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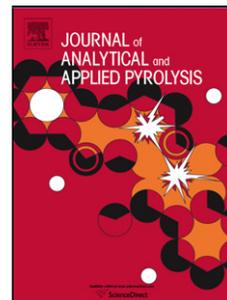
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# Fast pyrolysis of hot-water-extracted and delignified silver birch (*Betula pendula*) sawdust by Py-GC/MS

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## HIGHLIGHTS

- Fast pyrolysis has been applied to various solid residues from hot-water-extracted birch sawdust
- Fast pyrolysis has been utilized in the integrated biorefinery concept of birch wood
- A basis of a rapid characterization method for lignocellulosics has been created

## Abstract

The thermochemical behavior of birch (*Betula pendula*) sawdust both untreated and after various chemical treatments (hot-water extraction, delignification, and hot-water extraction followed by delignification) 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 feedstock samples with varying mass portions of the structural constituents (cellulose, hemicelluloses, and lignin) were determined at 500 °C and 700 °C at hold times of 5 s and 20 s. The formation of pyrolysis products was shown to be characteristically dependent on feedstock composition as well as on pyrolysis conditions. This kind of approach was of practical importance with respect to efforts not only to develop rapid characterization tools for lignocellulosics, but also to new biorefinery possibilities to produce bio-oils, for example, enriched either with aliphatic or aromatic constituents.

**Keywords:** Pyrolysis-gas chromatography; Silver birch; Hot-water extraction; Soda-AQ delignification; Condensable products

## 1. Introduction

Forest lignocellulosic biomass represents a renewable and sustainable alternative for replacing fossil resources for manufacturing chemicals, energy, and other products [1-4]. In many biorefinery processes, various pretreatment technologies, including mechanical upgrading, heating, or chemical treatment, play an important role [3,5-9]. Therefore, in an integrated forest biorefinery concept, one interesting approach, mainly for recovering valuable carbohydrates-derived material, is to apply hot-water extraction (“autohydrolysis”) to wood chips or sawdust prior to further processing, such as pulping [8,10-12]. It can be concluded that all these types of fractionation possibilities also offer, for example, a wide range of potential feedstocks for thermochemical conversions [13-15].

Thermochemical conversions of lignocellulosic materials have been investigated under a variety of conditions and from several points of view. These rather unselective techniques result in the formation of gases, condensable liquids (tars), and charcoal, whose relative proportions depend on the chosen treatment method and the specific reaction conditions [3]. For example, fast pyrolysis of lignocellulosics, carried out in the complete or near complete absence of an oxidizing agent with a relative high heating rate and a short reaction time typically at 500-700 °C, represents a straightforward method that produces a particularly high yield of liquid biofuels and chemicals [16,17]. Furthermore, it has been established that the individual main polymeric wood components, carbohydrates (cellulose and hemicelluloses) and lignin, are showing their characteristic degradation behavior during heating [18-22]; for example, carbohydrates typically form anhydrosugars, furans, and monomeric phenols via dehydration, whereas lignin partially loses its aliphatic side chains and degrades.

In this study, the fast pyrolysis of untreated and hot-water-extracted (HWE) silver birch (*Betula pendula*) sawdust as well as the soda-anthraquinone(AQ)-delignified pulps originated from these untreated and treated feedstocks was investigated by pyrolysis-gas chromatography-mass spectrometry (Py-GC/MS). The main aims were, on the one hand, to clarify the relative performance of these feedstocks during pyrolysis and, on the other hand, to evaluate the suitability of this analytical pyrolysis method as a rapid tool for roughly detecting chemical changes that take place in the feedstocks during applied chemical treatments. For obtaining these targets, the chemical composition of condensable product fractions formed under varying pyrolysis conditions was determined.

## 2. Experimental

### 2.1. Raw materials and their analyses

The untreated ( $B_{ref}$ ) and HWE (at 170 °C for 38 min with a yield of 71.9 % [23]) ( $B_{HWE}$ ) silver birch (*Betula pendula*) sawdust (<5 mm) as well as the soda-AQ-cooked pulps of untreated ( $P_{ref}$ ) and of HWE ( $P_{HWE}$ ) birch feedstocks were investigated.

The soda-AQ delignification experiments were carried out in a laboratory-scale oil-heated batch digester (CRS Autoclave System 420, CRS Reactor Engineering AB, Stenkullen, Sweden) equipped with 1.25-L rotating stainless-steel autoclaves. The treatment conditions were as follows: alkali (NaOH) charge 18 % based on oven-dried (o.d.) feedstock, AQ charge 0.1 % based on o.d. feedstock, temperature 170 °C, time 90 min, and liquor-to-feedstock ratio 5 L/kg. At the end of each cook, the autoclaves were removed from the oil bath and cooled rapidly with cold tap water. The spent cooking liquor (black liquor) was then separated from the pulp by pressing it through a nylon-woven fabric bag. The pulp obtained was thoroughly washed with

water, and the amount of removed organic material was calculated based on charged o.d. feedstock; yields for  $P_{\text{HWE}}$  and  $P_{\text{ref}}$  were 53.5 % and 51.6 %, respectively.

For the chemical analyses [24], untreated air-dried and hot-water-treated sawdust samples and pulps were ground with a Retsch SM 100 cutting laboratory mill (Retsch GmbH, Haan, Germany) equipped with a bottom sieve with trapezoidal holes (perforation size <1.0 mm) and stored in plastic bags. Prior to analyses, the moisture content was determined according to TAPPI T264 cm-97 standard in an oven at 105 °C. All analyses were carried out with two parallel samples, and the results were calculated as percentages of the dry sample.

The extractives content of the ground samples (about 1.5 g) was determined according to the TAPPI T280 pm-99 standard with acetone in a Soxhlet apparatus (extraction time 4 h with 6-10 percolations per hour). The extract was concentrated nearly to dryness by vacuum evaporation with a rotary evaporator (Heidolph VV2000, Gemini BV Laboratory, Apeldoorn, Netherlands), and drying was finalized before weighing by means of a gentle nitrogen stream.

The lignin content of the extractives-free ground samples was calculated as the sum of the “acid-insoluble (Klason) lignin” and the “acid-soluble lignin” according to the TAPPI T222 om-98, T249 cm-00, and T250 UM standards. The acid-soluble lignin content was determined with a Beckman DU 640 UV/Vis spectrophotometer (Beckman Instruments Inc., Fullerton, CA, USA) at 205 nm after quantitative dilution of the sulfuric acid hydrolysate until the absorbance  $A$  was in the range of 0.3-0.8. The concentration of the dissolved lignin  $c$  (g/L) was calculated as

$$c = A/(a \cdot b), \quad (1)$$

where  $a$  is the absorptivity (110 L/(gcm)) [25] and  $b$  is the length of the light path (cm).

Acid hydrolysis of the extractives-free ground samples was performed according to the TAPPI T249 cm-00 standard, and the resulting monosaccharides were analyzed as their per(trimethylsilyl)ated derivatives using a gas chromatography (GC) system comprising an HP 5890 Series II Plus GC apparatus (Hewlett Packard Company, Wilmington, NC, USA) equipped with a flame-ionization detector (FID). The silylation was made with a mixture of 99 % *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA, Regis Technologies, Morton Grove, IL, USA) and 1 % trimethylchlorosilane (TMCS, Regis Technologies) in pyridine and the mixture was shaken for 60 min [26]. Xylitol (Fluka Chemical Corporation, Seelze, Germany) served as an internal standard (IS). The column was a DP-1701 capillary column (60 m x 0.32 mm with a film thickness of 0.25 µm; Agilent Technologies, Palo Alto, CA, USA). For each monosaccharide, an IS was calibrated based on a separate run with the corresponding model monosaccharide: arabinose, xylose, galactose, glucose, and mannose (all from Fluka Chemical Corporation, Seelze, Germany). It was then possible to perform chromatogram peaks identification and obtain the mass-based response factor between each monosaccharide and the corresponding IS.

## 2.2. Pyrolysis experiments

About 0.5 mg of samples were pyrolyzed in a quartz tube (3.0 cm x 1.0 mm i.d., between quartz wool) at a heating rate of 20 °C/ms using a CDS Pyroprobe 1000 resistively heated coil filament pyrolyzer coupled to an HP 5890 II gas chromatograph (Py-GC, Hewlett Packard Company, Wilmington, NC, USA). The column was a ZB-35HT (Inferno) capillary GC column (30 m x 0.25 mm with a film thickness of 0.25 µm). Detection was carried out with an HP 5970 mass spectrometric detector under electron ionization (70 eV) with 2.92 scan/s in the 30-550 m/z

interval. For the identification of chromatogram peaks, the mass spectra (based on the National Institute of Standards and Technology (NIST) mass spectral library) were used.

The pyrolysis temperatures were 500 °C and 700 °C and in each case, the temperature was kept constant for either 5 s or 20 s. A splitless capillary injection port was used for the sample feed. The GC oven temperature program in the analyses of pyrolysis products was as follows: 2 min at 40 °C, 4 °C/min to 190 °C, 10 °C/min to 320 °C, and 10 min at 320 °C. Helium was used as carrier gas with a gas flow rate of 1 mL/min and as an inert atmosphere in the pyrolysis interface. The Py-GC interface temperature was 250 °C, and the injector temperature was 280 °C.

Quantitative analysis was conducted according to other recent studies [27-30] so that pure compounds (the total number was 48) were used as external standards to relatively quantify all the identified peaks from pyrolysis products (Py-GC/MS) by comparing the products to a set of standard samples of known concentration. The chromatogram peak identification was also partly confirmed based on the retention times and mass spectra of these pure compounds. Several standard methanol or acetone solutions in the concentration range of 0.05-8 mg/mL were prepared, and in all cases, the selected concentrations (five concentrations per each compound) depended on the standard's chromatographic response (GC/MS). The coefficients of determination ( $r^2$ ) values of the linear calibration curves were between 0.97-0.99 when a plot of instrument response (peak area, y-axis) vs. concentration of standard solution (in  $\mu\text{g}$ , x-axis) was performed. Each response factor represented the slope of the line between the response for a given standard and the origin. Therefore, the relative mass response of a target compound compared to the mass of the corresponding external standard. However, the simultaneous use of all 48 standards was rather complicated in all cases (Table S1 in Supplementary data), and to make this approach more appropriate and less tedious, the standards were classified into five groups (Table S2 and Fig. S1 in Supplementary data) if their relative standard deviation (RSD) of the response factors was less than or equal to 20 % [31]; thus, the slopes of the calibration curves for each standard were agreeably close to one another [28]. These average response factors were then used for the relatively quantitative determination of "similar products" (e.g., either for isomeric compounds or for compounds with similar molecular masses or structures). For example, in this case, the standards 2-methyl-2-cyclopenten-1-one, 4-hydroxy-5-methyl-3(2*H*)-furanone, 3-hydroxy-2-methyl-4*H*-pyran-4-one, and levoglucosan were, respectively, used for 2-hydroxy-2-cyclopenten-1-one, 3-hydroxy-2-penteno-1,5-lactone, pyran-type compounds, and anhydrosugars.

### 3. Results and discussion

#### 3.1. Raw materials

Chemical compositions of the reference initial and differently-treated (i.e., HWE, delignified, and HWE and delignified) birch feedstocks are presented in Table 1. The results indicated that 20-25 % of carbohydrates (mono-, oligo, and polysaccharides) and 30-35 % of the initial lignin were removed by hot-water treatment. This soluble fraction can be utilized for many purposes, and some potential possibilities will be separately investigated in forthcoming studies. The results also suggested that cellulose was rather stable during the treatment, but the loss of xylan, the main hardwood hemicellulose component consisting of xylose moieties, seemed to be 65-70 %. As expected, the typical losses of Klason and acid-soluble lignins were about 25 % and 60 %, respectively.

respectively. In practice, due to this treatment, the mass ratio of carbohydrates to lignin in the wood matrix increased from 3.1 to 3.5. In contrast, the corresponding mass ratio of aldohexose units (galactose, glucose, and mannose) to aldopentose units (arabinose and xylose) in the fraction of carbohydrates increased from 2.1 to 6.1.

TABLE 1

The chemical composition data on pulps (i.e.,  $B_{\text{ref}} \rightarrow P_{\text{ref}}$  and  $B_{\text{HWE}} \rightarrow P_{\text{HWE}}$ ) are shown in Table 1. In the former reference case ( $B_{\text{ref}} \rightarrow P_{\text{ref}}$ ), the total removal of carbohydrates was about 30 % (about 20 % for glucose and about 45 % for xylose), and the degree of delignification was about 95 %. The mass ratio of carbohydrates to lignin in the wood matrix clearly increased from 3.1 to 42.9, but the corresponding mass ratio of aldohexose units to aldopentose units in the fraction of carbohydrates increased only slightly from 2.1 to 2.9. However, in the latter case ( $B_{\text{HWE}} \rightarrow P_{\text{HWE}}$ ), it was noted that under the same delignification conditions as in case of  $B_{\text{ref}} \rightarrow P_{\text{ref}}$ , the HWE feedstock was more effectively delignified (about 98 %) than the corresponding untreated feedstock. Additionally, a higher removal of carbohydrates (about 35 %; for glucose, about 30 % and for xylose, about 65 %) was obtained. The mass ratio of carbohydrates to lignin in the wood matrix significantly increased from 3.5 to 113.7, and the corresponding mass ratio of aldohexose units to aldopentose units in the fraction of carbohydrates increased from 6.1 to 12.1. The chemical compositions of sulfur-free black liquors formed were not studied here in detail, and the recovery and utilization of the alkali-catalyzed degradation products of carbohydrates (mainly aliphatic carboxylic acids) and lignin in these liquors will be separately studied.

All these chemical treatments carried out according to the principles of integrated biorefinery concepts (i.e., to integrate a hot-water extraction stage to sulfur-free chemical pulping) resulted in various samples, in which the mass ratio of their principal chemical components (cellulose, hemicelluloses, and lignin) varied in a relatively wide range. Therefore, it could be concluded that these lignocellulosic samples were also very suitable as raw material samples for the present pyrolysis investigation.

### 3.2. Pyrolysis experiments

The integrated chromatographic system GC/MS applied was capable of resolving most of the main hydrophilic and lipophilic compounds released from birch samples during pyrolysis, and about 80 compounds were identified. In general, pyrolysis tests under the same conditions led to reproducible results, and a typical pyrogram profile for each sample could be obtained; examples of different samples are given in Figs. 1 and 2. Thus, it could be expected that the total amounts and the relative proportions of varying compounds or compound groups were characteristically dependent on the sample preparation and pyrolysis conditions. This finding was valid, although the total number of pyrolysis products that are normally recovered and identified from laboratory-scale pyrolyzers is known to be low [21].

FIGURE 1

FIGURE 2

It is also known that the characteristic feature for all the pyrolysates of lignocellulosics is a prominent amount of fixed gases and volatile products, such as carbon monoxide, carbon dioxide, methanol, acetaldehyde, acetic acid, glycolaldehyde, acetol, and certain  $<C_5$ -hydrocarbons and/or their derivatives [18, 21]. In this study, however, only the higher-molar-mass condensable products that were formed “rather selectively” from individual constituents were included. For example, acetic acid (a substituent of xylan) is not a relevant indicator of xylan because hot-water extraction and cooking remove it (via acetylation) more than the xylan backbone degrades itself.

For simplicity, the dominant GC-amenable pyrolysis products were classified into several compound groups (Table 2), and the formation of these monomer-related fragments were determined in different cases. It is evident that important contributions of postulated mechanisms for the degradation products in the pyrolysis of wood-derived components have been shown in many investigations [17-21]. Based on these data, it could be roughly concluded that the classes of anhydrosugar, cyclopentenone, furan, lactone, and pyrone derivatives originated from carbohydrates and those of catechol, benzenediol, guaiacol, phenol, and syringol derivatives originated from lignin. The characteristic classes of naphthalene and fatty acid derivatives were obtained from extractives and indene derivatives from xylan, whereas the class of other aromatics (benzene derivatives) was probably formed from all wood constituents.

TABLE 2

### 3.3. Practical considerations

In the case of  $B_{ref}$ , a pyrolysis time of 5 s at 500 °C and 700 °C resulted in the highest pyrolysis yields similar to those obtained from  $B_{HWE}$  and  $P_{ref}$  at 500 °C for 5 s (Fig. 3). Typically, the yield was found to decrease or remain almost similar when the pyrolysis temperature increased from 500 °C to 700 °C. As a general trend, the pyrolysis yields were higher for reference samples (i.e.,  $B_{ref} > B_{HWE}$  and  $P_{ref} > P_{HWE}$ ), mainly indicating a higher relative portion of hemicelluloses in these samples (Table 1). The overall treatment yield of samples was 71.9, 51.6, and 38.5 % of the initial  $B_{ref}$  dry matter for  $B_{HWE}$ ,  $P_{ref}$ , and  $P_{HWE}$ , respectively. This trend was also reflected in the pyrolysis yields that decreased in order:  $B_{ref} > B_{HWE} \approx P_{ref} > P_{HWE}$ .

FIGURE 3

The main feedstock chemical constituents degrade on heating at different rates [32]. Under the pyrolysis conditions of this study, varying amounts of carbohydrates- and lignin-derived low-molar-mass products were formed from these high-molar-mass polymers and could be partly found in pyrolysates. In addition, part of the devolatilized pyrolysis products might be selectively condensed before reaching the GC column. The results, for example, indicated that the formation of lactones from carbohydrates was especially enhanced at 500 °C, and at 700 °C a slightly more diverse spectrum of products, including compounds, such as indenenes, naphthalenes are probably formed from certain cyclic aliphatic extractives, and fatty acids, was detected (Fig. 3). Table 3 shows the ratio aliphatic products to aromatic products obtained in our experiments. As a typical

trend, more aromatic products were formed under harsher conditions: 700 °C/20s > 700 °C/5s > 500 °C/20s > 500 °C/5s. Thus, as expected from the sample compositions (Table 1), the maximum portion of aliphatic compounds, 85-95 %, was detected for pulps ( $P_{\text{ref}}$  and  $P_{\text{HWE}}$ ) at 500 °C/5s and the minimum one, 50-55 %, for delignification feedstocks ( $B_{\text{ref}}$  and  $B_{\text{HWE}}$ ) at 700 °C/5s and 20s.

TABLE 3

It could be roughly considered that the compound groups A, C, F, L, and Y (Table 2) were mainly formed from carbohydrates, F and L from xylan, and G and S from lignin. Based on this assumption, the ratio carbohydrates to lignin under the pyrolysis conditions studied (Fig. 3) was 2.2 ( $B_{\text{ref}}$ ) and 2.3 ( $B_{\text{HWE}}$ ) (the corresponding values from the data in Table 1 were 3.1 and 3.5) and, on the other hand, xylan to lignin 1.3 ( $B_{\text{ref}}$ ) and 1.4 ( $B_{\text{HWE}}$ ) (the value evaluated from the data in Table 1, 0.6-1.1). However, due to many reasons, the straightforward estimation for the ratio carbohydrates to xylan was difficult; an example was the values 1.8 ( $P_{\text{ref}}$ ) and 2.7 ( $P_{\text{HWE}}$ ) (from Table 1, about 3.9 and 13.0, respectively).

Since a number of significant pyrolysis products could be measured simultaneously, a single pyrolysis run gave fingerprint data for characterization of feedstock materials. Of the main products, 3-hydroxy-2-penteno-1,5-lactone (I, the compound group L from hemicelluloses), 3-methyl-1,2-cyclopentanedione (II, C from hemicelluloses), furfural (III, F from xylan), levoglucosan (IV, A from cellulose), 4-allylsyringone (V, S from syringyl lignin), and isoeugenol (VI, G from guaiacyl lignin) are commonly found in pyrolysates (Table 2 and Fig. 4). It was concluded that a correlation exists between the formation of a number of the products and the chemical composition of feedstock. In this case, for example, at 500 °C/5s and 700 °C/5s for  $B_{\text{ref}}$  and  $B_{\text{HWE}}$ , the GC peak area ratio (I+II+III+IV)/(V) (i.e., carbohydrates/lignin) was 14.3 and 9.6 (from Table 3.5 and 3.1) and that of (I+II+III+IV)/(V+VI) 5.7 and 3.2, respectively. At 500 °C/5s for  $B_{\text{ref}}$  and  $B_{\text{HWE}}$ , the corresponding ratio (I+III)/(V+VI) (i.e., xylan/lignin) was 4.2 and 6.2 (from Table 1, about 0.6 and 1.1), respectively.

FIGURE 4

Based on these preliminary results, this fast pyrolysis method seemed to offer a potential tool for feedstock characterization. However, it is evident that for obtaining a good correlation (i.e., the determination of relevant factors) between the pyrolysis and chemical composition data, a wide range of experiments within the same feedstock type is necessary. In this method, practical information was obtained by using the concentration (i.e., GC peak area) ratios of the selected pyrolysis products, thus eliminating the need to measure their absolute concentrations. In contrast, another approach would be to use only a specific single compound for this purpose; however, in this case, to obtain repeatable results, the knowledge about its absolute concentration is required.

#### 4. Conclusions

Today, one of the most promising biorefinery techniques is based on hot-water extraction, by which wood chips are treated and partially solubilized prior to sulfur-free alkaline pulping. In

this study, according to this integrated biorefinery concept, birch sawdust from hot-water extraction and delignification have been pyrolyzed (at 500 °C and 700 °C for 5 s and 20 s) to create novel data on condensable low-molar-mass pyrolysis products obtained from these feedstocks and, on the other hand, on possibilities for developing a rapid characterization method for lignocellulosics. In this case, the hydrolysates contained significant amounts of acetic acid, xylose (together with xylose oligomers), and low-molar-mass lignin, which can be utilized in different biorefinery processes.

The composition of feedstock materials as well as pyrolysis conditions have a clear effect on the composition of condensable pyrolysis products, and the characteristic fragmentation patterns for each differently-treated feedstock can be detected. Thus, the effects of the main constituents (cellulose, hemicelluloses, and lignin) in the feedstock materials on the distribution of pyrolysis products are typically seen; lignin-containing materials (untreated and hot-water-extracted sawdust) under harsher pyrolysis conditions result in the pronounced formation of aromatics, whereas aliphatic products can be principally obtained under milder pyrolysis conditions from carbohydrates-containing materials (especially those after delignification).

The pyrolysis experiments also clearly indicate that a simultaneous gas-chromatographic determination of the main low-molar-mass pyrolysis products offers detailed information about the chemical composition of feedstock materials. This finding provides a good basis for further development of a feasible characterization method for lignocellulosics.

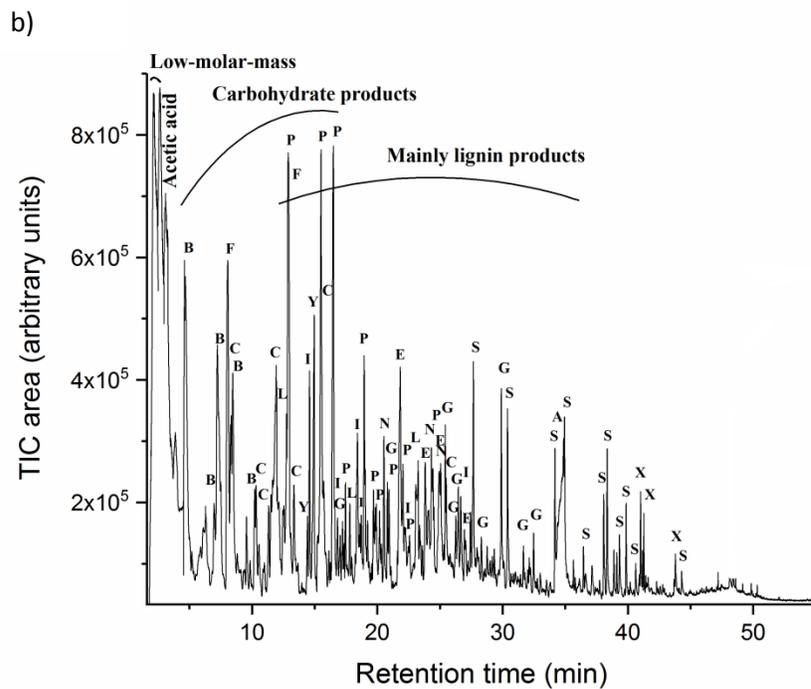
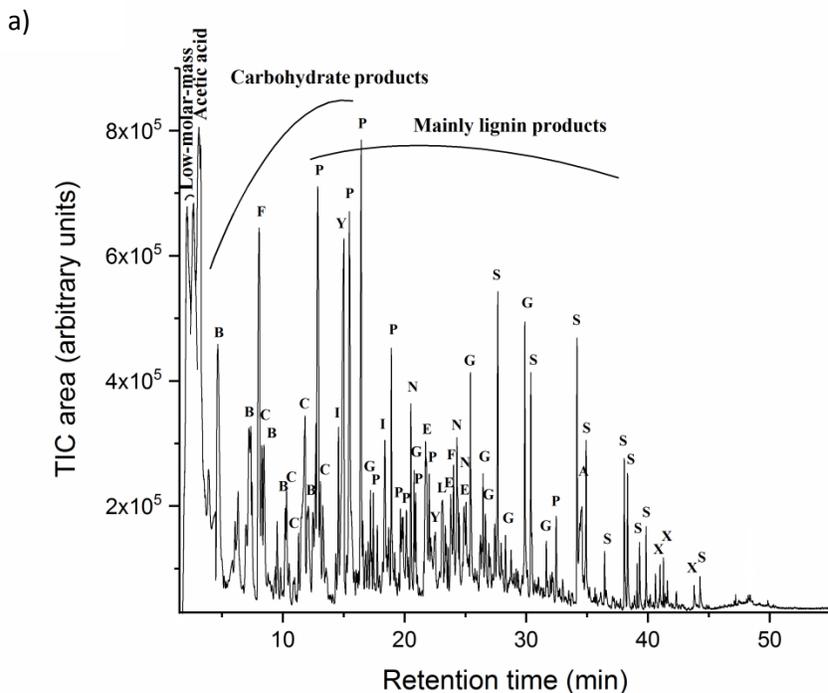
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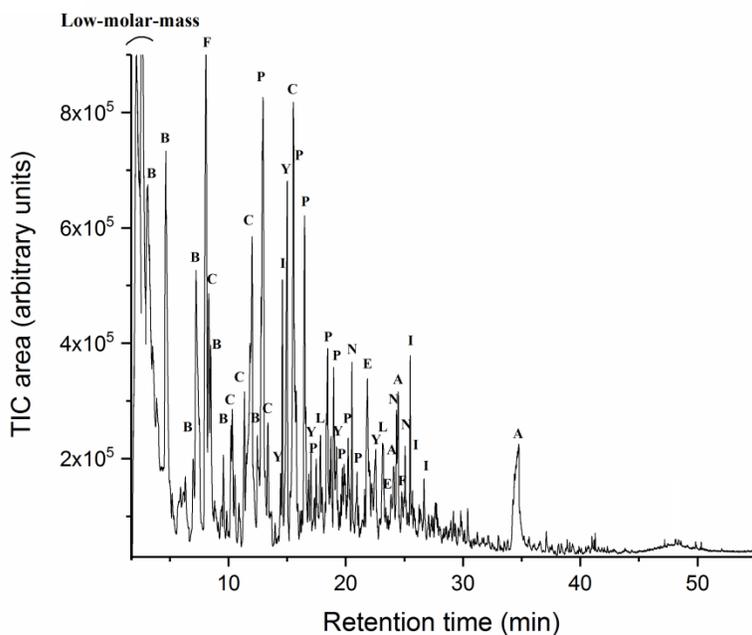
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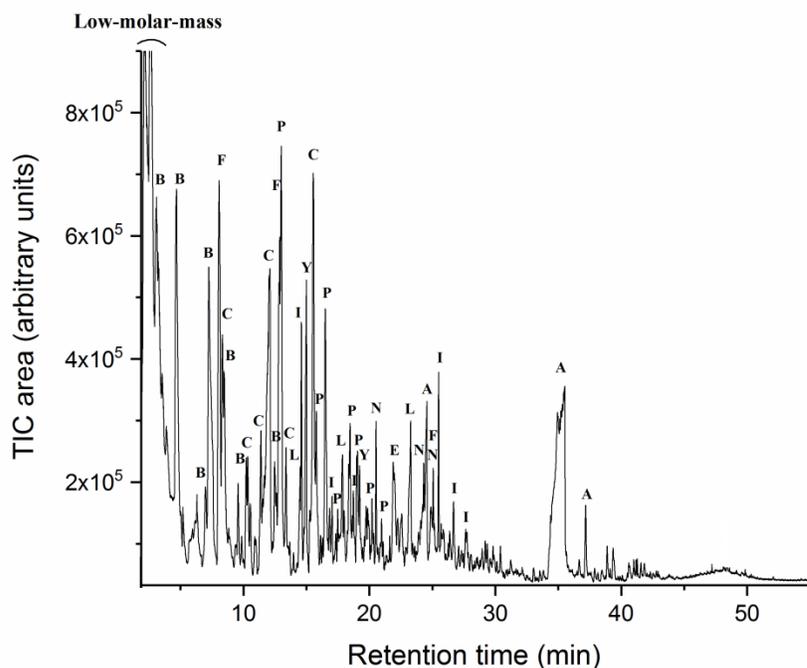
**Fig. 1.** The main products formed in the pyrolysis experiments (700 °C and 20 s) with untreated (a) and hot-water-extracted (b) birch sawdust. Letters indicate compound groups to which identified products belong: A (anhydrosugar derivatives), B (benzene derivatives), C (cyclopentenone derivatives), E (catechol and benzenediol derivatives), F (furan derivatives), G

(guaiacol derivatives), I (indene derivatives), L (lactone derivatives), N (naphthalene derivatives), P (phenol derivatives), S (syringol derivatives), X (fatty acids derivatives), and Y (pyrone derivatives).

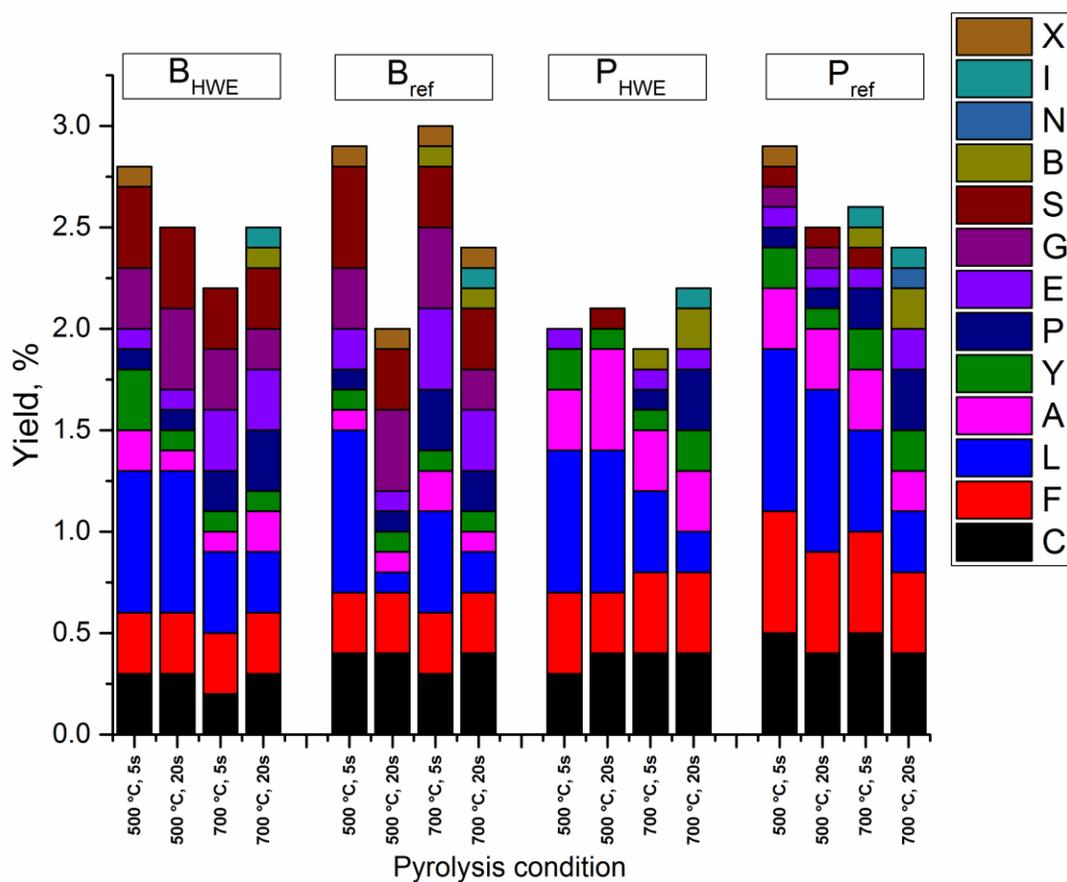
a)



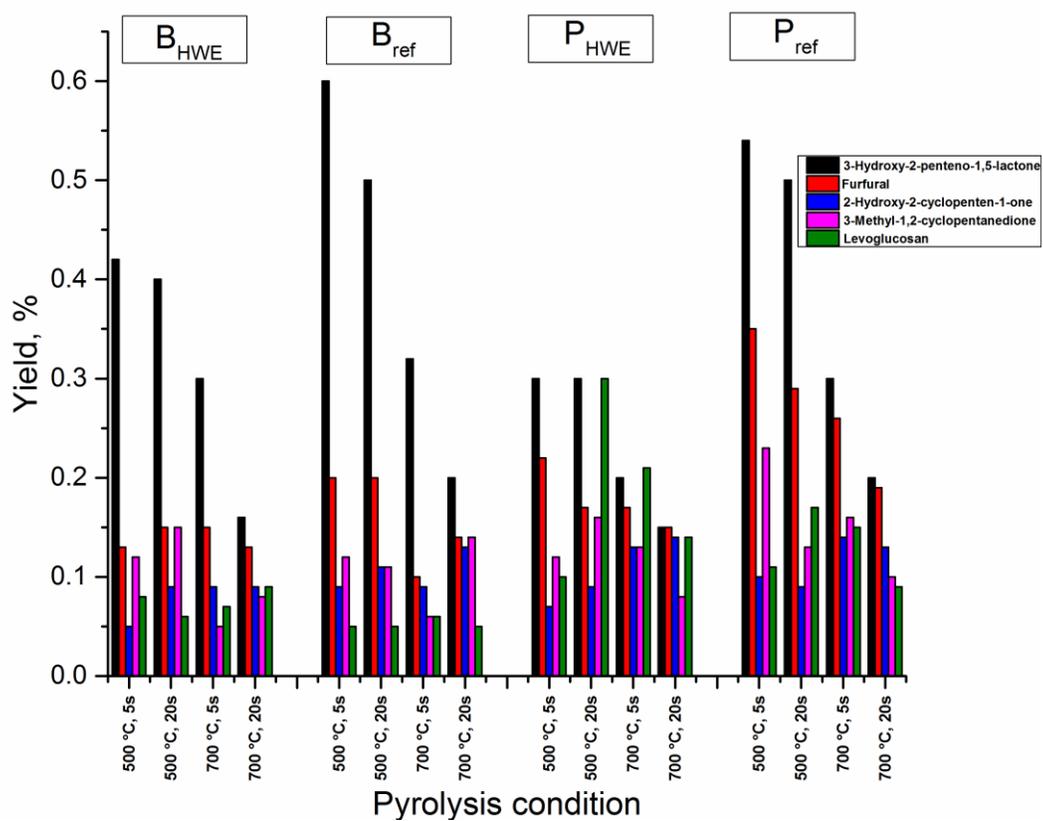
b)



**Fig. 2.** The main products formed in the pyrolysis experiments (700 °C and 20 s) with soda-AQ-delignified pulps of untreated (a) and of hot-water-extracted (b) birch sawdust. For the letter symbols, see Fig. 1.



**Fig. 3.** Effect of pyrolysis temperature and residence time on yields of various product groups. For the letter symbols, see Fig. 1.



**Fig. 4.** Effects of pyrolysis temperature and residue time on yields of prominent pyrolysis products.

**Table 1**

Chemical composition of the initial and differently-treated birch sawdust (% of the sample<sup>a</sup> dry solids)

Components	B <sub>HWE</sub>	B <sub>ref</sub>	P <sub>HWE</sub>	P <sub>ref</sub>
Carbohydrates <sup>b</sup>	72.7	67.5	88.7	91.5
Arabinose	0.1	0.4	-	-
Galactose	0.6	1.0	1.0	0.8
Glucose	60.8	43.4	80.6	66.8
Mannose	1.0	1.4	0.3	0.4
Xylose	10.2	21.3	6.8	23.5
Lignin	20.7	22.1	0.8	2.1
Klason	18.2	17.6	0.2	1.2
Acid-soluble	2.5	4.5	0.6	0.9
Extractives	2.8	2.9	0.7	0.6
Others	3.8	7.5	9.8	5.8
Total	100.0	100.0	100.0	100.0

<sup>a</sup> B<sub>HWE</sub> and B<sub>ref</sub> refer to hot-water-extracted and untreated sawdust, respectively, and P<sub>HWE</sub> and P<sub>ref</sub> refer to the soda-AQ-delignified pulps of hot-water-extracted and untreated sawdust, respectively.

<sup>b</sup> Monosaccharide units are presented as their anhydro forms.

**Table 2**

The main products formed in the pyrolysis experiments with differently-treated birch sawdust

Product	Retention time (min)	Group symbol
Anhydrosugars		A
1,4:3,6-Dianhydro- $\alpha$ -D-glucopyranose	24.0	
1,6-Anhydro- $\beta$ -D-glucopyranose (levoglucosan) *	34.5	
Benzene derivatives		B
Toluene *	4.6	
<i>o</i> -Xylene *	7.3	
Cyclopentenone derivatives		C
Cyclopent-2-en-1-one *	8.3	
2-Methylcyclopent-2-en-1-one *	10.3	
2-Cyclopenten-1,4-dione	11.2	
2-Hydroxycyclopent-2-en-1-one	11.8	
3-Methyl-1,2-cyclopentanedione *	15.4	
Catechol derivatives		E
1,2-Dihydroxybenzene (catechol) *	21.7	
1,2-Dihydroxy-3-methylbenzene *	23.7	
1,2-Dihydroxy-3-methoxybenzene *	24.3	
1,2-Dihydroxy-4-methylbenzene	24.8	
1,4-Dihydroxy-2,5-dimethylbenzene	26.9	
Furan derivatives		F
Furfural (furan-2-carbaldehyde) *	8.0	
5-Methylfurfural *	12.8	
2,5-Furandicarboxaldehyde *	19.1	
5-(Hydroxymethyl)furfural *	24.7	
Guaiacol derivatives		G
2-Methoxyphenol (guaiacol) *	17.2	
2-Methoxy-4-methylphenol *	20.7	
4-Ethenyl-2-methoxyphenol	25.4	
2-Methoxy-4-(prop-2-en-1-yl)phenol (eugenol) *	26.4	
2-Methoxy-4-(prop-1-en-1-yl)phenol (isoeugenol) *	28.3	
Indene derivatives		I
1 <i>H</i> -Indene *	14.6	
1-Methyl-1 <i>H</i> -indene	18.4	
2,3-Dihydro-1 <i>H</i> -inden-1-one	25.6	
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 *	17.8	
1-Hydroxy-3,6-dioxabicyclo[3.2.1]octan-2-one	23.2	
Naphthalene derivatives		N
Naphthalene *	20.5	

1-Methylnaphthalene	24.3	
Phenol derivatives		P
Phenol *	12.9	
2-Methylphenol *	15.5	
4-Methylphenol *	16.4	
2,4-Dimethylphenol	18.9	
3,5-Dimethylphenol *	19.7	
4-(Prop-2-en-1-yl)phenol	24.5	
Syringol derivatives		S
2,6-Dimethoxyphenol (syringol) *	27.6	
4-Allyl-4-methyl-2,6-dimethoxyphenol	30.3	
1-(4-Hydroxy-3-methoxyphenyl)ethan-1-one *	32.4	
4-Ethenyl-2,6-dimethoxyphenol	34.1	
4-Allyl-2,6-dimethoxyphenol (4-allylsyringol) *	34.9	
4-Hydroxy-3,5-dimethoxybenzaldehyde	38.3	
1-(4-Hydroxy-3,5-dimethoxyphenyl)ethanal	39.3	
4'-Hydroxy-3',5'-dimethoxyacetophenone *	39.8	
3-(4-Hydroxy-3,5-dimethoxyphenyl)prop-2-enal	44.3	
Pyrone derivatives		Y
Pyran-2-one	14.5	
3-Hydroxy-2-methylpyran-4-one *	19.3	
3,4-Dihydro-6-methyl-2 <i>H</i> -pyran-2-one	22.4	
Fatty acid derivatives		X
Hexadecanoic acid	40.9	
9,12-Octadecadienoic acid	43.8	

\*Confirmed by the pure standards.

**Table 3**

Percentage ratio aliphatic compounds/aromatic compound in pyrolysates (for abbreviations, see Table 1)

Condition	B <sub>HWE</sub>	B <sub>ref</sub>	P <sub>HWE</sub>	P <sub>ref</sub>
500 °C/5 s	67/33	63/37	95/5	87/13
500 °C/20 s	62/38	65/35	95/5	84/16
700 °C/5 s	52/48	50/50	89/11	81/19
700 °C/20 s	50/50	56/44	73/27	71/29