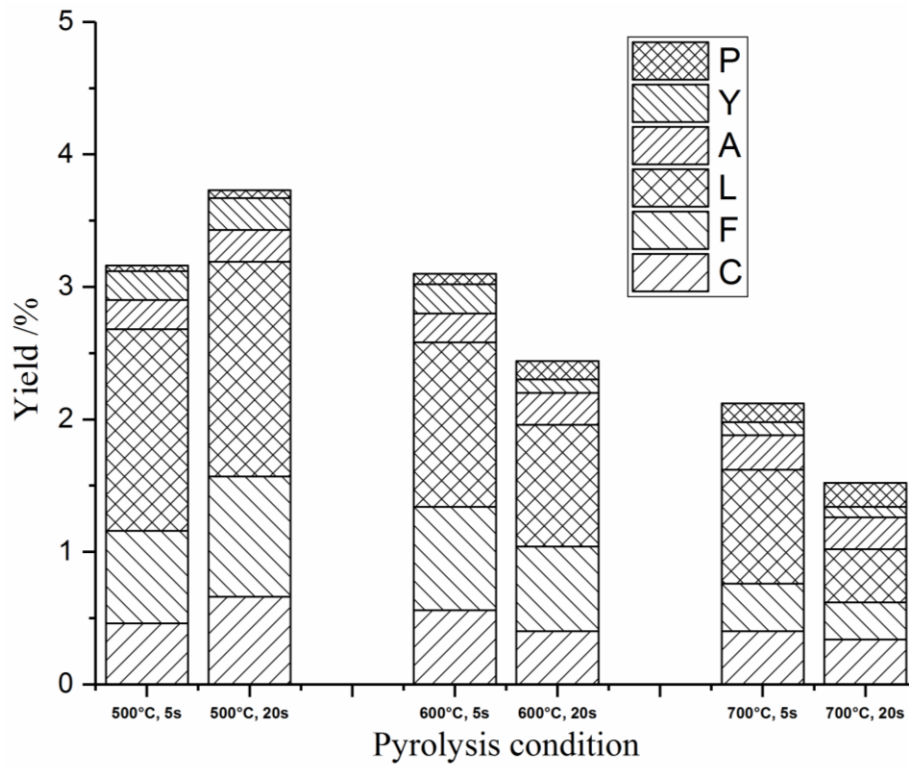
5-(Hydroxymethyl)furfural <sup>c</sup>	24.7	+	-	-	
Guaiacol derivatives					G
2-Methoxyphenol (guaiacol) <sup>c</sup>	17.2	-	-	+	
2-Methoxy-4-methylphenol <sup>c</sup>	20.7	-	-	+	
Lactone derivatives					L
5 <i>H</i> -Furan-2-one	12.7	+	+	+	
3-Hydroxy-2-penteno-1,5-lactone	15.0	+	-	+	
4-Hydroxy-2,5-dimethylfuran-3-one <sup>c</sup>	17.8	+	-	+	
1-Hydroxy-3,6-dioxabicyclo[3.2.1]octan-2-one	23.2	+	+	-	
Linear ketone derivatives					LK
Methyl acrylate	5.3	-	-	+	
1-Hydroxy-2-butanone	5.7	+	-	+	
2-Methylbut-2-enal	6.4	+	+	-	
Valeraldehyde	7.3	+	+	-	
Phenol derivatives					P
Phenol <sup>c</sup>	12.9	+	+	+	
2-Methylphenol <sup>c</sup>	15.5	+	+	+	
4-Methylphenol <sup>c</sup>	16.4	+	+	+	
2,4-Dimethylphenol	18.9	+	+	+	
4-Ethenylphenol	22.1	-	-	+	
Syringol derivatives					S
2,6-Dimethoxyphenol (syringol) <sup>c</sup>	27.6	-	-	+	
Pyrone derivatives					Y
Pyran-2-one	14.5	+	-	-	
3-Hydroxy-2-methylpyran-4-one <sup>c</sup>	19.3	+	-	-	
Dihydro-6-methyl-2 <i>H</i> -pyran-3(4 <i>H</i> )-one	22.4	+	+	+	

246 <sup>a</sup> + Indicates the presence of this compound.

247 <sup>b</sup> RT refers to retention time.

248 <sup>c</sup> Confirmed by pure standards.

249 Most of these pyrolysis products have been detected earlier in related studies after pyrolysis of polysaccharides-  
250 containing samples or polysaccharides, although in different proportions [4–6,14-17,23,29,51,56-58,60]. In our  
251 previous pyrolysis studies with birch wood [4] and spruce wood [5] as well as okra and miscanthus [6], there were  
252 several pyrolysis products, such as guaiacol, syringyl, naphthalene, and fatty acid derivatives, that originated from  
253 lignin and extractives. However, in this back up study, guaiacol and syringyl derivatives were detected only for  
254 xylan, indicating that the xylan preparation used contained some minor guaiacyl-syringyl-type lignin impurities. As  
255 a typical trend, in each case, the yield of GC-detectable pyrolysis products decreased steadily toward harsher  
256 pyrolysis conditions enhancing the formation of char and volatiles. Hence, the pyrolysis temperature should be  
257 shortened to maximize the yield of pyrolysis products (Figs. 4-6). All the compound groups with different relative  
258 formation rates were detected within the temperature range studied (500 °C, 600 °C, and 700 °C), except  
259 anhydrosugar derivatives (mainly LG and levoglucosanone), which were prominently obtained only from cellulose.  
260

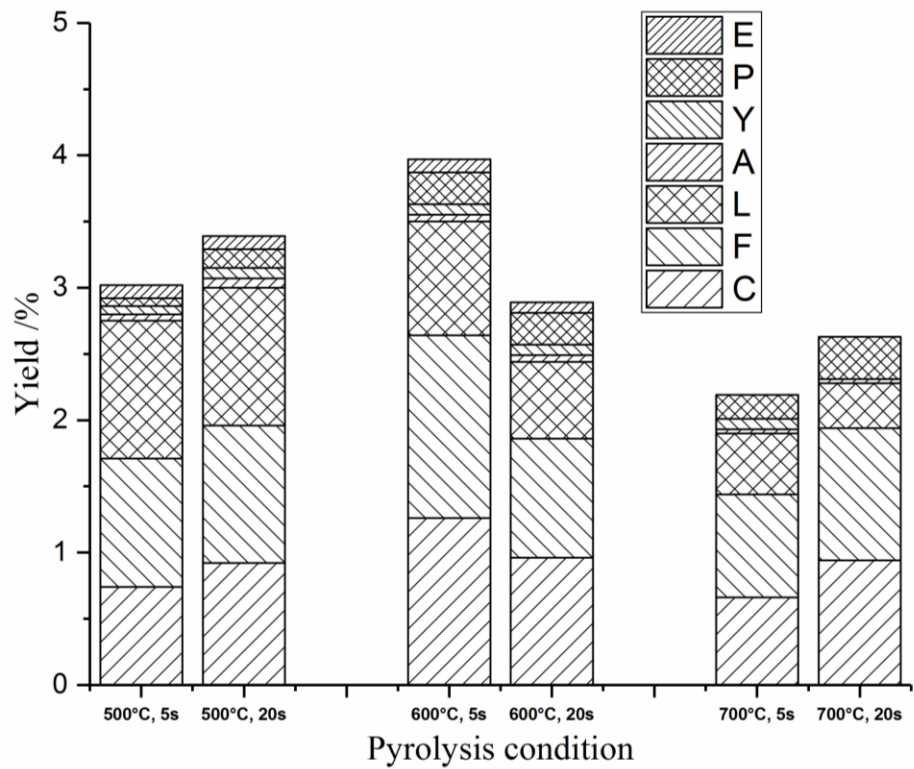


261

262 **Fig. 4.** Effects of pyrolysis temperature and residence time on yields of main product groups from cellulose. For the  
 263 letter symbols, see Fig. 3.

264

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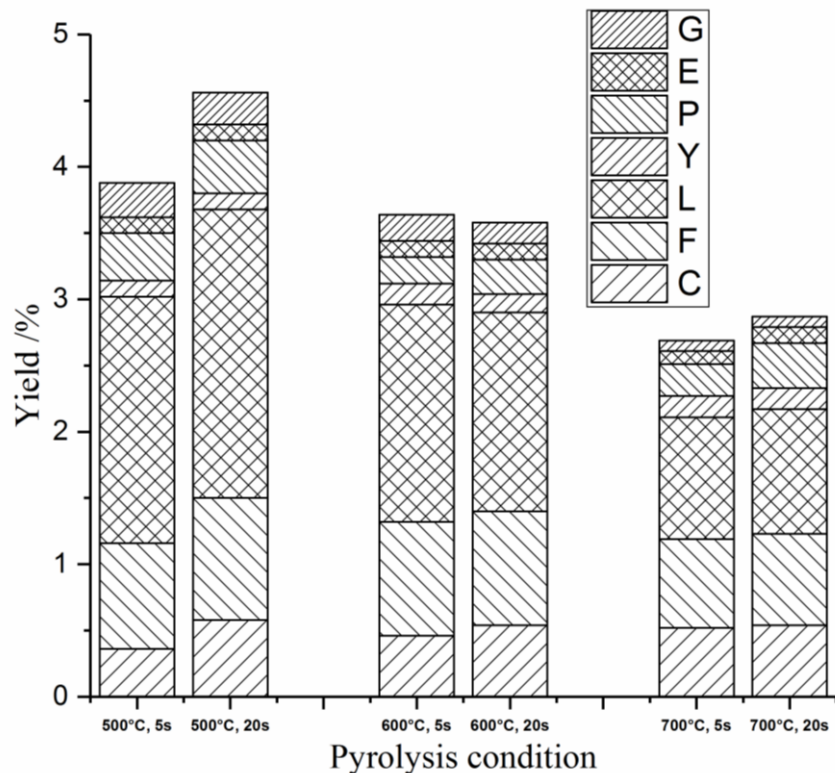


266

267 **Fig. 5.** Effects of pyrolysis temperature and residence time on yields of main product groups from glucomannan. For  
 268 the letter symbols, see Fig. 3.

269

270



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272 **Fig. 6.** Effects of pyrolysis temperature and residence time on yields of main product groups from xylan. For the  
 273 letter symbols, see Fig. 3.

274

275 Figure 7 shows the formation examples of the selected main pyrolysis products from model substances and their

276 formation decreased at the longer holding time (20 s) and the higher reaction temperature (700 °C). It could be noted

277 that, for example, 3-hydroxy-2-penteno-1,5-lactone (lactone) was primarily formed from xylan (also partly from

278 cellulose), 5H-furan-2-one (lactone) from glucomannan (also partly from cellulose), 3-methylcyclopentane-1,2-

279 dione (cyclopentenone) from glucomannan, furfural (furan) from cellulose and xylan, and 5-HMF (furan) from

280 cellulose. Based on the our previous studies [4-6], of these major pyrolysis products, especially 3-hydroxy-2-

281 penteno-1,5-lactone was produced by a factor of three from hardwood [4] than from softwood [5] indicating the

282 presence of a higher portion of xylan in hardwood. However, its yield from hardwood was still less than that from

283 xylan, probably due to an effect of its integration with cellulose and lignin. In the case of 5H-furan-2-one, its

284 formation was less in spruce than pure glucomannan due to their interaction. On the other hand, it decreased in

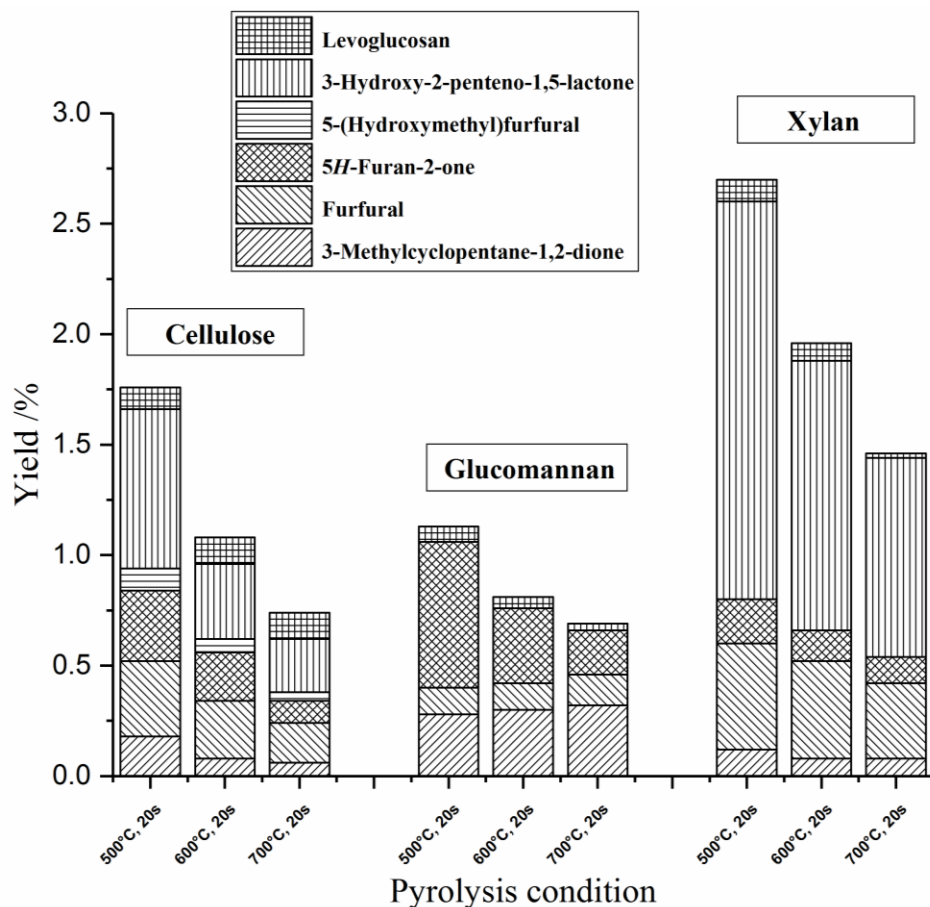
285 delignified glucomannan-poor softwood samples even by a factor of six, and it could be claimed that this compound

286 originated from glucomannan more readily than from cellulose. A decreasing trend of LG formation in untreated and

287 treated softwood samples manifested that it was formed from both glucomannan and cellulose, but more from



288 cellulose. Also 3-methylcyclopentane-1,2-dione and furfural, are prominent products from birch wood and spruce  
 289 wood as well as non-wood [6].  
 290



291  
 292 **Fig. 7.** Effects of temperature and time on yields of some prominent pyrolysis products.  
 293

294 *3.3. Formation of pyrolysis products*

295 It was expected that the total amounts and the relative proportions of varying compounds and compound groups  
 296 were characteristically dependent on pyrolysis conditions, although the total yield of pyrolysis products that are  
 297 normally recovered and identified from laboratory-scale pyrolyzers is generally known to be low [61,62]. A great  
 298 number of studies have been performed to clarify the reaction networks between the basic structural unit of  
 299 cellulose, D-glucose, or  $\beta$ -(1 $\rightarrow$ 4)-glycosidic bond-containing low-molar-mass model compounds (e.g., to clarify the  
 300 role of the dehydration and retroaldol condensation reactions of anhydrosugars and the cleavage of glycosidic  
 301 bonds) [11,46,32]. Typically, the products of cellulose pyrolysis in the classic lumped kinetic models are roughly

302 divided into gases, tar, and char, rather than utilizing the detailed compound distribution. Earlier kinetic studies have  
 303 been carried out under a variety of pyrolysis conditions, leading to somewhat conflicting data with a wide range of  
 304 kinetic parameters [37]. Hence, it can be concluded that the kinetics and elementary-reaction chemistry of  
 305 carbohydrate pyrolysis are still debated [29].

306 A comprehensive clarification of the myriad pyrolysis reaction routes for cellulose and hemicelluloses was  
 307 beyond the scope of this study. Instead, the practical aim was to clarify the chemical composition of condensable  
 308 liquids obtained from these feedstocks at varying temperatures for evaluating the chemical usefulness of the  
 309 corresponding fractions. Table 3 illustrates the relative formation of the major product groups (lactone, furan, and  
 310 cyclopentenone derivatives) from cellulose, glucomannan, and xylan under varying pyrolysis conditions, whereas  
 311 the corresponding formation of the minor product groups (phenolic, pyrone, and anhydrosugar derivatives) is shown  
 312 in Table 4.

313

314 Table 3. Relative proportions (%) of major product groups obtained from cellulose, glucomannan, and xylan under  
 315 varying pyrolysis conditions. The values given in parentheses refer to yields (% of the initial feedstock dry matter).<sup>a</sup>

Product group <sup>b</sup>	Cellulose	Glucomannan	Xylan
500 °C			
L	46 (1.8)	33 (1.1)	48 (2.0)
F	23 (0.8)	31 (1.0)	20 (0.8)
C	16 (0.5)	26 (0.8)	11 (0.4)
600 °C			
L	39 (1.1)	21 (1.5)	43 (1.5)
F	26 (0.7)	33 (1.1)	24 (0.8)
C	17 (0.5)	32 (1.1)	14 (0.5)
700 °C			
L	33 (0.6)	17 (0.4)	33 (0.7)
F	18 (0.4)	37 (0.9)	24 (0.7)
C	21 (0.4)	33 (0.6)	19 (0.6)

316 <sup>a</sup> Data from Figs. 4-6, calculated average values for heating times of 5 and 20 s.

317 <sup>b</sup> L refers to lactone derivatives, F to furan derivatives, and C to cyclopentenone derivatives.

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324

325 Table 4. Relative proportions (%) of minor product groups obtained from cellulose, glucomannan, and xylan under  
 326 varying pyrolysis conditions.<sup>a</sup>

Product group <sup>b</sup>	Cellulose	Glucomannan	Xylan
500 °C			
P	1.3	3.1	9.0
Y	6.7	2.1	2.8
A	6.7	1.8	-
600 °C			
P	4.0	7.1	6.3
Y	5.6	2.4	4.2
A	8.5	1.5	-
700 °C			
P	9.3	10	10
Y	5.0	2.3	5.7
A	14	1.2	-

327 <sup>a</sup> Data from Figs. 4-6, calculated average values for heating times of 5 and 20 s.

328 <sup>b</sup> P refers to phenolic derivatives, Y to pyrone derivatives, and A to anhydrosugar derivatives.

329

330 Tables 3 and 4 indicate that no distinct compound group was selectively formed at certain temperatures and the  
 331 major product groups lactone, furan, and cyclopentenone derivatives accounted for 72-85% (from cellulose), 86-  
 332 90% (from glucomannan), and 76-81% (from xylan) of the total amount of pyrolysis products determined. In  
 333 practice, this finding means that if a mixture of cellulose, glucomannan, and xylan with equal proportions would be  
 334 pyrolyzed at 500 °C, about half of the condensable liquids will consist of lactone derivatives. In the case of  
 335 cellulose, the proportion of lactone derivatives decreased, and that of anhydrosugar derivatives increased steadily as  
 336 the temperature increased. For glucomannan and xylan, the proportion of lactone derivatives also decreased and the  
 337 proportion of cyclopentenone derivatives was slightly depressed toward the maximum temperature. However, for all  
 338 model substances, no significant changes in the proportion of furan derivatives could be detected. The corresponding  
 339 major product groups were also prominent ones identified in our earlier pyrolysis experiments, especially at 500 °C,  
 340 with wood and non-wood feedstocks [4–6] existing together with the lignin-derived significant product groups,  
 341 guaiacol, and syringyl derivatives. Particularly in the wood pyrolysis cases, estimated in view of the present results,  
 342 approximate calculations suggested that the proportions of these compound groups were almost equal to the  
 343 expected ones.

344

#### 345 4. Conclusions

346 Pyrolysis-based technologies can be described as direct thermochemical conversion methods of lignocellulosic  
 347 biomass carried out in the complete or near complete absence of an oxidizing agent (air or oxygen) typically at 500-

348 700 °C to provide complex fractions of gases, condensable liquids, and char. In many biorefinery concepts, pyrolysis  
349 has been applied to prepare fuels and platform chemicals. The pyrolytic degradation of biomass is dominated by the  
350 behavior of its structural components, carbohydrates (cellulose and hemicelluloses, such as glucomannan and xylan)  
351 and lignin.

352 In this study, the analytical pyrolysis of cellulose, glucomannan, and xylan was carried out at 500, 600, and 700  
353 °C. In each case, the condensable liquids formed were analyzed in detail and classified into several characteristic  
354 compound groups. The results revealed that despite some general formation trends, due to many parallel reaction  
355 paths, no compound group was selectively formed at certain temperatures, and the major product groups lactone (the  
356 most prominent fraction), furan, and cyclopentenone derivatives accounted for 72-85% (from cellulose), 86-90%  
357 (from glucomannan), and 76-81% (from xylan) of the total amount of pyrolysis products determined. This study also  
358 confirmed by thermogravimetric analyses that within the temperature range studied, cellulose was thermally more  
359 stable than the heterogeneous hemicelluloses. All these findings supported those from versatile earlier research and  
360 facilitated the creation of a more coherent picture of this complicated area. These kinds of data are of practical  
361 importance with respect to efforts to develop new biorefinery possibilities for renewable resources.

362

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366

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## Supplementary data S1: Yield of cellulose pyrolysis products (%)

Pyrolysis products	RT <sup>a</sup> /min	500 °C, 5 s	500 °C, 20 s	600 °C, 5 s	600 °C, 20 s	700 °C, 5 s	700 °C, 20 s
Toluene	4.6	-	-	-	0.02	0.02	0.04
2-Methylbut-2-enal	6.4	0.32	0.36	-	0.08	-	-
Furfural	8.0	0.28	0.34	0.28	0.26	0.22	0.18
Cyclopent-2-en-1-one	8.1	0.06	0.08	0.06	0.08	0.08	0.08
Furanmethanol	8.2	-	-	0.04	-	-	-
Ethenylbenzene	8.3	-	-	-	-	0.02	0.02
5-Methyl-3 <i>H</i> -furan-2-one	9.1	0.1	0.1	-	-	-	-
1-Acetoxypropan-2-one	9.3	0.12	-	0.28	-	-	-
Cyclohexanone	9.7	0.02	0.04	0.02	0.02	-	-
2-Methylcyclopent-2-en-1-one	10.3	0.02	-	0.06	-	0.04	0.04
1-(2-Furyl)ethanone	10.4	-	-	0.04	0.01	-	-
2-Cyclopenten-1,4-dione	11.2	-	0.06	0.02	0.04	0.02	0.02
2-Hydroxycyclopent-2-en-1-one	11.6	0.16	0.22	0.2	0.14	0.14	0.1
5 <i>H</i> -Furan-2-one	12.5	0.46	0.32	0.34	0.22	0.1	0.1
Phenol	12.7	0.04	0.04	0.04	0.06	0.06	0.1
5-Methylfurfural	12.7	0.02	0.12	0.04	0.06	0.06	0.06
Pyran-2-one	14.2	-	-	-	0.06	0.06	0.06
3-Methyl-5 <i>H</i> -furan-2-one	14.4	0.06	0.1	0.1	0.1	0.22	-
1 <i>H</i> -Indene	14.5	-	-	-	-	-	0.02
2 <i>H</i> -Pyran-2,6(3 <i>H</i> )-dione	14.6	0.14	-	-	-	-	-
3-Hydroxy-2-penteno-1,5-lactone	15.0	0.58	0.72	0.52	0.34	0.3	0.24
3-Methylcyclopentane-1,2-dione	15.4	0.2	0.26	0.2	0.12	0.12	0.1
2-Methylphenol	15.5	-	-	-	0.02	0.02	0.02
4-Methylphenol	16.4	-	0.02	0.02	0.04	0.04	0.04
4-Methyl-5 <i>H</i> -furan-2-one	17.9	0.1	0.12	0.1	0.1	0.1	-
4-Hydroxy-2,5-dimethylfuran-3-one	18.1	0.06	0.08	0.06	0.04	0.02	-
Methylfuran-2-carboxylate	18.1	0.08	0.08	0.06	0.06	0.04	-
1-Methyl-1 <i>H</i> -indene	18.3	-	-	-	-	-	0.02
2-Hydroxy-3-ethylcyclopent-2-en-1-one	18.5	-	-	0.02	-	-	-
2,4-Dimethylphenol	18.9	-	-	0.02	0.02	0.02	0.02
3-Hydroxy-2-methylpyran-4-one	19.0	0.1	0.1	0.08	-	-	-
2,5-Furandicarboxaldehyde	19.1	-	-	0.16	0.16	-	-
Levoglucosenone	19.8	0.03	0.03	0.03	0.03	0.03	0.03
Naphthalene	20.4	-	-	-	-	-	0.02
2,3-Dihydroxybenzaldehyde	20.5	0.1	0.1	0.1	-	-	-
3,5-Dihydroxy-2-methylpyran-4-one	21.5	-	0.08	-	-	-	-
Dihydro-6-methyl-2 <i>H</i> -pyran-3(4 <i>H</i> )-one	22.4	0.12	0.14	0.12	0.1	0.1	0.08
(1 <i>R</i> ,5 <i>S</i> )-1-Hydroxy-3,6-dioxabicyclo[3.2.1]octan-2-one	23.0	0.16	0.18	0.12	0.12	0.12	0.06
1,4:3,6-Dianhydro- $\alpha$ -D-glucopyranose	23.8	0.06	0.06	0.06	0.06	0.06	0.06
2,3-Anhydro-D-mannose	24.2	0.06	0.08	0.06	0.06	0.06	0.04
5-(Hydroxymethyl)furfural	24.6	0.1	0.1	0.06	0.06	0.04	0.04
2,3-Dihydro-1 <i>H</i> -indene-1-one	25.4	-	-	-	0.02	-	-
Levoglucosan	34.5	0.1	0.1	0.1	0.12	0.14	0.12

<sup>a</sup> RT refers to retention time (min).

## Supplementary data S2: Yield of glucomannan pyrolysis products (%)

Pyrolysis products	RT <sup>a</sup> /min	500 °C, 5 s	500 °C, 20 s	600 °C, 5 s	600 °C, 20 s	700 °C, 5 s	700 °C, 20 s
Toluene	4.6	0.02	0.02	0.04	0.02	0.02	0.04
2-Methylbut-2-enal	6.4	0.44	0.44	0.76	0.28	-	-
1,2-Dimethylbenzene	7.2	-	-	-	-	-	0.02
Pentanal	7.3	3.92	2.96	3.48	2.88	2.44	2.68
Furfural	7.9	0.1	0.12	0.18	0.12	0.12	0.14
Cyclopent-2-en-1-one	8.1	0.06	0.1	0.12	0.1	0.08	0.1
Furanmethanol	8.2	0.22	0.22	0.46	0.12	0.08	0.16
5-Methyl-3 <i>H</i> -furan-2-one	9.1	0.1	0.1	-	-	-	-
1-Acetoxy-propan-2-one	9.3	0.4	0.12	-	0.2	0.16	0.2
Cyclohexanone	9.7	0.02	0.02	0.04	-	-	-
2-Methylcyclopent-2-en-1-one	10.3	0.04	0.06	0.08	0.06	0.04	0.06
1-(2-Furyl)ethanone	10.4	0.04	0.05	0.06	0.03	0.04	0.05
2-Cyclopenten-1,4-dione	11.2	0.04	0.04	0.06	0.04	0.02	0.02
2-Hydroxycyclopent-2-en-1-one	11.6	0.18	0.18	0.24	0.18	0.12	0.14
2-Methylethenylbenzene	12.2	-	-	-	-	-	0.02
5 <i>H</i> -Furan-2-one	12.7	0.62	0.66	0.54	0.34	0.22	0.2
Phenol	12.8	0.02	0.08	0.1	0.1	0.08	0.12
5-Methylfurfural	12.8	0.02	-	-	0.08	0.08	0.1
5-Methyl-5 <i>H</i> -furan-2-one	12.9	0.06	0.1	-	-	-	-
3-Methylcyclopent-2-en-1-one	13.1	0.04	0.06	0.08	0.08	0.04	0.06
2,3-Dimethylcyclopent-2-en-1-one	13.4	-	0.02	0.04	0.04	-	0.02
3-Methyl-5 <i>H</i> -furan-2-one	14.4	0.12	-	0.1	0.1	0.1	-
1 <i>H</i> -Indene	14.5	-	-	-	-	-	0.02
2,3-dimethylcyclopent-2-en-1-one	14.8	0.1	0.12	0.12	0.1	-	-
3-Methylcyclopentane-1,2-dione	15.4	0.28	0.28	0.4	0.3	0.2	0.32
2-Methylphenol	15.5	-	0.02	0.02	0.02	0.04	0.04
2-Hydroxy-3,5-dimethylcyclopent-2-en-1-one	15.6	0.02	0.02	0.06	0.04	0.02	0.06
4-Methylphenol	16.4	0.02	0.04	0.06	0.08	0.06	0.1
2-Methoxyphenol	17.2	0.04	0.04	-	-	-	-
3-Ethylcyclopent-2-en-1-one	17.2	-	-	0.04	0.02	0.02	-
2,6-Dimethylphenol	17.4	-	-	0.02	0.02	-	0.02
4-Methyl-5 <i>H</i> -furan-2-one	17.6	0.1	0.1	0.12	0.1	0.1	0.1
4-Hydroxy-2,5-dimethylfuran-3-one	17.6	-	0.04	0.04	-	-	-
Methylfuran-2-carboxylate	17.7	0.06	0.06	0.08	0.06	-	0.06
2-Hydroxy-3-ethylcyclopent-2-en-1-one	18.3	0.06	0.14	0.14	0.12	0.1	0.14
1-Methyl-1 <i>H</i> -indene	18.6	-	-	-	-	-	0.02
2,4-Dimethylphenol	18.9	0.02	0.02	0.04	0.02	0.02	0.04
3-Ethylphenol	19.6	-	-	-	-	-	0.04
3,5-Dimethylphenol	20.1	-	-	0.02	0.02	0.02	0.02
Naphthalene	20.5	-	-	-	-	-	0.02
2,3-Dihydroxybenzaldehyde	20.5	0.1	0.1	0.1	0.08	-	-
1,2-Dihydroxybenzene	21.7	-	-	-	-	-	0.06
Dihydro-6-methyl-2 <i>H</i> -pyran-3(4 <i>H</i> )-one	22.2	0.06	0.08	0.08	0.08	0.08	-
(1 <i>R</i> ,5 <i>S</i> )-1-Hydroxy-3,6-dioxabicyclo[3.2.1]octan-2-one	23.0	0.04	0.04	0.04	0.04	0.04	0.04
1-Methylnaphthalene	24.3	-	-	-	-	-	0.02
4-Ethyl-2-methoxyphenol	24.3	-	-	0.04	-	-	-
Levoglucozan	34.5	0.05	0.07	0.05	0.05	0.03	0.03

<sup>a</sup> RT refers to retention time (min).

## Supplementary data S3: Yield of xylan pyrolysis products (%)

Pyrolysis products	RT <sup>a</sup> /min	500 °C, 5 s	500 °C, 20 s	600 °C, 5 s	600 °C, 20 s	700 °C, 5 s	700 °C, 20 s
Toluene	4.6	0.01	0.01	0.02	0.02	0.04	0.04
Methyl prop-2-enoate	5.3	3.26	4.16	2.42	1.94	1.28	1.52
1-Hydroxybutan-2-one	5.7	1.16	1.00	1.48	1.00	1.04	1.00
1,2-Dimethylbenzene	7.2	-	-	-	-	-	0.02
Furfural	8.0	0.32	0.48	0.4	0.44	0.32	0.34
Cyclopent-2-en-1-one	8.1	-	0.08	0.08	0.08	0.08	0.08
Ethenylbenzene	8.4	-	-	-	-	0.02	0.04
Furanmethanol	8.6	0.06	0.02	0.06	0.02	-	-
5-Methyl-3H-furan-2-one	9.1	0.1	0.1	0.06	0.1	-	-
1-Acetoxy-propan-2-one	9.3	0.12	0.2	0.36	0.24	0.16	0.24
Cyclohexanone	9.7	-	0.02	0.02	0.02	0.02	0.02
2-Methylcyclopent-2-en-1-one	10.3	0.1	0.08	0.1	0.08	0.06	0.06
2-Cyclopenten-1,4-dione	11.2	0.02	0.02	0.04	0.02	0.02	0.02
2-Hydroxycyclopent-2-en-1-one	11.6	0.08	0.12	0.14	0.12	0.14	0.12
5H-Furan-2-one	12.5	0.18	0.2	0.28	0.14	0.16	0.12
Phenol	12.9	0.28	0.28	0.08	0.1	0.1	0.16
3-Methylcyclopent-2-en-1-one	13.1	0.02	0.04	0.04	0.04	0.02	0.02
3-Hydroxy-2-penteno-1,5-lactone	15.0	1.52	1.8	1.22	1.22	0.72	0.9
3-Methylcyclopentane-1,2-dione	15.4	0.1	0.14	0.16	0.12	0.12	0.14
2-Methylphenol	15.5	-	-	0.02	0.02	0.02	0.02
2-Hydroxy-3,5-dimethylcyclopent-2-en-1-one	15.6	0.02	0.02	0.02	-	-	-
4-Methylphenol	16.4	0.02	0.04	0.04	0.06	0.06	0.08
2-Methoxyphenol	17.2	0.04	0.06	0.04	0.04	0.04	0.04
4-Methyl-5H-furan-2-one	17.9	0.04	0.04	0.04	0.02	0.02	0.02
4-Hydroxy-2,5-dimethylfuran-3-one	18.1	0.02	0.04	0.04	0.02	0.02	0.02
2-Hydroxy-3-ethylcyclopent-2-en-1-one	18.3	0.02	0.06	0.06	0.06	0.06	0.08
2,4-Dimethylphenol	18.9	-	0.02	0.02	0.02	0.02	0.02
2-Ethylphenol	19.6	0.04	0.04	0.02	0.04	0.02	0.02
2,3-Dihydroxybenzaldehyde	20.5	0.12	0.12	0.12	0.12	0.1	0.12
2-Methoxy-4-methylphenol	20.7	0.04	0.04	0.04	0.02	0.04	0.04
1,2-Dihydroxybenzene	21.5	-	-	-	-	-	0.04
4-Ethenylphenol	22.1	0.02	0.02	0.02	0.02	0.02	0.04
Dihydro-6-methyl-2H-pyran-3(4H)-one	22.4	0.12	0.12	0.16	0.14	0.16	0.16
2',5'-Dihydroxyacetophenone	23.4	0.08	0.1	0.08	0.08	-	-
2-Methoxy-4-ethylphenol	23.5	0.04	0.04	0.02	0.02	-	-
1,2-Dihydroxy-3-methylbenzene	23.7	-	-	-	-	-	0.08
1-Methylnaphthalene	24.2	-	-	-	-	-	0.02
4-Ethenyl-2-methoxyphenol	25.4	0.06	0.06	0.06	0.04	0.04	0.04
2,6-Dimethoxyphenol	27.6	0.04	0.04	0.04	0.04	0.02	0.02
Levoglucosan	34.5	0.16	0.1	0.08	0.08	0.04	0.02
Dibutyl benzene-1,2-dicarboxylate	42.3	0.02	0.02	-	-	-	-

<sup>a</sup> RT refers to retention time (min).

Supplementary data S4: Classification of pyrolysis products including peak identification and calibration information

Compound	RT <sup>a</sup> /min	Major ion(s) ( <i>m/z</i> )	Quantification <sup>b</sup>	r <sup>2</sup> Value <sup>c</sup>	Slope
<b>Linear ketones, acids, esters derivatives (&lt;C5)</b>					
Acetic acid	3.7	43, 60	Standard	0.96	4.1
Butanal	3.9	57, 72	Standard	0.99	4.1
Methyl acrylate	5.3	55, 86	Acetic acid		
1-Hydroxy-2-butanone	5.7	57, 88	Butanal		
2-Methylbut-2-enal	6.4	55, 84	Butanal		
Pentanal	7.2	58, 86	Butanal		
1-Acetoxypropan-2-one	9.3	57, 86, 116	Acetic acid		
<b>Benzene derivatives</b>					
Toluene	4.6	51, 65, 91	Standard	0.99	298.5
1,2-Dimethylbenzene	7.3	91, 106	Standard	0.99	230.0
Ethynylbenzene	8.4	78, 104	Standard	0.96	191.7
<b>Furan derivatives</b>					
Furfural (furan-2-carbaldehyde)	8.0	39, 95, 96	Standard	0.99	42.9
Furanmethanol ((furan-2-yl)methanol)	8.6	53, 69, 81, 98	Standard	0.99	94.2
1-(2-Furyl)ethanone	10.5	95, 110	5-Methylfurfural		
5-Methylfurfural	12.8	53, 109, 110	Standard	0.98	62.2
Methyl furan-2-carboxylate	18.1	39, 95, 126	Furfural (furan-2-carbaldehyde)		
4-Hydroxy-2,5-dimethylfuran-3-one	18.1	43, 57, 85, 128	Standard	0.99	41.6
2,5-Furandicarboxaldehyde	19.1	53, 67, 95, 124	Standard	0.99	83.0
5-(Hydroxymethyl)furfural	24.7	39, 97, 109, 126	Standard	0.97	73.0
<b>Lactone derivatives</b>					
5-Methyl-3 <i>H</i> -furan-2-one	9.1	55, 70, 98	Standard	0.99	56.0
5 <i>H</i> -Furan-2-one	12.7	39, 55, 84	Standard	0.99	24.8
3-Methyl-5 <i>H</i> -furan-2-one	14.5	69, 98	5-Methyl-3 <i>H</i> -furan-2-one		
3-Hydroxy-2-penteno-1,5-lactone	15.0	58, 85, 114	4-Hydroxy-5-methylfuran-3-one	0.97	35.2
4-Methyl-5 <i>H</i> -furan-2-one	17.9	69, 98	5-Methyl-3 <i>H</i> -furan-2-one		
(1 <i>R</i> ,5 <i>S</i> )-1-Hydroxy-3,6-dioxabicyclo[3.2.1]octan-2-one	23.2	57, 69, 85, 116, 144	4-Hydroxy-2,5-dimethylfuran-3-one		
<b>Cyclopentenone derivatives</b>					
Cyclopent-2-en-1-one	8.3	39, 82	Standard	0.98	118.4
Cyclohexanone	9.9	55, 69, 98	Standard	0.99	51.2
2-Methylcyclopent-2-en-1-one	10.3	53, 67, 96	Standard	0.99	65.2
2-Cyclopenten-1,4-dione	11.2	54, 68, 98	2-Methylcyclopent-2-en-1-one		
2-Hydroxycyclopent-2-en-1-one	11.8	55, 69, 98	2-Methylcyclopent-2-en-1-one		
3-Methylcyclopent-2-en-1-one	13.3	53, 67, 96	2-Methylcyclopent-2-en-1-one		
2,3-Dimethylcyclopent-2-en-1-one	14.8	67, 82, 95, 110	2-Methylcyclopent-2-en-1-one		
3-Methylcyclopentane-1,2-dione	15.4	55, 69, 83, 112	Standard	0.98	43.6
2-Hydroxy-3,5-dimethylcyclopent-2-en-1-one	15.6	69, 83, 97, 111, 126	2-Methylcyclopent-2-en-1-one		
3-Ethylcyclopent-2-en-1-one	17.2	67, 81, 95, 110	2-Methylcyclopent-2-en-1-one		

2-Hydroxy-3-ethylcyclopent-2-en-1-one	18.5	55, 69, 83, 126	2-Methylcyclopent-2-en-1-one		
<b>Phenol derivatives</b>					
Phenol	12.9	66, 94	Standard	0.98	55.1
2-Methylphenol	15.5	39, 51, 79, 107	Standard	0.99	85.0
4-Methylphenol	16.4	39, 51, 79, 108	Standard	0.99	82.0
2,6-Dimethylphenol	17.4	77, 107, 122	Standard	0.98	128.6
2-Ethylphenol	18.3	63, 77, 107, 122	2,6-Dimethylphenol		
2,4-Dimethylphenol	18.9	65, 77, 107, 122	2,6-Dimethylphenol		
3-Ethylphenol	19.6	77, 107, 122	3,5-Dimethylphenol		
3,5-Dimethylphenol	19.8	77, 107, 122	Standard	0.98	87.6
2,3,6-Trimethylphenol	22.0	77, 91, 121, 136	Standard	0.98	222.0
4-Ethenylphenol	22.1	65, 91, 120	3,4-Dimethylphenol		
<b>Pyran derivatives</b>					
Pyran-2-one	14.3	39, 68, 96	3-Hydroxy-2-methylpyran-4-one		
2 <i>H</i> -Pyran-2,6(3 <i>H</i> )-dione	14.8	55, 84, 112	3-Hydroxy-2-methylpyran-4-one		
3-Hydroxy-2-methylpyran-4-one	19.0	43, 55, 71, 126	Standard	0.98	74.5
3,5-Dihydroxy-2-methylpyran-4-one	21.8	68, 85, 113, 142	3-Hydroxy-2-methylpyran-4-one		
Dihydro-6-methyl-2 <i>H</i> -pyran-3(4 <i>H</i> )-one	22.4	56, 84, 114	3-Hydroxy-2-methylpyran-4-one		
<b>Indene derivatives</b>					
1 <i>H</i> -Indene	14.5	63, 89, 116	Standard	0.99	211.2
1-Methyl-1 <i>H</i> -indene	18.4	115, 130	1 <i>H</i> -Indene		
2,3-Dihydro-1 <i>H</i> -indene-1-one	25.6	78, 104, 132	1 <i>H</i> -Indene		
<b>Guaiacol derivatives</b>					
2-Methoxyphenol (guaiacol)	17.2	53, 81, 109, 124	Standard	0.99	79.2
2-Methoxy-4-methylphenol	20.7	67, 123, 138	Standard	0.99	275.0
2-Methoxy-4-ethylphenol	23.5	137, 152	2-Methoxy-4-methylphenol		
2-Methoxy-4-ethenylphenol	25.4	51, 77, 107, 135, 150	Standard	0.97	251.5
<b>Anhydrosugar derivatives</b>					
(1 <i>S</i> ,5 <i>R</i> )-6,8-Dioxabicyclo[3.2.1]oct-2-en-4-one (levoglucosenone)	19.8	39, 68, 98	Levoglucosan		
1,4:3,6-Dianhydro- $\alpha$ -D-glucopyranose	24.0	69, 86, 98, 144	Levoglucosan		
2,3-Anhydro-D-mannose	24.5	69, 71, 85, 97, 144	Levoglucosan		
1,6-Anhydro- $\beta$ -D-glucopyranose (levoglucosan)	34.5	60, 73, 126, 145	Standard	0.99	67.0
<b>Naphthalene derivatives</b>					
Naphthalene	20.5	51, 102, 128	Standard	0.99	178.8
1-Methylnaphthalene	24.3	71, 115, 142	Naphthalene		
<b>Catechol derivatives</b>					
2,3-Dihydroxybenzaldehyde	20.5	51, 64, 92, 120, 138	Standard	0.99	119.0
1,2-Dihydroxybenzene (catechol)	21.7	64, 81, 110	Standard	0.98	57.3

2',5'-Dihydroxyacetophenone (1-(2,5-dihydroxyphenyl)ethanone)	23.4	69, 109, 137, 152	2,3-Dihydroxybenzaldehyde		
1,2-Dihydroxy-3-methylbenzene	23.7	51, 78, 106, 124	Standard	0.97	155.0
1,2-Dihydroxy-3-methoxybenzene	24.4	97, 125, 140	Standard	0.97	159.0
<b>Syringyl derivatives</b>					
2,6-Dimethoxyphenol (syringol)	27.6	96, 139, 154	Standard	0.99	76.3

In all cases, the intercept was 0.0.

<sup>a</sup> RT refers to retention time (min).

<sup>b</sup> Quantification is done by pure compounds.

<sup>c</sup>  $r^2$  refers to coefficient values.