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ORIGINAL

Fast pyrolysis of hot-water-extracted and delignified Norway spruce (*Picea abies*) sawdust by Py–GC/MS

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Abstract

The thermochemical behavior of Norway spruce (*Picea abies*) sawdust as such and after various chemical treatments (hot-water extraction, delignification, and hot-water extraction followed by delignification) was investigated by analytical pyrolysis–gas chromatography–mass spectrometry. In each case, the yields of major GC-amenable condensable products were semi-quantitatively measured, and the individual compounds were classified into several compound groups. The formation of these groups from feedstock samples with varying mass portions of their structural constituents (carbohydrates and lignin) was determined at 500 °C and 700 °C with a residence time 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 uncover new biorefinery possibilities to produce bio-oils, for example, enriched either with aliphatic or aromatic constituents.

Introduction

The main constituents of lignocellulosic materials consist of carbohydrates (cellulose and hemicelluloses) and lignin together with a minor proportion of extractives (Alén 2011a; Fengel and Wegener 1989; Saka 2001; Sjöström 1993). Pyrolysis is one of the thermochemical conversion methods of biomass carried out in the complete or near complete absence of an oxidizing agent (air or oxygen) typically at 500–700 °C to provide complex fractions of gases, condensable liquids (tars), and char (solid residue)

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(Alén 2011b). It has been established that during pyrolysis, each constituent shows a unique thermochemical behavior (Alén et al. 1996, 2002; Anca-Couce 2016; Bai and Kim 2016; Kan et al. 2016; Kawamoto 2017; Lappi 2012; Lédé 2012; Patwardhan 2010; Piskorz et al. 1986; de Wild 2015; Yang et al. 2007; Zhou et al. 2017). In previous experiments, for developing novel biorefinery concepts, the fast pyrolysis of hot-water-extracted and pulped hardwood sawdust was studied (Ghalibaf et al. 2017). However, the lignin and hemicelluloses present in softwoods differ chemically from those in hardwoods (Alén 2011a). Additionally, softwoods generally contain more lignin [25–30% of dry solids (DS)] and less hemicelluloses (25–30% of DS) than hardwoods; the content of hardwood lignin and hemicelluloses are usually in the range of 20–25% and 30–35% of DS, respectively. Based on these facts, the thermal behavior of softwoods and hardwoods can be expected to be somewhat different, even under mild pyrolytic conditions. It can also be concluded that a better understanding of these specific thermochemical differences will be of benefit to the further development of processes that utilize renewable wood-derived resources for producing particularly condensable liquids through pyrolysis.

The primary aim of this study was to apply fast pyrolysis to untreated and hot-water-extracted (HWE) ("autohydrolyzed") Norway spruce (*Picea abies*) sawdust as well as the soda-anthraquinone (AQ)-cooked pulps originated from these untreated and treated feedstocks by analytical pyrolysis–gas chromatography–mass spectrometry (Py–GC/MS). In each case, the ultimate goal was to study the selective formation of specific product groups. However, it is known that in practice, soda-AQ process is mainly used for non-woods and hardwoods due to the less reactive softwood lignin against this sulfur-free process (Alén 2011b; Feng and Alén 2001; Finell and Nilsson 2004; Lehto et al. 2016). On the other hand, it has been shown that the autohydrolysis stage of wood may facilitate the lignin removal in the subsequent alkaline delignification, and the sulfur-free cooking is possible (Bajpai 2012; Hendriks and Zeeman 2009; Lehto et al. 2016). In this research, the aim was a high removal of material (mainly hemicelluloses) during the hot-water-extraction phase and a low degree of delignification of the soda-AQ cooking phase; this approach resulted in a relatively narrow ratio of differently treated carbohydrates to lignin of the HWE feedstock and pulp (i.e., with a high content of residual lignin). Hence, in this study, the explorative research point of view was primarily emphasized.

The main idea behind this study was to evaluate the suitability of this rapid analytical method for detecting chemical changes that were taking place in the feedstocks during the different chemical treatments performed (i.e., through their pyrolysis product profile) and, on the other hand, with respect to biorefinery aspects to assess the relative suitability of these alternative feedstocks for pyrolytic valorization. In this phase, as was also the case for the corresponding hardwood samples (Ghalibaf et al. 2017), only the straightforward formation of condensable products was investigated.

Materials and methods

Feedstock materials and their analyses

Untreated (S_{ref}) and HWE (S_{HWE}) Norway spruce (*Picea abies*) sawdust (< 5 mm) as well as soda-AQ-cooked pulps of untreated (P_{ref}) and of HWE (P_{HWE}) spruce feedstocks were investigated. Hot-water extraction was performed in three stages (Lehto et al. 2016): (1) at 160 °C for 40 min, (2) at 170 °C for 60 min, and (3) at 180 °C for 180 min.

The soda-AQ cooking 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 cooking conditions were as follows: alkali (NaOH) charge 20% on oven-dried (o.d.) feedstock, AQ charge 0.1% on o.d. feedstock, cooking temperature 170 °C, cooking time 30 min, and liquor-to-feedstock ratio 5 L/kg. At the end of each cooking, 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 into a nylon-woven fabric bag. The pulp obtained was thoroughly washed with water, and the amount of removed organic material was calculated on the basis of o.d. initial and cooked feedstock; yields for P_{ref} and P_{HWE} were, respectively, 60.0% and 64.9% of material charged into reactors.

For the chemical analyses, air-dried untreated and HWE 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 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, The Netherlands), and drying was finalized prior to weighing by means of a gentle nitrogen stream.

Acid hydrolysis of the extractives-free ground samples was performed according to TAPPI T249 cm-00 standard, and the resulting monosaccharides were analyzed as their per(trimethylsilyl)ated derivatives using a gas chromatography (GC) system as described elsewhere (Alén et al. 1984; Niemelä and Alén 1999).

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 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; the absorptivity value was 120 L/(gcm) (Swan 1965).

Pyrolysis experiments and product analyses

About 0.5 mg of samples was pyrolyzed in a quartz tube (3.0 cm × 1.0 mm inner diameter, between quartz wool) under an inert atmosphere in the heated interface 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 pyrolysis temperatures were 500 °C and 700 °C and in each case, the temperature was kept constant for both 5 s and 20 s. The GC conditions were the same as those applied earlier to a similar purpose (Ghalibaf et al. 2017). 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 proper interpretation of the mass spectra (based on the National Institute of Standards and Technology (NIST) mass spectral library) was used. Quantitative analysis was conducted according to an earlier study (Ghalibaf et al. 2017), so that pure compounds (the total number was 37) were used as external standards to relatively quantify all the 75 identified peaks from pyrolysis products (Py–GC/MS) by comparing the products to a set of standard samples of known concentration (Table S1 in Supplementary Material).

Results and discussion

Feedstocks

Chemical compositions of the spruce sawdust samples (i.e., S_{ref}, S_{HWE}, P_{ref}, and P_{HWE}) are presented in Table 1. The yield of hot-water extraction was about 72% of o.d. feedstock, indicating that about 90% of hemicelluloses (mono-, oligo-, and polysaccharides) and 10% of the initial lignin were removed by this treatment. In practice, this also meant that the hydrolyzate primarily contained mannose moieties from the principal softwood hemicellulose component, glucomannan, with a minor amount of xylose moieties from xylan; in contrast, the cellulose was rather stable during this treatment. Due to the hot-water extraction, the mass ratio of carbohydrates to lignin in the softwood matrix decreased from 2.0 to 1.6, whereas the corresponding mass ratio of aldohexose units (galactose, glucose, and mannose) to aldopentose units (arabinose and xylose) in the fraction of carbohydrates increased from 6.1 to 24.7. It can be concluded that the suitability of the soluble carbohydrates, as such or after further enzymatic hydrolysis, for the production of a wide range of platform chemicals is high, for example, by fermentation (Alén 2011b; Alvira et al. 2010; Cherubini 2010; Hörhammer et al. 2011; Ragauskas et al. 2006). Additionally, the main monosaccharide moiety, mannose, can also be converted into many potential chemicals (*e.g.,* mannitol and mannonic acid) by conventional chemical methods (Alén 2011b). Some attractive possibilities will be separately studied in forthcoming investigations.

The chemical composition data (Table 1) on pulps (i.e., $S_{\mathrm{ref}} \rightarrow P_{\mathrm{ref}}$ and $S_{\mathrm{HWE}} \rightarrow P_{\mathrm{HWE}}$) indicated that high carbohydrate losses were obtained in the

Table 1 Chemical composition of the initial and differently treated spruce sawdust samples (% of the feedstock[a] dry solids)

Component	S^{a}_{ref}	S^{a}_{HWE}	P^{a}_{ref}	P^{a}_{HWE}
Carbohydrates[b]	60.6	59.2	76.1	61.8
Arabinose	1.4	–	0.7	–
Galactose	1.4	–	1.2	0.6
Glucose	40.0	55.9	61.3	59.9
Mannose	11.9	1.0	6.9	0.3
Xylose	5.9	2.3	6.0	1.0
Lignin	29.8	36.8	17.8	37.4
Klason	29.4	36.6	17.3	37.1
Acid-soluble	0.4	0.2	0.5	0.3
Extractives	1.2	4.0	0.5	0.8
Others	8.4	0.0	5.6	0.0
Total	100.0	100.0	100.0	100.0

[a] S_{ref} and S_{HWE} refer to untreated and HWE spruce sawdust, respectively, and P_{ref} and P_{HWE} refer to the soda-AQ-cooked pulps of untreated and HWE spruce feedstocks, respectively

[b] Monosaccharide units are presented as their anhydro forms

beginning of the cooking, and delignification proceeded slowly (Lehto et al. 2016). This rather low selectivity meant that in the former case (i.e., $S_{ref} \rightarrow P_{ref}$), the approximate carbohydrate and lignin losses were, respectively, 25% and 64% of the initial amount, and in the latter case (i.e., $S_{HWE} \rightarrow P_{HWE}$), 32% and 34% of the initial amount, respectively. This finding also suggested, probably due to a more open structure of the HWE wood matrix, slightly higher reactivity of the carbohydrate fraction. On the other hand, highly prolonged hot-water extraction seemed to alter the structure of lignin in such a way that in this case, its dissolution was clearly hindered during the subsequent alkaline pulping (Lehto et al. 2016). Additionally, it should be pointed out that a more reactive, low-molar-mass fraction of lignin was already partly dissolved during hot-water extraction. The mass ratio of carbohydrates to lignin in the wood matrix increased during delignification from 2.0 to 4.3 ($S_{ref} \rightarrow P_{ref}$) and from 1.6 to 1.7 ($S_{HWE} \rightarrow P_{HWE}$).

During alkaline pulping, the most significant alkali-catalyzed degradation reactions of carbohydrates include the well-known peeling reactions of reducing end units and the alkaline hydrolysis of glycosidic bonds between monosaccharide moieties in carbohydrate chains, which results in the formation of numerous hydroxy monocarboxylic and hydroxy dicarboxylic acids (Alén 2011a; Alén et al. 1985; Niemelä 1990; Niemelä et al. 1985; Sjöström 1991, 1993). The recovery and utilization of these hydroxy acids will be separately studied and are not reported here. Additionally, the pyrolysis of black liquors from the sulfur-free delignification (Lehto et al. 2016) to produce low-molar-mass aromatics will be investigated in detail in forthcoming studies.

It is evident that all these chemical treatments with spruce sawdust samples were carried out according to the principles of integrated biorefinery concepts (i.e., to integrate a hot-water extraction stage into sulfur-free chemical pulping) and led to various samples, in which the mass ratio of carbohydrates to lignin was at three different levels: 1.6 (S_{HWE} and P_{HWE}), 2.0 (S_{ref}), and 4.3 (P_{ref}). When comparing the fractions of lignin with each other (as well as those of carbohydrates), their structural chemical composition might be varied to some extent. However, it could generally be concluded that these samples were very suitable for the purpose of the present pyrolysis investigation.

Pyrolysis of spruce samples

It was possible to resolve most of the main hydrophilic and lipophilic compounds—about 75 compounds were identified—released from spruce samples during pyrolysis by the chromatographic system (GC/MS) applied. Pyrolysis experiments under the same conditions resulted in reproducible results, and a typical pyrogram profile for each sample could be obtained; examples of different pyrograms are given in Figs. 1 and 2. It is generally known that the total amount of pyrolysis products that are normally recovered and identified from laboratory-scale pyrolysis is low (Lappi 2012). However, in spite of this, 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.

In this study, only the higher-molar-mass condensable products that were formed rather selectively from individual feedstock constituents were studied, thus excluding fixed gases and volatile low-molar-mass products generally characteristic for all the pyrolysates of lignocellulosics. For simplicity, the main GC-amenable pyrolysis products were classified into various compound groups (Table 2), and the formation of these monomer-containing fragments were determined in different cases. The postulated mechanisms for their formation from the main wood constituents have been shown in many investigations (Anca-Couce 2016; Kawamoto 2017; Lappi 2012; Lédé 2012; Patwardhan 2010; Piskorz et al. 1986). In general, it could be roughly concluded that the groups of anhydrosugar, cyclopentenone, furan, indene, lactone, and pyrone derivatives originated from carbohydrates and those of catechol and benzenediol, guaiacol, and phenol derivatives from lignin. The groups of other aromatics (benzene and naphthalene derivatives) were probably formed from all wood components.

Practical considerations

In the case of S_{ref}, pyrolysis times of 5 s and 20 s at 500 °C resulted in the highest pyrolysis yields (3.5–3.8%) similar to that obtained from S_{HWE} at 500 °C for 20 s (Fig. 3). Typically, the yield was found to decrease when the pyrolysis temperature increased from 500 to 700 °C. Additionally, as the general trend, pyrolysis yields were higher at both temperatures for undelignified sawdust than for pulps—at 500 °C for 5 s and 20 s: $S_{\mathrm{ref}} > S_{\mathrm{HWE}} > P_{\mathrm{ref}} > P_{\mathrm{HWE}}$ and at 700 °C for 5 s: $S_{\mathrm{HWE}} > S_{\mathrm{ref}} > P_{\mathrm{ref}} > P_{\mathrm{HWE}}$, and at 700 °C for 20 s: $S_{\mathrm{ref}} \sim S_{\mathrm{HWE}} \sim P_{\mathrm{ref}} > P_{\mathrm{HWE}}$—also indicating the overall treatment yield of samples 72% (S_{HWE}), 60% (P_{ref}), and 47% (P_{HWE}) of the initial S_{ref} DS (100%).

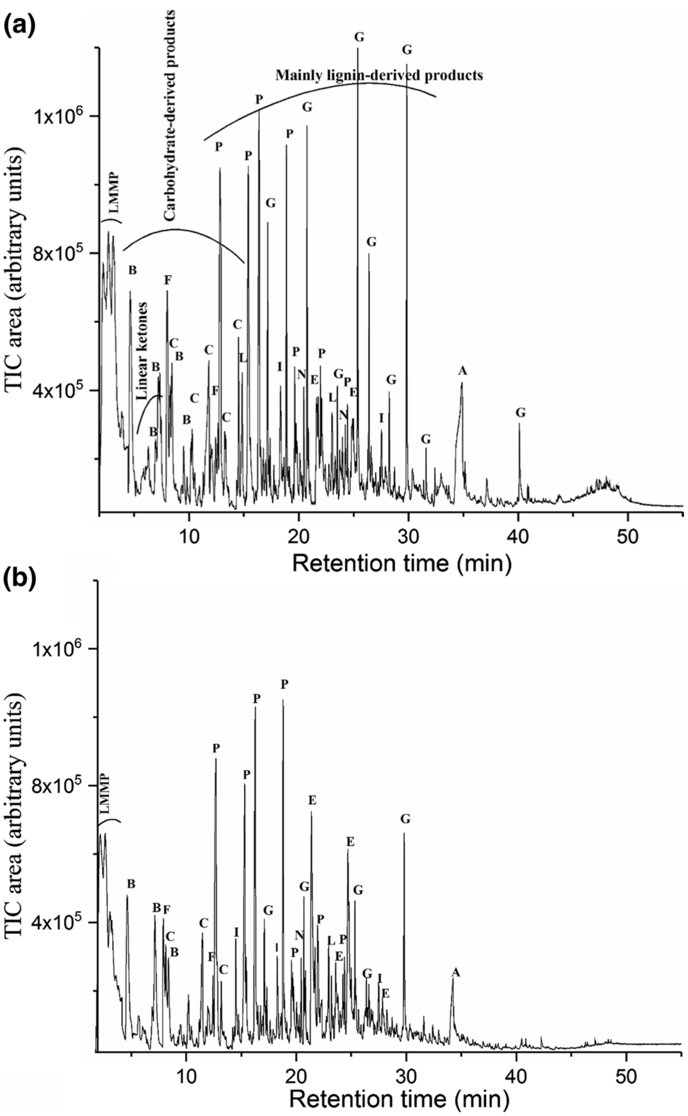

Fig. 1 Main products formed in the pyrolysis experiments (700 °C and 20 s) with untreated (**a**) and HWE (**b**) spruce sawdust. Letters indicate compound groups to which identified products belong: *A* (anhydrosugar derivatives), *B* (benzene derivatives), *C* (cyclopentenone derivatives), *E* (catechol and benzenediol derivatives), *F* (furan derivatives), *G* (guaiacol derivatives), *I* (indene derivatives), *L* (lactone derivatives), *N* (naphthalene derivatives), and *P* (phenol derivatives). LMMP (low-molar-mass products)

Under the pyrolysis conditions of this study, due to their different degradation rates from high-molar-mass wood polymers, varying amounts of carbohydrates- and lignin-derived low-molar-mass products were formed and could be partly detected in pyrolysates. Additionally, part of the devolatilized pyrolysis products might be selectively condensed before reaching the GC column. The results, for example,

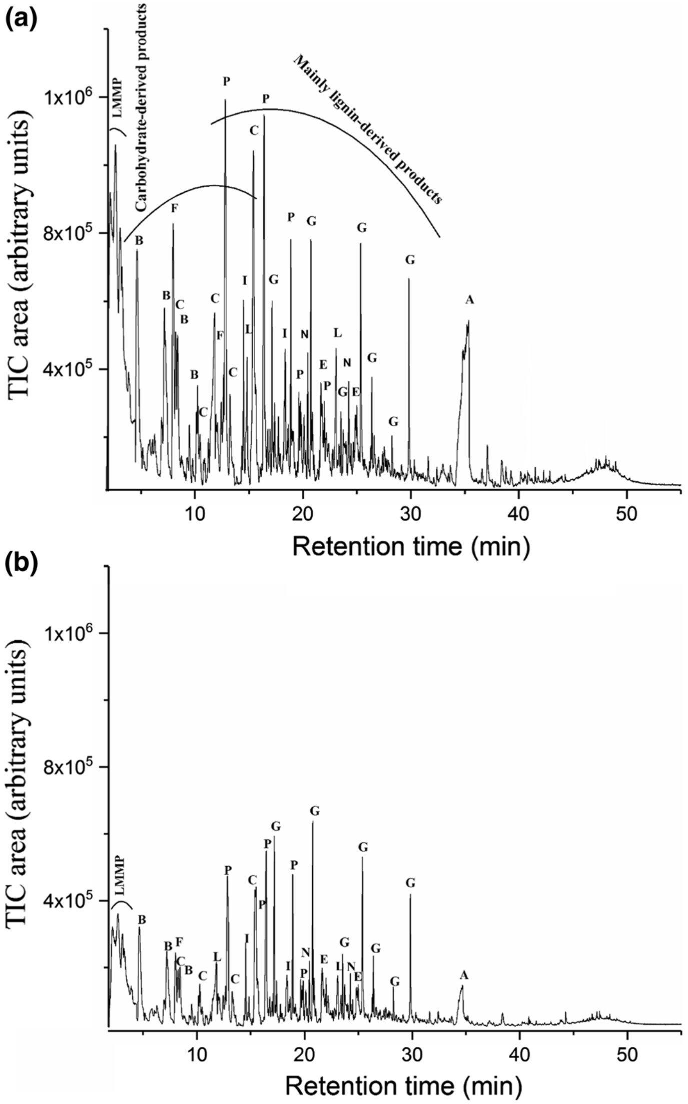

Fig. 2 Main products formed in the pyrolysis experiments (700 °C and 20 s) with the soda-AQ-delignified pulps of untreated (**a**) and of HWE (**b**) spruce feedstocks. For the letter symbols, see Fig. 1

suggested that the formation of lactones from carbohydrates, similarly to phenols from lignin, was enhanced when increasing the temperature from 500 to 700 °C. Table 3 shows the ratio of aliphatic products to aromatic products obtained in the experiments. As a typical trend, more aromatic products were formed under harsher conditions, especially at 700 °C for 5 s. Thus, as expected from the sample compositions (Table 1), the minimum and maximum portions of aliphatic compounds—33% and 58%, respectively—were detected for the pulps P_{HWE} and P_{ref}, respectively.

Table 2 Main products formed in the pyrolysis experiments with differently treated spruce sawdust

Product	Retention time (min)	Group symbol
Anhydrosugars		
1,6-Anhydro-*β*-D-glucopyranose (levoglucosan)*	34.5	*A*
Benzene derivatives		
Toluene*	4.6	*B*
Cyclopentenone derivatives		
Cyclopent-2-en-1-one*	8.3	*C*
Cyclohexanone*	9.9	
2-Methylcyclopent-2-en-1-one*	10.3	
2-Hydroxycyclopent-2-en-1-one	11.8	
3-Methyl-1,2-cyclopentanedione*	15.4	
Catechol derivatives		
Benzene-1,2-diol (catechol)*	21.7	*E*
3-Methylbenzene-1,2-diol*	23.7	
4-Methylbenzene-1,2-diol	24.8	
Furan derivatives		
Furfural (furan-2-carbaldehyde)*	8.0	*F*
5-Methylfurfural*	12.8	
2,5-Furandicarboxaldehyde*	19.1	
5-(Hydroxymethyl)furfural*	24.7	
Guaiacol derivatives		
2-Methoxyphenol (guaiacol)*	17.2	*G*
2-Methoxy-4-methylphenol*	20.7	
4-Ethenyl-2-methoxyphenol	25.4	
4-Propyl-2-methoxyphenol	26.3	
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		
1*H*-Indene*	14.6	*I*
1-Methyl-1*H*-indene	18.4	
Lactone derivatives		
5*H*-Furan-2-one	12.7	*L*
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		
Naphthalene*	20.5	*N*
1-Methylnaphthalene	24.3	
Phenol derivatives		
Phenol*	12.9	*P*
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	

Table 2 (continued)

*Confirmed by pure standards

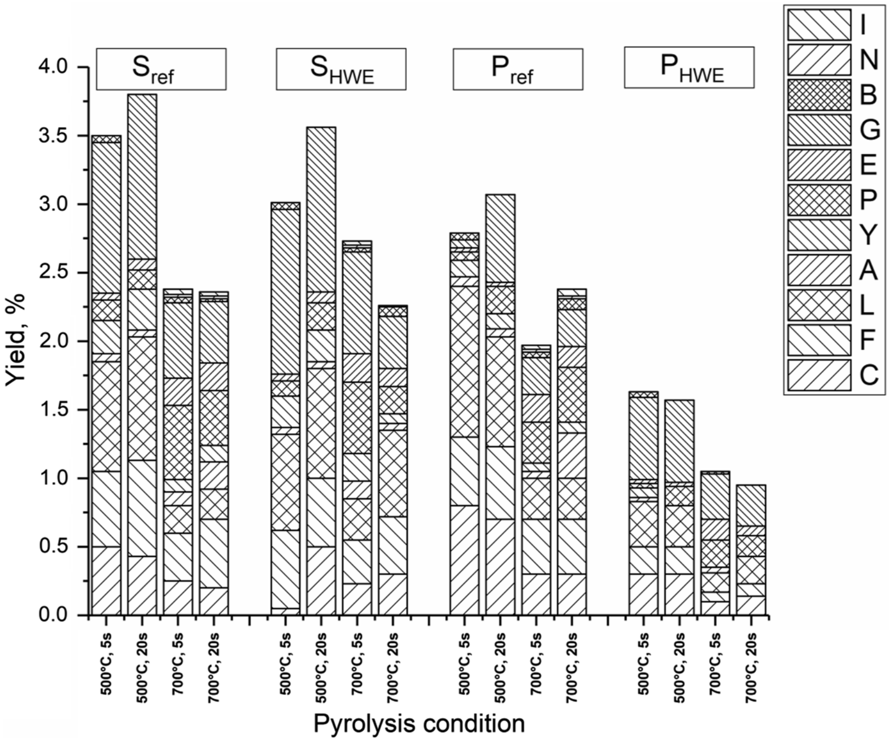

Fig. 3 Effects of temperature and residence time on yields of various product groups. For the letter symbols, see Fig. 1

Table 3 Percentage ratio aliphatic compounds/aromatic compounds in pyrolysates (for abbreviations, see Table 1)

Condition	S_{ref}	S_{HWE}	P_{ref}	P_{HWE}
500 °C/5 s	61/39	53/47	93/7	57/43
500 °C/20 s	63/37	58/42	72/28	51/49
700 °C/5 s	43/57	44/56	58/42	33/67
700 °C/20 s	54/46	65/35	61/39	45/55

It could be roughly considered that the compound groups A, C, F, L, and Y are mainly formed from carbohydrates, and E, G, and P from lignin (Table 2). Based on this assumption, the ratios of carbohydrates to lignin under the pyrolysis conditions at 500 °C for 20 s (Fig. 3) were 1.7 (S_{ref}), 1.4 (S_{HWE}), 3.2 (P_{ref}), and 1.0 (P_{HWE}); they indicated a rather good comparative correlation since the corresponding values from the data in Table 1 were 2.1, 1.6, 4.4, and 1.7, respectively. It was evident that hot-water extraction as well as delignification caused some chemical changes in the

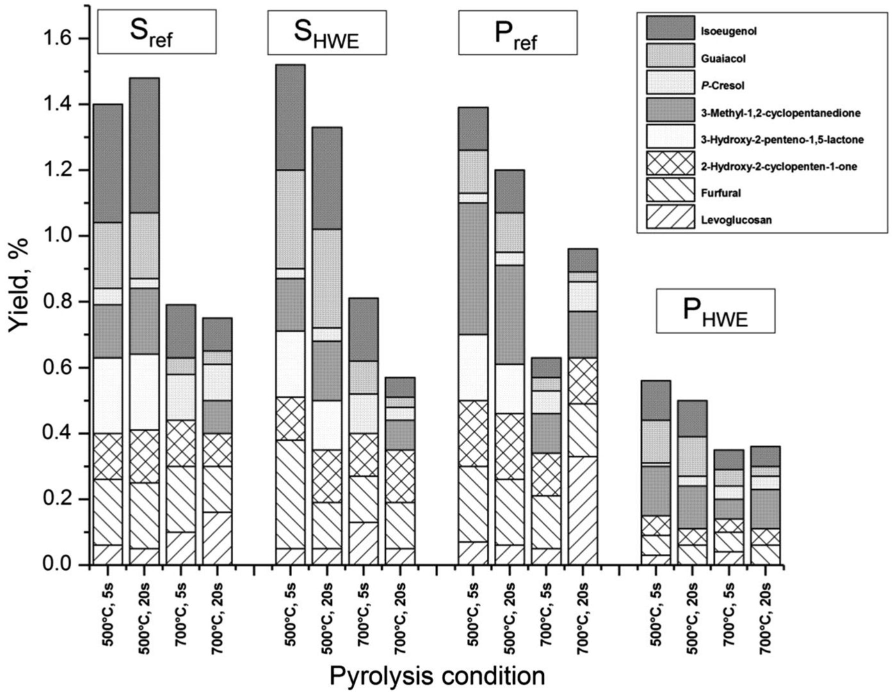

Fig. 4 Effects of temperature and residue time on yields of prominent pyrolysis products

fractions of carbohydrates and lignin in the feedstock matrix, thus partly reflecting also to some extent the formation of individual products during pyrolysis.

Since a number of prominent pyrolysis products could be measured simultaneously, a single pyrolysis run created fingerprint data for the characterization of feedstock materials. Of the selected main products (Fig. 4), 3-methyl-1,2-cyclopentanedione (I), 3-hydroxy-2-pentone-1,5-lactone (II), 2-hydroxy-2-cyclopenten-1-one (III), furfural (IV), and levoglucosan (V) are originated from carbohydrates, and isoeugenol (2-methoxy-4-propenylphenol, VI), guaiacol (2-methoxy phenol, VII), and *p*-cresol (4-methylphenol, VIII) from lignin. Furthermore, it was concluded that a correlation also exists between the formation of a number of these fingerprint products and the chemical composition of feedstocks. In this case, for example, at 700 °C for 5 s, the straightforward ratio (I + II + III + IV + V)/(VI + VII + VIII) (i.e., carbohydrates/lignin) was 1.3 (S_{ref}), 1.3 (S_{HWE}), 4.5 (P_{ref}), and 1.3 (P_{HWE}). However, it was possible to test many other ratios as well and representative correlations could be achieved, for example, when the ratio (I + III + IV + V)/(VI + VII) (→ 2.1 (S_{ref}), 1.4 (S_{HWE}), 4.6 (P_{ref}), and 1.8 (P_{HWE})) was used.

Softwoods generally contain less hemicelluloses than hardwoods (Alén 2011a). However, they differ not only in the content of total hemicelluloses but also in the percentages of individual hemicellulose constituents; in softwoods mainly glucomannan (containing glucose and mannose units) and in hardwoods mainly xylan (containing xylose units). In comparison with a previous study (Ghalibaf et al.

2017), these chemical compositions also have some influence on the distribution of pyrolysis products. For example, typically, three times higher amounts of the xylan-derived 3-hydroxy-2-penteno-1,5-lactone are formed from hardwood than softwood; the percentage amount of xylose in birch sawdust (i.e., in B_{ref}) is 21.3 (Ghalibaf et al. 2017) and 5.9 in S_{ref} (Table 1). Furthermore, anhydrosugars (e.g., levoglucosan) detected only in the pyrolysis of hexoses (i.e., D-glucose, D-mannose, and D-galactose) are formed 1.2 times more from S_{ref} than from B_{ref} at 500 °C for 5 s (the hexose portions are 53.3% and 45.9%, respectively). Additionally, the softwood lignins are principally formed from *trans*-coniferyl alcohol-type units (i.e., guaiacyl lignin), whereas hardwood lignins are mainly originated from almost equal amounts of *trans*-coniferyl alcohol-type and *trans*-sinapyl alcohol-type moieties (i.e., guaiacyl–syringyl lignin). Hence, for example, no syringols could be obtained from softwood pyrolysis.

Hence, based on these preliminary results, this pyrolysis technique also seemed to offer a potential tool for spruce-derived feedstocks. However, it was obvious that for obtaining a good correlation (i.e., the determination of relevant factors) between the pyrolysis and chemical composition data, a wider range of experiments within the same feedstock type would be necessary. In this method, practical information could be obtained by using the 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; in this case, to obtain repeatable results, the knowledge of its absolute concentration is needed.

Conclusion

One of the most promising biorefinery concepts is based on the hot-water extraction of fibrous feedstocks followed by sulfur-free pulping. In the present study, according to this integrated biorefinery approach, spruce sawdust from hot-water extraction and soda-AQ delignification were 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, to clarify possibilities for developing a rapid characterization method for lignocellulosics. The most important findings were as follows:

- During the first phase (hot-water extraction) with a high removal of carbohydrates, the hydrolysates contained a major amount of mannose moieties-containing material from the principal softwood component, glucomannan, and a minor amount of xylose moieties-containing material from xylan. This carbohydrate-derived fraction can be readily converted into many potential products by typical biochemical and chemical methods.
- In the second stage (a mild soda-AQ delignification) with a low removal of lignin, the black liquors contained fractions of degraded lignin and aliphatic carboxylic acids from carbohydrates. Their recovery and utilization for many purposes are possible.
- The compositions of feedstock materials (initial, HWE, and HWE followed by delignification) as well as pyrolysis conditions had a clear effect on the forma-

tion of condensable pyrolysis products, and the characteristic fragmentation patterns for each differently treated feedstock could be detected. The main compound groups were lactone and furan derivates from carbohydrates and guaiacol and phenol derivatives from lignin. For example, higher amounts of 3-hydroxy-2-penteno-1,5-lactone and 3-methyl-1,2-cyclopentanedione were formed at 500 °C from the samples S_{ref} and P_{ref}, whereas levoglucosan was formed from S_{ref} and P_{ref} at 700 °C (20 s). Lignin-derived products were generated more readily at 500 °C (5 s and 20 s) from S_{ref} and S_{HWE}.

- Two treatment methods, such as hot-water extraction and soda-AQ delignification, resulted in the removal of carbohydrates and lignin in different amounts. This fact also had some effect on the ratio aliphatic compounds/aromatic compound in the pyrolysis product fraction. However, as a general trend, the relative portion of aromatic compounds was increased under harsher pyrolysis conditions (especially at 700 °C for 5 s). At 500 °C, the ratio of aliphatic compounds to aromatic compounds was 51–93/7–49, whereas at 700 °C, more aromatics were formed, and the corresponding ratio is 33–65/35–67.
- A simultaneous gas-chromatography determination of the main low-molar-mass fingerprint products offered detailed information about the chemical composition of feedstock materials. This finding provides a good basis for further development of a feasible characterization method for spruce-derived lignocellulosics.

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