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ANALYTICAL PYROLYSIS OF WOOD AND NON-WOOD MATERIALS FROM INTEGRATED BIOREFINERY CONCEPTS

BY

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Doctor of Philosophy

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ABSTRACT

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Wood and non-wood differ with respect to their anatomical, physical, and chemical properties, even among their species, resulting in different behaviors during thermal conversion. Hence, understanding the degradation of these feedstocks by pyrolysis is attractive to establish biorefinery possibilities for renewable resources. Additionally, biomass pretreatment technology plays an important role in many biorefinery processes. Therefore, an approach that integrates such pretreatment with pyrolysis offers an attractive, novel method for improving the end-product spectrum (e.g., enriched either with aliphatic or aromatic constituents). Furthermore, a rapid analytical method for biomass feedstocks characterization was preliminarily developed through their pyrolysis product profiles for detecting chemical changes that were taking place in these feedstocks during different chemical treatments.

In the primary stage of this research, the effect of pyrolysis conditions on the pyrolysis products of differently-treated feedstocks, from hot-water extraction ("autohydrolysis") and soda-anthraquinone (AQ) delignification was investigated. The further aim was to clarify the difference in the pyrolysis products of wood materials, including hardwood and softwood, with non-wood materials as well as the pretreatment impact on these feedstocks. Hence, the thermochemical behavior of woody silver birch (*Betula pendula*) and Norway spruce (*Picea abies*) sawdust, and non-woody okra (*Abelmoschus esculentus*) and miscanthus (*Miscanthus* x *giganteus*) stalks, 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). The formation of the pyrolysis products from feedstock samples with varying mass portions of the structural constituents (cellulose, hemicelluloses, and lignin) were determined at 500 ^{o}C and 700 ^{o}C at hold times of 5 s and 20 s. In all cases, major GC-amenable condensable products were measured semi-quantitatively and classified into several product groups. Additionally, the formation of pyrolysis products was found to be characteristically dependent on feedstock composition and pyrolysis conditions.

In the final stage of research, the main aim was to achieve a better understanding of the studies on lignocellulosic with respect to their main carbohydrate constituents (cellulose and hemicelluloses, including glucomannan and xylan) by the same instrument under the same pyrolysis conditions. Among the 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.

Keywords: Silver birch, Norway spruce, Okra, Miscanthus, Cellulose, Glucomannan, Xylan, Carbohydrates, Condensable products, Pyrolysis-gas chromatography

LIST OF ORIGINAL PUBLICATIONS

This thesis is covered by the following original publications, which are referred to in the text by Roman numerals (I-IV):

I Ghalibaf, M., Lehto, J., and Alén, R. (2017). Fast pyrolysis of hot-water-extracted and delignified silver birch (*Betula pendula*) sawdust by Py-GC/MS. *Journal of Analytical and Applied Pyrolysis*, 127C, 17–22.

II Ghalibaf, M., Lehto, J., and Alén, R. (2018). Fast pyrolysis of hot-water-extracted and delignified Norway spruce (*Picea abies*) sawdust by Py-GC/MS. *Wood Science and Technology*, *in press*, DOI: 10.1007/s00226-018-1064-4.

III Ghalibaf, M., Ullah, S., and Alén, R. (2018). Fast pyrolysis of hot-water-extracted and soda-AQ-delignified okra (*Abelmoschus esculentus*) and miscanthus (*Miscanthus* x *giganteus*) stalks by Py-GC/MS. *Biomass and Bioenergy*, 118, 172-179.

IV Ghalibaf, M., Doddapaneni, T.R.K.C., and Alén, R. (2018). Pyrolytic behavior of lignocellulosics-based polysaccharides. *Journal of Thermal Analysis and Calorimetry*, *in press*, DOI: 10.1007/s10973-018-7919-y.

Author's contribution

The experimental work and preliminary planning in publications I-IV were conducted by the author and written by Maryam Ghalibaf, Raimo Alén, Joni Lehto, Saleem Ullah, and Tharaka Rama Krishna C. Doddapaneni, who contributed as co-authors. The author, together with Joni Lehto in publications I and II and Saleem Ullah in publication III, performed the chemical analyses of the corresponding materials. Tharaka Rama Krishna C. Doddapaneni made the thermogravimetric analysis in publication IV.

SUPPORTING PUBLICATIONS

Ghalibaf, M., Lehto, J., and Alén, R. (2015). Fast pyrolysis of differently-treated birch (*Betula pendula*) sawdust by Py-GC/MSD. Biorefinery I: Chemicals and Materials from Thermo-Chemical Biomass Conversion and Related Processes, Engineering Conferences International, ECI Conference, Chaniá, Crete, Greece, 27 September- 2 October.

Ghalibaf, M., Lehto, J., and Alén, R. (2015). Fast pyrolysis of differently-treated spruce (*Picea abies*) sawdust by Py-GC/MSD. 6th Nordic Wood Biorefinery Conference, NWBC, Helsinki, Finland, 19-22 October.

Ghalibaf, M., Ullah, S., and Alén, R. (2016). Fast pyrolysis of differently-treated okra (*Abelmoschus esculentus*) stalks by Py-GC/MSD. 21st International Symposium on Analytical and Applied Pyrolysis. Pyro, Nancy, France, 9-12 May.

Alén, R., Lehto, J., Kumar, H., Ullah, S., Ghalibaf, M., and Halmemies, E. (2018). Chemical aspects on integrated biorefineries in the pulp industry. Baltic Conference Series, bcs18s, Stockholm, Sweden, 14-17 May.

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To my beloved son

PREFACE

The experimental work of this doctoral thesis was conducted in the Laboratory of Applied Chemistry at the Department of Chemistry, University of Jyväskylä, from March 2013 to May 2017.

I would firstly like to give my deepest thanks to my supervisor, Professor Raimo Alén. His guidance and knowledge in my research field has been a valuable resource for me as a student. Thank you for providing opportunities to explore my interests, enhance my understanding.

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مامان و بابا عزیزم دستتون را میبوسم و به شما افتخار میکنم.

Jyväskylä, July 2018

Maryam Ghalibaf

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LIST OF ABBREVIATIONS

5-HMF	5-hydroxymethylfurfural
5-MF	5-methyl-2-furaldehyde
A	anhydrosugar derivatives
AQ	anthraquinone
B	benzene derivatives
B_{HWE}	hot-water-extracted birch feedstock
B_{ref}	untreated birch feedstock
BSTFA	*N,O*-bis(trimethylsilyl)trifluoroacetamide
C	cyclopentenone derivatives
DGP	1,4:3,6-dianhydro-α-D-glucopyranose
DP	degree of polymerization
DTG	derivative thermogravimetric
E	catechol and benzenediol derivatives
F	furan derivatives
FF	2-furaldehyde
FID	flame ionization detector
FTIR	Fourier transform infrared spectroscopy
G	guaiacol derivatives
gal	galactopyranose
GC	gas chromatography
GC × GC	two-dimensional gas chromatography
glc	glucopyranose
GlcA	4-*O*-methylglucuronic acid
HPAEC	high performance anion exchange chromatography
HPLC	high performance liquid chromatography
HWE	hot-water-extracted
I	indene derivatives
IS	internal standard
L	lactone derivatives
LG	levoglucosan
LGO	levoglucosanone
LMMP	low-molar-mass products
Man	mannopyranose
M_{HWE}	hot-water-extracted miscanthus feedstock
M_{ref}	untreated miscanthus feedstock
MS	mass spectrometry
MWL	milled wood lignin
N	naphthalene derivatives
NIST	National Institute of Standards and Technology
NMR	nuclear magnetic resonance
o.d.	oven-dried

$\mathrm{O_{HWE}}$	hot-water-extracted okra feedstock
$\mathrm{O_{ref}}$	untreated okra feedstock
P	phenol derivatives
PAD	pulses amperometric detection
$\mathrm{PB_{HWE}}$	soda-AQ-delignified pulps of hot-water-extracted birch feedstock
$\mathrm{PB_{ref}}$	soda-AQ-delignified pulps of untreated birch feedstock
$\mathrm{P_{HWE}}$	soda-AQ-delignified pulps of hot-water-extracted feedstock
$\mathrm{PM_{HWE}}$	soda-AQ-delignified pulps of hot-water-extracted miscanthus feedstock
$\mathrm{PM_{ref}}$	soda-AQ-delignified pulps of untreated miscanthus feedstock
$\mathrm{PO_{HWE}}$	soda-AQ-delignified pulps of hot-water-extracted okra feedstock
$\mathrm{PO_{ref}}$	soda-AQ-delignified pulps of untreated okra feedstock
$\mathrm{P_{ref}}$	soda-AQ-delignified pulps of untreated feedstock
$\mathrm{PS_{HWE}}$	soda-AQ-delignified pulps of hot-water-extracted spruce feedstock
$\mathrm{PS_{ref}}$	soda-AQ-delignified pulps of untreated spruce feedstock
Py-GC/MS	pyrolysis-gas chromatography/mass spectrometry
Ref	untreated feedstock
RSD	relative standard deviation
S	syringol derivatives
SEC	size exclusion chromatography
$\mathrm{S_{HWE}}$	hot-water-extracted spruce feedstock
Sref	untreated spruce feedstock
TAPPI	Technical Association of the Pulp and Paper Industry
TGA	thermogravimetric analysis
TMCS	trimethylchlorosilane
TOF	time-of-flight
UV/Vis	ultraviolet/visible
X	fatty acid derivatives
Xyl	xylopyranose
Y	pyrone derivatives

1 INTRODUCTION

Forest lignocellulosic biomass materials represent a renewable and sustainable alternative for replacing fossil resources for manufacturing chemicals, energy, and other products [Goldstein, 1980; Kamm and Kamm, 2004; Kamm et al., 2006; FitzPatrick et al., 2010; Vertès et al., 2010; Alén, 2011a,b; Bridgwater, 2012; Pandey et al., 2015; Fang and Smith, 2016]. At the same time, an improved use of more versatile biomass resources is of great importance. For example, non-wood based raw materials, such as annual crops, can be also applied as an effective fibrous alternative to the decreasing forest wood resources in most developing regions [Alén, 2011b; Jahan et al., 2013]. Potential agricultural feedstocks, such as okra and miscanthus stalks, may offer interesting raw materials for lignocellulosic biorefineries. Okra is one of the most important vegetables and is widely grown, and its edible green seed pods play an essential role in the human diet by supplying carbohydrates, minerals, and vitamins [Çalişir et al., 2005; Kumar et al., 2013; García et al., 2014]. Post-harvest okra stalk residues have traditionally been an unused fraction of the total harvest, although their utilization for fiber in pulps [Atik, 2002; Jahan et al., 2012], composites [de Rosa et al., 2010], and ethanol production [Egüés et al., 2012] has been studied to some extent. In contrast, miscanthus is currently of great importance as a commercial energy crop in the sustainable production of biofuel products and chemicals due to its vast production worldwide and its high dry-matter yield [Lewandowski et al., 2000; Clifton-Brown et al., 2004; Hong et al., 2011; Le Ngoc Huyen et al., 2010; Brosse et al., 2012], together with the suitability of its fiber for paper production [Ververis et al., 2004; Bauer et al., 2012]. However, only a limited amount of data on the chemical composition of the pyrolysis vapors of okra and miscanthus stalks is still available.

In general, one of the most promising integrated biorefining approaches, mainly utilized for recovering valuable wood-derived carbohydrates, is based on different pretreatment processes [van Heiningen, 2006; Carvalheiro et al., 2008; Kumar et al., 2009; Zhu et al., 2010; Bajpai, 2012; Park and Kim, 2012; Alén, 2015; Lehto, 2015; Akhtar et al., 2016; da Silva et al., 2016; Kumar and Sharma, 2017], such as hot-water extraction conducted prior to delignification [Mendes et al., 2009; Chirat et al., 2012; Lehto and Alén, 2013; Martin-Sampedro et al., 2014; Alén, 2015; Lehto, 2015; Lehto et al., 2016; Loaiza et al., 2016]. Typically, using such pretreatments, it is possible to obtain potential by-streams and simultaneously to increase the reactivity of feedstock material resulting in enhanced pulping performance together with spent liquors having attractive chemical compositions. Hence, these kinds of integrated biorefinery concepts allow the efficient utilization of all major feedstock constituents (cellulose, hemicelluloses, and lignin) to be considered when planning target-oriented and economic processes for the manufacture of useful products from fibrous materials.

It can be concluded that all these types of fractionation possibilities also offer, for example, a wide range of potential feedstocks for thermochemical conversions [Hodgson et al., 2010, 2011; Konttinen et al., 2011; Butler et al., 2013; Collard and Blin, 2014; Mante et al., 2014; Mimmo et al., 2014; Jiang et al., 2016; Zhurinsh et al., 2017]. Furthermore, it has been established that the individual main polymeric components, carbohydrates (cellulose and hemicelluloses) and lignin, show their characteristic degradation behavior during heating [Shafizadeh, 1985; Piskorz et al., 1986; Alén et al., 1996, 2002; Bridgwater et al., 1999; Yang et al., 2007; Patwardhan, 2010; Lappi, 2012; Lédé, 2012; Custodis et al., 2014; de Wild, 2015; Anca-Couce, 2016; Bai and Kim, 2016; Kan et al., 2016; Kawamoto, 2017; Wang and Luo, 2017; Zhou et al., 2017]. For example, carbohydrates typically form anhydrosugars, furans, and monomeric phenols via dehydration, whereas lignin partially loses its aliphatic side chains and degrades. Thermochemical conversions of these 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 [Alén, 2011a]. For example, fast pyrolysis of lignocellulosics, carried out in the complete or near-complete absence of an oxidizing agent with a relatively high heating rate and a short reaction time, typically at 500-700 ^{o}C, represents a straightforward method that produces a particularly high yield of liquid biofuels and chemicals [Radlein et al., 1991; Bridgwater, 2002].

Despite the fact that the pyrolysis analysis of untreated wood is well documented, there are only a few studies dealing with pretreated wood and non-wood materials. These previous findings suggest the following: First, various biomasses could act differently during thermal conversion and pretreatment processes; second, biomass pretreatment could have a major influence on pyrolysis products. Hence, a comparative study between the integration of pretreated wood and non-wood with pyrolysis might be needed to assess the relative suitability of these alternative feedstocks for pyrolytic valorization with respect to biorefinery aspects. On the other hand, such a study might be needed to evaluate the suitability of this analytical pyrolysis as a rapid tool for detecting chemical changes that take place in the feedstocks during the different chemical treatments performed.

2 OBJECTIVES OF THE STUDY

Wood and non-wood behave differently during heating due to the types of cells, their percentages and arrangments. Hence, as a primary aim of the study, the effect of feedstocks as well as pyrolysis conditions on yield and composition of the condensable pyrolysis products was investigated by pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) in publications I-III. The observed phenomena in publications I-III were verified by the model compounds in publication IV. As a secondary aim of the study, the suitability of this technique as a rapid tool was studied. The experimental research originally planned could be divided into the following subtasks:

To determine the chemical composition of untreated and treated wood and non-wood feedstocks (publications I-III).

To study the pyrolytic behavior of differently-treated softwood and hardwood samples at 500-700 °C (prepared according to the "integrated forest biorefinery concepts") (publications I and II).

To investigate the pyrolytic behavior of differently-treated non-wood feedstocks at 500-700 °C (publication III).

To detect the influence of changes caused by hot-water treatment and soda-AQ delignification on the composition of pyrolysis products (publications I-III).

To investigate the pyrolytic and thermogravimetric behavior of the model substances cellulose and hemicelluloses (glucomannan and xylan) for outlining their main pyrolysis degradation paths (publication IV).

To develop a rapid potential tool for feedstock characterization by finding out correlations between the chemical composition and pyrolysis data (publications I-III).

3 CHEMICAL COMPOSITION OF LIGNOCELLULOSIC BIOMASS

Lignocellulosic wood and non-wood biomasses ascribe to plants or plant-based materials, which are a source of renewable energy and chemicals and are not used for food [Clifton-Brown et al., 2004; Dhyani and Bhaskar, 2017; Wang et al., 2017]. Hardwood- and softwood-derived feedstocks comprise whole trees and forest residues, while non-wood feedstocks are classified into agricultural residues, natural-growing plants, and crops according to their origin. In general, biomass feedstocks vary in appearance and reaction characteristics, although the chemical compositions are similar. All biomass feedstocks are comprised of cellulose, hemicelluloses, and lignin with minor amounts of extractives and inorganics (Table 1). The percentage of each constituent varies significantly among biomass feedstocks depending on the species (genetic differences), growing conditions, and presence of specialized tissues within individual plants [Alén, 2000, 2011a,c Huber et al., 2006].

TABLE 1 Chemical composition of wood and non-wood feedstocks (% of the feedstock dry solids) [Alén, 2011c]

Component	Hardwood	Softwood	Non-wood
Carbohydrates	70-80	65-75	50-80
Cellulose	40-45	40-45	30-45
Hemicelluloses	30-35	25-30	20-35
Lignin	20-25	25-30	10-25
Extractives	<5	<5	5-15
Proteins	<0.5	<0.5	5-10
Inorganics	0.1-1	0.1-1	0.5-10

Hardwoods have a higher proportion of hemicelluloses than softwoods, but softwoods have a higher proportion of lignin [Demirbaş, 2005; Alén, 2011b]. Hardwoods, softwoods, and non-woods differ not only in the content of total hemicelluloses but also in the percentages of individual hemicellulose constituents: in hardwoods and non-woods, mainly xylan (containing xylose units); in softwoods, mainly glucomannan (containing mannose and glucose units). Furthermore, it has been reported that hardwoods and softwoods are different due to their cell types as well as the different structure of hemicelluloses and lignin.

It has been realized that hardwoods and non-woods show some similarities. For example, hardwood fibers are shorter (short-core fibers), and many of the non-wood fibers are also similar to the short fiber in hardwoods, which also reflects the variations in the hemicellulosic composition in non-wood (consists of more xylan than glucomannan) [Ververis et al., 2004]. The degree of polymerization (DP) of non-wood hemicelluloses is lower than of wood hemicelluloses. Non-woods contain lower lignin contents compared with woods. The accumulation of carbohydrates and lignin decreases from the base to the top, which depends on various species of non-wood plants as well as the harvesting time [Atik, 2002; Shatalov and Pereira, 2002; Duldulao et al., 2010; Le Ngoc Huyen et al., 2010; Jahan et al., 2012].

3.1 Carbohydrates

3.1.1 Cellulose

Cellulose is a linear homopolysaccharide of cellobiose monomers composed of two β-D-glucopyranose moieties linked together by (1→4)-glycosidic bonds (Figure 1). Its DP is from 10,000 to 15,000, depending on molar masses (1.6 and 2.4 million Da, respectively) and molecular lengths (5.2 and 7.7 µm, respectively). Cellulose molecules consist of highly ordered (crystalline) or less-ordered (amorphous) regions, which results from intra- and intermolecular hydrogen bonding. The amorphous phase is thermally less stable than the crystalline phase. The stability of cellulose during different chemical treatments is also due to its high crystallinity [Kadla and Gilbert, 2000; Alén, 2011b].

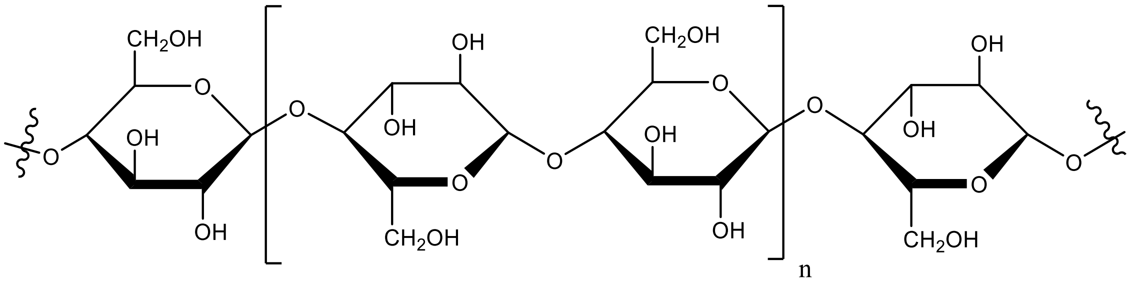


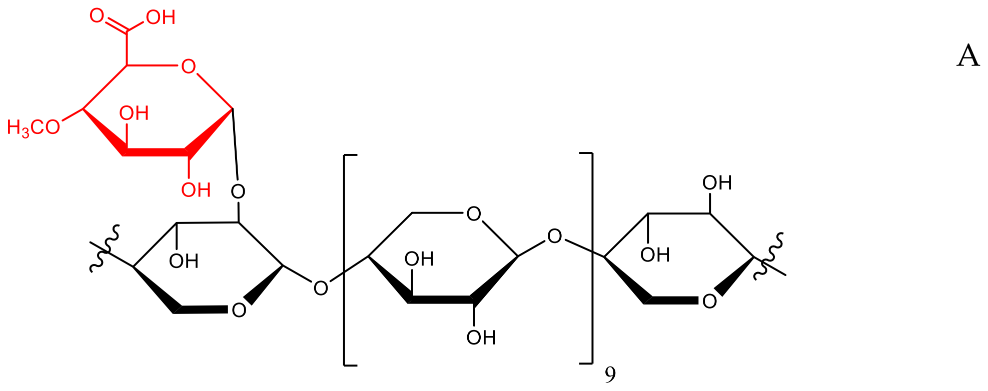
FIGURE 1 Structure of cellulose [Moulijn et al., 2015].

3.1.2 Hemicelluloses

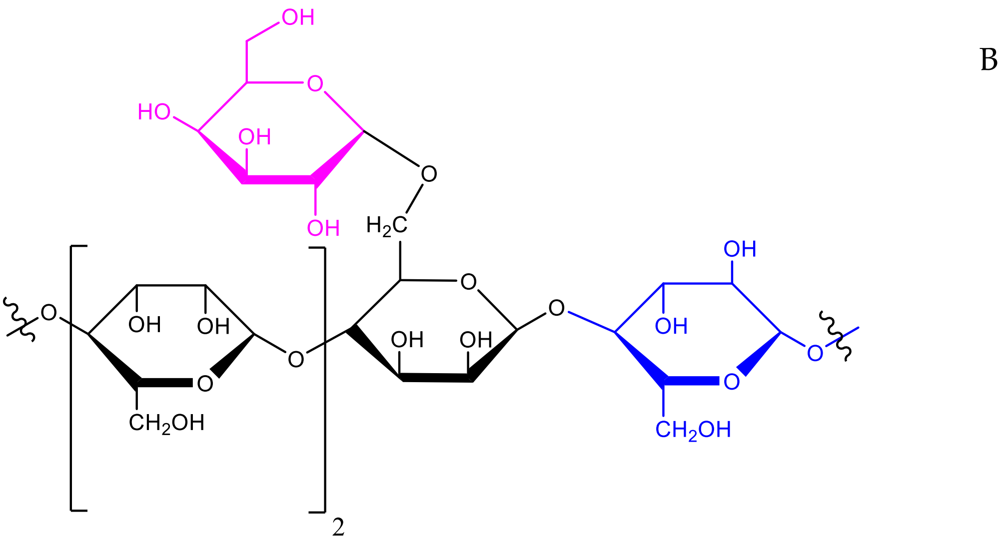
Hemicelluloses are heteropolysaccharides, whose composition depends on the plant species. The chemical and thermal stability of hemicelluloses is lower in comparison with cellulose due to lower DP (100-200) and lack of crystallinity [Alén, 2011c]. Xylose, mannose, glucose, galactose, and arabinose are the main monosaccharides moieties. These building blocks are hexoses (mannose, glucose, and galactose), pentoses (xylose and arabinose), and deoxyhexoses.

Hardwood hemicelluloses components primarily consist of xylan (glucuronoxylan) and galactoglucomannan (glucomannan), whereas softwood hemicelluloses mostly consist of glucomannan and arabinoglucuronoxylan (xylan) (Figure 2). The percentages of glucomannan and xylan vary in hardwoods and softwoods. In hardwoods, the content of xylan and glucomannan is 20-30 % and <5 % of the dry wood solids, respectively, whereas, in softwoods, the corresponding contents are 5-10 % and 15-20 % of the dry wood solids. Xylan and glucomannan also vary in the acetyl group content in hardwoods and softwoods. In hardwoods, the percentage of acetyl group content in xylan reaches 8-17 % of the total xylan, and glucomannan is not acetylated. In contrast, in softwoods, the percentage of acetyl group content in glucomannan reaches 6 % of the total glucomannan, and xylan is not acetylated. Additionally, softwood xylan contains much more uronic acid substituents than hardwood xylan [Sjöström and Westermark, 1999; Alén, 2011c].

Xylans contain a linear building unit of β-(1→4)-linked β-D-xylopyranose units with branches composing 4-*O*-methyl-α-D-glucuronic acid, α-D-glucuronic acid, and α-L-arabinofuranose, whose amounts are strongly dependent on the biomass species [Gröndahl et al., 2003; Saha, 2003]. Glucomannans contain a linear building unit of β-D-glucopyranose and β-D-mannopyranose with β-(1→4)—linkages and branches composing α-D-galactopyranose [Fengel and Wegener, 1989; Alén et al., 2011c]. Among the hemicelluloses, xylan has a lower thermal stability than glucomannan [Alén et al., 1996].



GlcA: Xyl 0.1: 1



Gal: Glc: Man 0.5: 1: 3.5

FIGURE 2 Partial chemical structures of A) xylan from hardwood and B) glucomannan from softwood (Xyl xylopyranose, 4-*O*-Me-GlcA 4-*O*-methylglucuronic acid, Man mannopyranose, Glc glucopyranose, and Gal galactopyranose) [Alén, 2011c].

3.2 Lignin

Lignin is a highly linked amorphous polymer consisting primarily of aromatic units that distinctly differ from the polysaccharide constituents of wood and non-wood biomass (Figure 3). Its chemical structure makes it different and more complex than the other macromolecular constituents of wood and non-wood [Alén, 2011c; Tian et al., 2016]. Lignins are biosynthetically derived mainly from three hydroxycinnamyl alcohol precursors (monolignols): *p*-coumaryl, coniferyl, and sinapyl alcohols, all of which are formed from D-glucose via the shikimic acid pathway. These intermadiates produce *p*-hydroxyphenyl, guaiacyl, and syringyl phenylpropanoid structural units, respectively, thus forming the main building blocks of the lignin polymer [Sjöström, 1993]. The units are attached by different ether and carbon-to-carbon bonds as follows: α-*O*-4 (phenolic and non-phenolic with methoxyl group), β-*O*-4 (phenolic) > β-*O*-4 (non-phenolic), and β-1 (phenolic and non-phenolic) > 5-5 (phenolic and non-phenolic). However, based on the product distribution, the breakage of the C_{β}-O bonds are overcome during depolymerization [Liu et al., 2011].

In general, lignin can be classified based on the type of its precursors into two major groups, such as guaiacyl-syringyl lignins (consists of hardwood lignins in almost equal amounts) and guaiacyl lignins (primarily consists of softwood lignins) [Azadi et al., 2013]. In contrast to wood, the secondary cell wall of grass plants characteristically contains core and non-core lignins [Bidlack et al., 1992]. The non-core lignin contains, for example, ferulic acid moieties that are usually esterified to carbohydrates and etherified to lignin, forming "ferulic bridges" [Atsushi et al., 1984; Scalbert et al., 1985; Sun et al., 2001; Buranov and Mazza, 2008; Miller et al., 2010]. Grass lignins are generally referred to as "guaiacyl-syringyl-type lignins" (like hardwood ones), even though they consist of somewhat unusual aromatic residues in significant amounts as well as a pronounced amount of *trans-p*-coumaryl alcohol units [Gellerstedt and Henriksson, 2008; Alén, 2011a]. However, acetylated lignin with a different degree of lignin acetylation is found in all non-woody plants, such as spirodienone, resinol, and phenylcoumaran. These categories may be divided into several subgroups as follows [Sarkanen and Hergert, 1971; Ibarra et al., 2007; del Río et al., 2008; Martínez et al., 2008; Villaverde et al., 2009; Bauer et al., 2012; Laskar et al., 2013]:

Guaiacyl lignins

- Standard guaiacyl lignins (softwood lignins)
- Lignins in *Pteridophyta*
- Lignins in *Cycadales*

Guaiacyl-syringyl lignins

- Standard guaiacyl-syringyl lignins (hardwood lignins)
- Lignins in coniferous *Gnetales*
- Tropical hardwood lignins
- Grass lignins
- Lignins in monocotyledons other than grasses

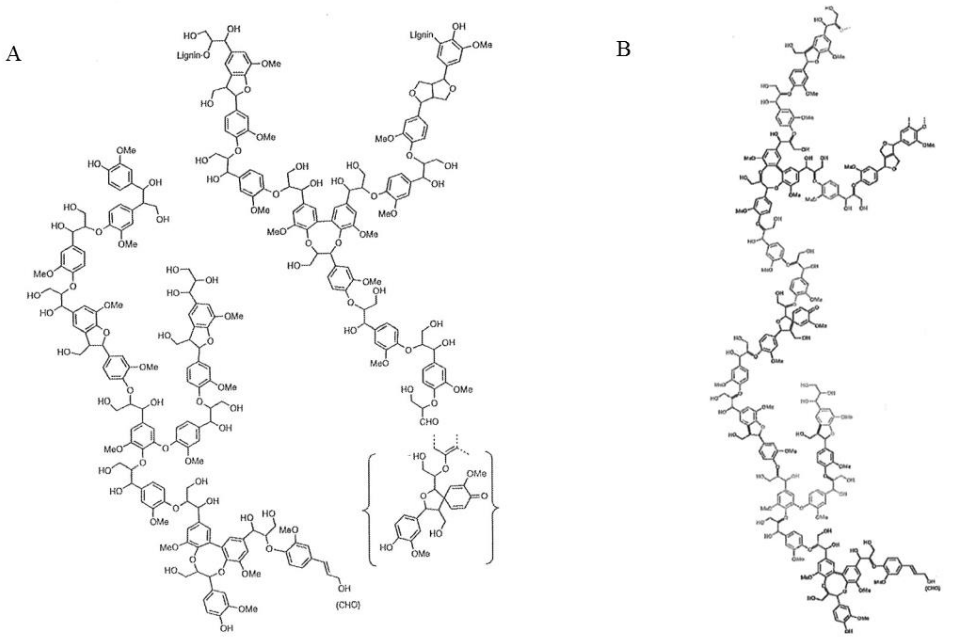


FIGURE 3 Suggested structures for softwood lignin A) illustrated by [Brunow et al., 1998] and B) illustrated by [Ralph et al., 2007].

3.3 Extractives and inorganics

Extractives are non-structural substances generated by plants and are mainly classified into hydrophobic aliphatic and hydrophilic phenolic compounds (Table 2). It is generally known that the composition of extractives varies widely from species to species, and the total amount of extractives as well as inorganic elements, even in a given species, may depend on growth conditions.

TABLE 2 Classification of organic extractives in wood [Alén, 2011c]

Aliphatic compounds	Phenolic compounds	Other compounds
Terpenes and terpenoids (e.g., resins acids and steroids)	Simple phenols Stilbenes Lignans	Sugars Cyclitols Tropolones
Esters of fatty acids (fats and waxes)	Isoflavones Flavonoids	Amino acids Alkaloids
Fatty acids	Condensed tannins	Coumarins
Alkanes	Hydrolysable tannins	Quinones

Hardwoods are composed mainly of fatty acids (60-90 %) [Ranzi et al., 2017]. Softwood plants are rich in resins, which consist mainly of 60-70 % terpenes together with fatty acids. Terpenes are hydrocarbons derived from isoprene monomers (×C_5H_8) as shown in Table 3. Phenolic compounds are more often found in ever-green plants than in annual crops.

TABLE 3 Classification of the main terpene types in wood tissues [Alén, 2000]

Name	Number of ($C_{10}H_{16}$) units	Molecular formula
Monoterpenes	1	$C_{10}H_{16}$
Sesquiterpenes	1.5	$C_{15}H_{24}$
Diterpenes	2	$C_{20}H_{32}$
Triterpenes	3	$C_{30}H_{48}$
Polyterpenes	>4	$>C_{40}H_{64}$

Inorganic compounds are present in low amounts, and they are important for the wood growth. Three common cations in wood are calcium, potassium, and magnesium, corresponding to about 80 % of the inorganic elements [Alén, 2000]. They are primarily present in the form of carbonates, silicates, phosphates, and oxalates [Blander et al., 1995; Rothpfeffer and Karltun, 2007].

4 THERMOCHEMICAL CONVERSION OF BIOMASS

4.1 General aspects

Thermochemical processes cause conversion of biomass into chemical products and energy, such as heat, electricity, and transport fuels. In general, thermochemical conversion of lignocellulosic biomaterials generates gases, condensable liquids, and solid products [Alén, 2011a]. The relative ratio of these products chiefly depend on the selected method and the specific reaction conditions. The methods are primaily classified as combustion, gasification, pyrolysis, and liquefaction [Konttinen et al., 2011], and the selection of method depends on certain factors, such as economics, the type of biomass feedstocks, and the desired products.

Gasification (above 900 °C with a long hold time) occurs in total or partial oxidation of the primary products. It results in the production of a mixture of gases for energy. In general, pyrolysis is the first stage in the gasification and combustion processes. In the formation of liquids, the liquefaction and pyrolysis processes are alike, although liquefaction occurs in higher pressures and reaction times (5-20 MPa, 30 min) and lower temperatures (300-350 °C).

4.2 Pyrolysis

Pyrolysis-based technologies can be described as direct thermochemical conversion methods of lignocellulosic biomass that takes place in the complete or near complete absence of an oxidizing agent (air or O_2) to provide complex fractions of gases, condensable liquids, and char [Alén, 2011a]. Traditional pyrolysis processes (slow pyrolysis) occur at 500-600 °C for long vapor residence times of 5-30 min to produce charcoal. However, fast pyrolysis processes carried out at 450-900 °C in a few seconds or less at a high heating rate of about 300 °C/min result in high yields of liquid platform chemicals.

4.2.1 Apparatus

4.2.1.1 Analytical (laboratory-scale) instruments

The final fragment distribution during pyrolysis depends greatly on the pyrolysis temperature. Therefore, reproducibility of the final pyrolysis temperature via a rapid temperature rise and accurate temperature control are the essential parameters in analytical pyrolysis. Analytical pyrolysis instruments are principally divided into two groups (Table 4) based on the method with which heat is introduced to the sample [Brettell, 2004; Kusch et al., 2005]. Selection of the pyrolyzer type depends on personal preference, experimental requirements, budget, or availability.

TABLE 4 Classification of analytical pyrolysis instruments

Pulse-mode pyrolyzers		**Isothermal furnace pyrolyzers**
Resistively heated filament pyrolyzers	**Curie Point pyrolyzers**	
- Resistively heated filament - Slow/rapid heating mode - Not good heat transfer - Solid/viscous liquid - Small sample size - Possible secondary reactions - Reproducible for small sample size - Easy to control the temperature - High resolution	- Inductively heated to temperature of ferromagnetic alloy - Rapid heating mode - Good heat transfer - Solid/liquid - Small sample size - Less secondary reactions - Reproducible for small sample size - Good resolution	- Continuously heated furnace - No heating mode (isothermal) - Poor heat transfer - Solid/liquid - Large sample size - Secondary reactions - Reproducible for small sample size - Hard to control the temperature - Low resolution

A resistively heated platinum filament pyrolyzer (the CDS instruments pyroprobe 1000) is shown as an example in Figure 4. It is utilized for quickly heating the sample, such as solids, semisolids, and viscous liquids, that are not soluble in a volatile solvent. In this model, heating rates are selectable in the range of 0.01 °C/ms to 20 °C/ms, temperature ranges are programmable between 1 °C and 1400 °C, and final hold times may be selected from 0.01 s to 99.99 s. The pyrolyzates can be readily transferred to analytical devices (e.g., to GC/MS) as long the filament is positioned correctly and the probe is sealed off from air. A heated interface is needed between the pyrolyzer and column; thus, the interface has its own heater to prevent condensation of pyrolyzate compounds and should have minimal volume. For this configuration, a valve is needed between the pyrolyzer and column; hence, insertion or removal of the filament can occur. To overcome nonrepeatable data, the pyrolysis conditions, sample size, and sample location must be controlled. For example, the samples are better centered between quartz wool in nearly the exact spot of the quartz tube for good reproducibility. In addition, maintenance should take place to prevent the contamination of both the sample and the lines [Brettell, 2004].

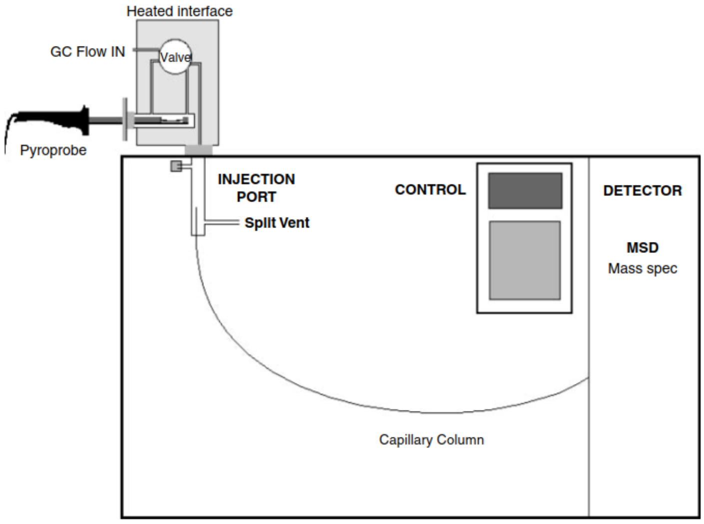


FIGURE 4 Example of a pyrolysis-gas chromatography/mass spectrometry unit [Wu et al., 2012].

4.2.1.2 Large-scale reactors

Various reactor configurations are required based on size limitations for effective high heat transfer rates and smooth operation. The technological strength and the market attractiveness of different types of reactors are presented in Figure 5. Fluidized-bed reactors are mostly utilized within the common pyrolysis reactor designs, operated in either bubbling or circulating mode. These systems have certain advantages, such as production of high-quality bio-oil, short residence time, and good heat transfer [Bridgwater et al., 2002; Bridgwater, 2012; Jahirul et al., 2012; Verma et al., 2012].

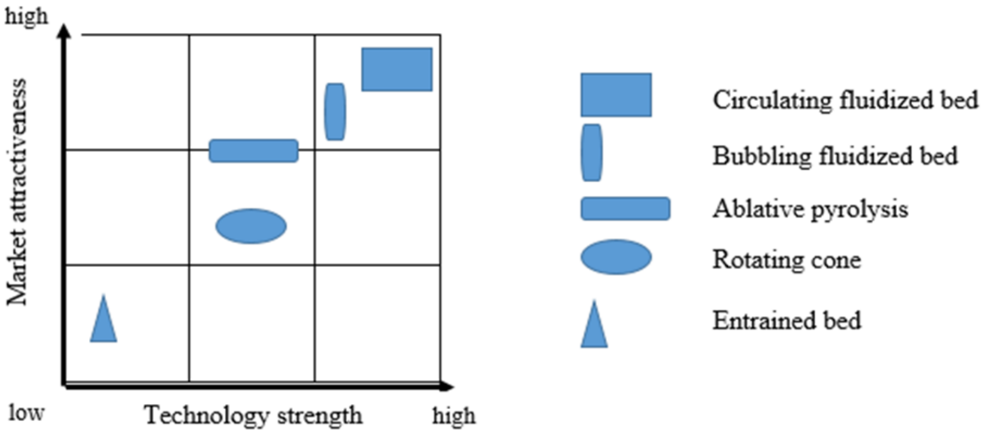


FIGURE 5 Status of pyrolysis reactors (modified image from Van de Velden et al. [2010]).

4.2.2 Chemical characterization of pyrolysis bio-oils

It is important to characterize the bio-oil as every bio-oil has different composition depending on the feedstock, applied pyrolysis conditions, and reactor configurations. Therefore, fast and cheap methods are required for pyrolysis liquid characterization. Micropyrolysis in combination with GC and MS is considered to be a powerful tool for the study of fast pyrolysis.

4.2.2.1 Conventional (one-dimensional) gas chromatography

The GC/MS or flame ionization detector (GC/FID) is still one of the most generally used techniques for the analysis of pyrolysis products due to its reasonable price and broad availability.

In general, improper chromatographic resolution, peak co-elution, unavailability of mass spectra of some bio-oil components in MS libraries, the lack of analytical standards (unknown response factors for the quantification), and the inability to analyze the nonvolatile compounds (e.g., sugar and lignin oligomers) are the significant obstacles of the GC characterization of pyrolysis liquid. Therefore, qualitative and quantitative bio-oil analysis is challenging work, and GC/MS analysis presents only limited information about the chemical composition of these oils.

Pyrolysis (Py-GC/MS) is normally applied to study the process of biomass pyrolysis and its degradation products on the lab-scale under varying conditions. The pyrolysates are directly introduced into the injector of the gas chromatograph where they are analyzed. However, the high-molar-mass components (resulting from their condensation in the transfer line between the pyrolyzer and gas chromatograph) are not detected in this method [Sobeih et al., 2008; Staš et al., 2014]. The characterization of bio-oils by this technique is very complex due to the strong peak co-elution. On the other hand, better chromatographic resolution and a significantly higher number of detected components can be obtained using two-dimensional gas chromatography (GC × GC) coupled with FID or time-of-flight mass spectrometry (TOF-MS), which is due to the application of two columns having different selectivity and refocusing the eluted components [Marsman et al., 2007].

4.2.2.2 Other techniques

In the basic research field, information on the chemical nature of pyrolysis liquids can be analyzed by combining a wide range of techniques, such as GC/MS (volatile compounds), high performance liquid chromatography mass spectrometry (HPLC) combined with MS (nonvolatile compounds) [Christensen et al., 2011], Fourier transform infrared spectroscopy (FTIR) (functional groups) [Scholze and Meier, 2001], size exclusion chromatography (SEC) (molecular mass distributions) [Hoekstra et al., 2011], and nuclear magnetic resonance (NMR) [Martínez et al., 2008].

5 PYROLYSIS–REACTION PATHS

5.1 General aspects

The study of pyrolysis behavior of the three main biomass substituents and their corresponding interaction is essential to understand the overall pyrolysis behavior of biomass. During pyrolysis under an inert atmosphere, biomass converts into low-degree-polymerized products by a series of complicated reactions, such as depolymerization, ring-opening, and cleavage of chemical bonds [Pastorova et al., 1994; Banyasz et al., 2001; Scheirs et al., 2001; McGrath et al., 2003; Van de Velden et al., 2010; Collard et al., 2012]. Dehydration reactions happen under the conditions of slow heat rates, low temperatures (<310 °C), and long residence times so that the molar-mass of feedstock is reduced to form a solid residue that contains aromatic polycyclic structures, which are principally benzene rings and the combination of these rings. This pathway takes place by intra- and intermolecular rearrangement reactions, which result in a higher thermal stability residue along with release of water or incondensable gases, such as H_2, CO, and CO_2. Depolymerization occurs in the cleavage of the bonds between the monomer units of polymers, resulting in the decreasing DP of the polymeric chains to form volatile molecules, condensable gases of monomers, dimers, and trimers.

When the volatile compounds formed are not stable at temperatures above 600 °C, they can proceed to secondary reactions, such as cracking or recombination [Morf et al., 2002; Wei et al., 2006; Van de Velden et al., 2010]. Cracking reactions form the lower-molar-mass molecules by cleavage of chemical bonds either within the volatile compounds or within the polymer [Evans and Milne, 1987; Blanco López et al., 2002; Neves et al., 2011]. Recombination takes place to form nonvolatile high-molar-mass molecules by combining the volatile compounds and can directly form secondary char [Morf et al., 2002; Wei et al., 2006; Hosoya et al., 2007; Neves et al., 2011].

In general, investigations of the mechanism dealing with pyrolysis reactions of biomass are primarily based on kinetics modeling, mainly irradiating the thermogravimetric behavior of biomass by thermogravimetric analysis (TGA), derivative thermogravimetric (DTG), and chemical reactions (the formation of the major products) [Wang et al., 2017]. The TG curves can represent the mass loss during the pyrolysis process and the final char residue, while the DTG curves describe the temperature related to the maximum reaction rate and determine the various stages in the pyrolysis process. These methods are widely applied techniques, especially when studying thermal stability of polymers. The kinetics of pyrolysis reactions can be influenced by certain factors, such as heating rate, temperature, pressure, the effect of ambient atmosphere, catalysts, pyrolysis reactor, chemical composition of feedstock, and a combination of these variables.

Figure 6 represents TG (i.e., mass change vs. temperature) and DTG (i.e., mass change/time vs. temperature) curves of pure cellulose, hemicelluloses, and lignin samples. The dissimilarities in pyrolysis behaviors of these three components are due to differences in their molecular structures and chemical natures. Hemicelluloses decompose earlier among the three biopolymers in the temperature range of 220-315 °C due to their low DP, while cellulose starts to decompose mainly in the temperature range of 315-400 °C with a minor formation of solid after 400 °C. Lignin decomposes slowly in a wide range of temperatures up to 900 °C with a high solid residue remaining at the end of lignin pyrolysis [Dhyani and Bhaskar, 2017]. Other studies [Moriana et al., 2014; Stefanidis et al., 2014] have reported temperature ranges of decomposition of xylan, glucomannan, and cellulose at 200-300 °C, 200-375 °C, and 280-360 °C, respectively. Dehydration reactions of xylan and glucomannan occur at 150-240 °C and 150-270 °C, respectively [Chen and Kuo, 2011]. Thus, the first mass loss at 100 °C refers to water evaporation and the breakage of weak side groups. The stability of lignin, cellulose, and hemicelluloses against heating increases in the following order: hemicelluloses > cellulose > lignin.

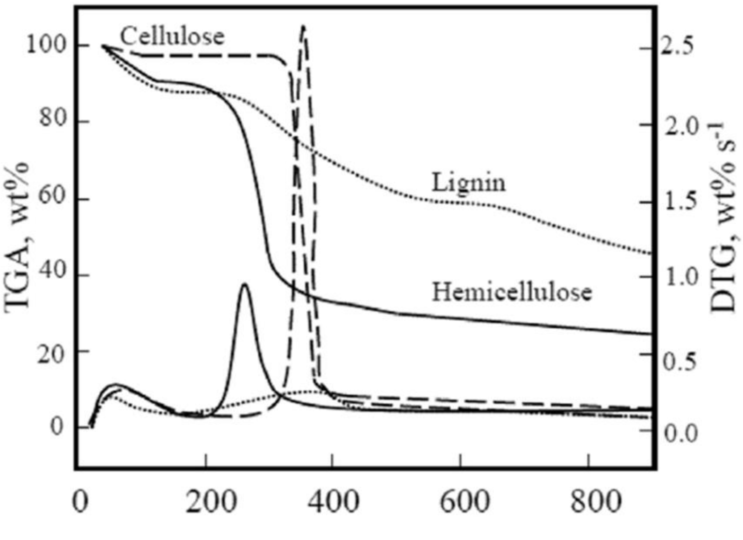


FIGURE 6 TGA/DTG curves of biomass components [Dhyani and Bhaskar, 2017].

5.2 Kinetic models for biomass pyrolysis

A comprehensive kinetic model for the three main biomass components is shown in Figure 7. The most common model for cellulose pyrolysis is the Broido-Shafizadeh model, which was later simplified by Shafizadeh and Bradbury [Bradbury et al., 1979]. It shows that parallel and competitive reactions exist in the generation of condensable volatiles (I) and char (II), and reaction path k_4 overcomes the reaction path k_3 at temperatures above 300 °C. Therefore, three demonstrative reactions, such as dehydration (k_1), depolymerization (k_2 and k_3), and fragmentation (k_4), are the main competitive reactions in different temperature ranges; this presumption is known as the Waterloo-mechanism [Piskorz et al., 1986; Boukis, 1997; Van de Velden et al., 2010]. At low temperatures, formation of sugars are facilitated, and eventually the cleavage of glycosidic bonds and some C–C bonds generates char (II), condensable volatiles (II), and gases. The presence of inorganics, which act as catalysts, strongly increase the production of char and linear small oxygenated products [Richards and Zheng, 1991; Liu et al., 2008; Kawamoto et al., 2009; Wang and Luo, 2017]. Wang et al. [2016] has also represented a single-step global reaction model for pyrolysis of cellulose.

In the case of hemicelluloses, a semi-global reaction model was introduced [Di Blasi and Lanzetta, 1997] so that first, at low temperature, xylan pyrolysis produces intermediate condensable volatiles; then, further volatiles and char are formed through intermediates. This model is also applicable for xylan and glucomannan at both high and low temperatures [Branca et al., 2013].

In the pyrolysis process of lignin, there are several mass loss peaks with a gentle variation tendency due to the wide distribution of bond energy and corresponding activation energies. A study of kraft lignin pyrolysis proposed three parallel reaction pathways for a short residence time to the production of gas, pyrolysis oil, and char. For a longer residence time, pyrolysis oil and some primary solid products undergo the secondary decomposition into gaseous products and cause an extra reaction pathway [Cho et al., 2012; Adam et al., 2013; Wang et al., 2017].

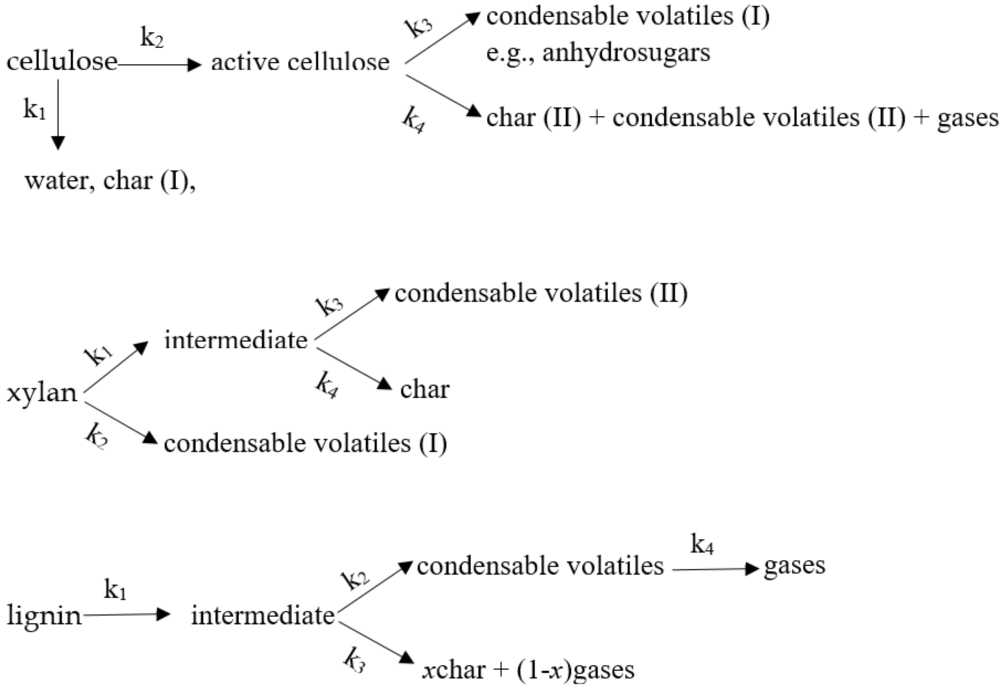


FIGURE 7 Kinetic models for pyrolysis of cellulose [Liu et al., 2008], xylan [Di Blasi and Lanzetta, 1997], and lignin [Wang et al., 2017].

5.3 Pyrolysis product distributions

5.3.1 Cellulose

During the cellulose pyrolysis, more than 100 components have been detected, and it is impossible to illustrate the mechanism of all corresponding reactions. Therefore, only mechanisms of the formation of several major products are considered here. Volatiles consist of anhydrosugars (such as levoglucosan [LG] and levoglucosanone [LGO]), furans (such as 5-hydroxymethylfurfural [5-HMF] and furfural), linear small oxygenated chemicals (hydroxyacetone and hydroxyacetaldehyde), and some gases (CO_2, CO, and CH_4). The longer the residence time and the higher the reaction temperature, the more secondary cracking reactions occur. Hence, the residence time should be shortened to maximize the yield of bio-oil [Drummond and Drummond, 1996; Luo et al., 2004].

A scheme of cellulose pyrolysis is presented in Figure 8. Ring-opening of glucopyranose units takes place to form open-chain structures, followed by dehydration and cyclization to generate 5-HMF, which further converts through the elimination of the hydroxymethyl group to produce furfural [Wang et al., 2012]. The cleavage of the hydroxymethyl group needs lower energy than the side aldehyde chain. However, 5-HMF and furfural are more likely yielded through competitive reactions rather than continuous reactions during the pyrolysis of glucose [Wang et al., 2017]. LG is produced by the cleavage of the β-

(1→4)-glycosidic linkage in the cellulose macromolecules, followed by an intramolecular rearrangement. LGO is formed by the dehydration of LG at a temperature of 250-400 °C, as well as by dehydration from glucose, to produce an intermediate with a carbon-carbon double bond, followed by dehydration via a six-membered hydrogen transfer, enol-keto tautomerization, and finally dehydration. The formation of 1,4:3,6-dianhydro-α-D-glucopyranose (DGP) is due to the double dehydration reactions of the hydroxyl groups in the glucopyranose units [Scheirs et al., 2001; Shin et al., 2001; Lin et al., 2009; Shen and Gu, 2009; Lu et al., 2011; Wang et al., 2012, 2017]. A decomposition product of monosaccharides (D- and DL-arabinose, D- and DL-xylose, and D-mannose) and alditols (D- and DL-arabinitol) at above 500 °C is 3-hydroxy-2-penteno-1,5-lactone [Räisänen et al., 2003].

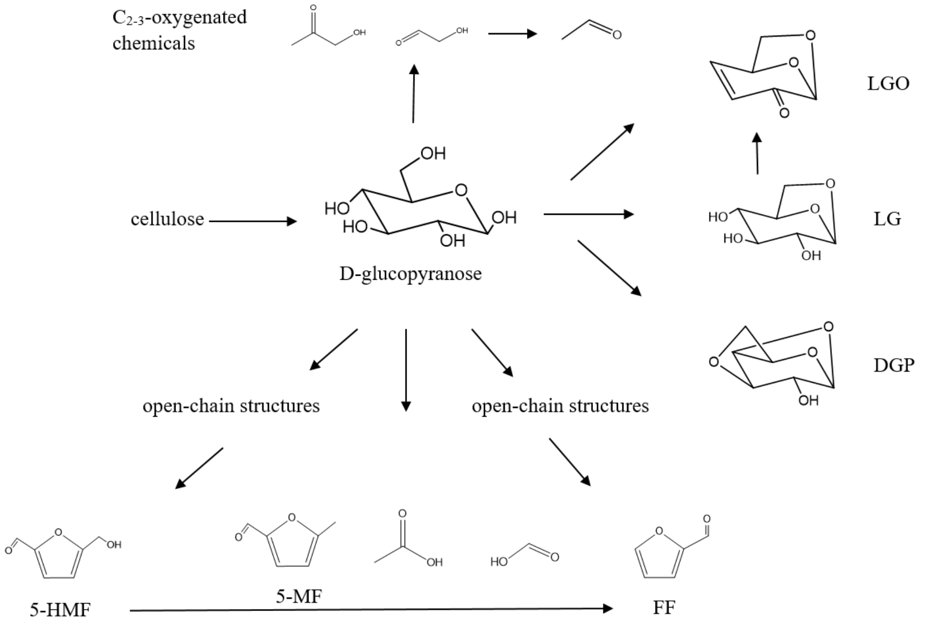


FIGURE 8 A modified decomposition pathway of cellulose pyrolysis [Wang and Luo, 2017]; LG levoglucosan, LGO levoglucosenone, DGP 1,4:3,6-dianhydro-α-D-glucopyranose, 5-HMF 5-hydroxymethylfurfural, 5-MF 5-methyl-2-furaldehyde, and FF 2-furaldehyde.

5.3.2 Hemicelluloses

The pyrolysis products of xylose can be classified as furans, mainly furfural (from pentoses; mostly D-xylose and L-arabinose) and 5-HMF (from hexoses; D-glucose, D-mannose, and D-galactose), anhydrosugars (principally include LG detected only in hexose pyrolysis), ketones (hydroxyacetone, furanones, pyranones, cyclopentanones, and cyclopentenones), some phenols, and gaseous products (CO_2, CO, and CH_4) [Wang and Luo, 2017]. The char yield from pentose pyrolysis is higher than that from hexose pyrolysis due to the additional hydroxymethyl in the hexose structure, which can form stabilized low-molar radicals and avoid further repolymerization with each other to form char [Šimkovic et al., 1988; Di Blasi and Lanzetta, 1997; Branca et al., 2013; Wang and Luo, 2017]. Fast pyrolysis of xylan results in higher char than that of cellulose due to the existence of different sugars (pentoses and hexoses) in its structure [Ponder and Richards, 1991; Zhu and Lu, 2010; Patwardhan et al., 2011a]. More gases, methanol, and acetic acid are formed from hemicelluloses than cellulose. Contrary to xylan, products of glucomannan decomposition are similar to those of cellulose decomposition [Alén et al., 1996; Di Blasi et al., 2010].

Pyrolysis conditions largely affect the product distribution. Yields of most furans decrease after 550 °C, except for methylfuran and furan, while the yield of 5-HMF decreases after 700 °C due to fragmentation reactions. The structure of residue leads to enhanced amounts of aromatics when temperature rises above 320 °C and 350 °C for xylan and glucomannan, respectively [Collard and Blin, 2014]. High temperatures can contribute to the formation of gaseous products. Another study [Alén et al., 1996] showed that, due to the poor thermal stability of xylan compared to that of glucomannan, with an increase in temperature, the yield of low-molar volatiles increased and the yield of lactones and furans declined. The production of CO_2 is mainly caused by decarboxylation of acetic acid and uronic acid [Ponder and Richards, 1991] while CO is produced by the decarboxylation of aldehydes and also from the decomposition of volatiles. CH_4 is generated from the decomposition of $O–CH_3$ groups.

Xylan pyrolysis has indicated that as the residence time increases in the time range of 2-20 s, the yield of acids and furans increases and decreases, respectively. The decomposition of volatiles to gaseous products can proceed within a longer residence time [Wang and Luo, 2017]. The reaction atmosphere influences product distribution by affecting decomposition temperature; for example, TG analysis shown that xylan decomposition temperature lowers and widens under synthesis gas compared with N_2 [Wang et al., 2008]. The degradation behavior of xylan under superheated steam atmosphere has shown that the yield of liquid products changes only a little while the formation of gaseous products increases distinctly [Giudicianni et al., 2013]. One other parameter is mineral matter, which promotes the formation of char and lighter compounds in bio-oils.

As clarified in Figure 9, first, the cleavage of the linked lignin fragments occurs; then, degradation to phenols takes place. Acetic acid is produced from the release of *O*-acetyl groups attached to the xylan linear backbone by deacetylation, pyrolytic ring scission, and side-chain cracking of hemicelluloses at temperatures lower than 300 °C via torrefaction [Prins et al., 2006]. Depolymerization and ring scission of xylan form ring-opened intermediates, which further produce linear ketone products, such as hydroxyacetone (via carbon chain fracture), furfural and furanones (by cyclization), and alicyclic ketones, such as cyclopentenones through the combination of C=C bonds [Wu et al., 2009; Peng and Wu, 2010; Shen et al., 2010; Patwardhan et al., 2011a; Dong et al., 2012]. Another major pyrolytic product is 3-hydroxy-2-penteno-1,5-lactone, which is yielded independently from the formation of furfural [Ohnishi et al., 1977]. The degradation of glycosidic linkages between monomer units of glucomannan results in various anhydrosugars (such as LG, levomannosan, levogalactosan from β-D-glucopyranose, β-D-mannopyranose, and α-D-galactopyranose, respectively) and more stable furan rings (such as 5-HMF, 5-MF, and furfural) [Alén et al., 1996; Branca et al., 2013].

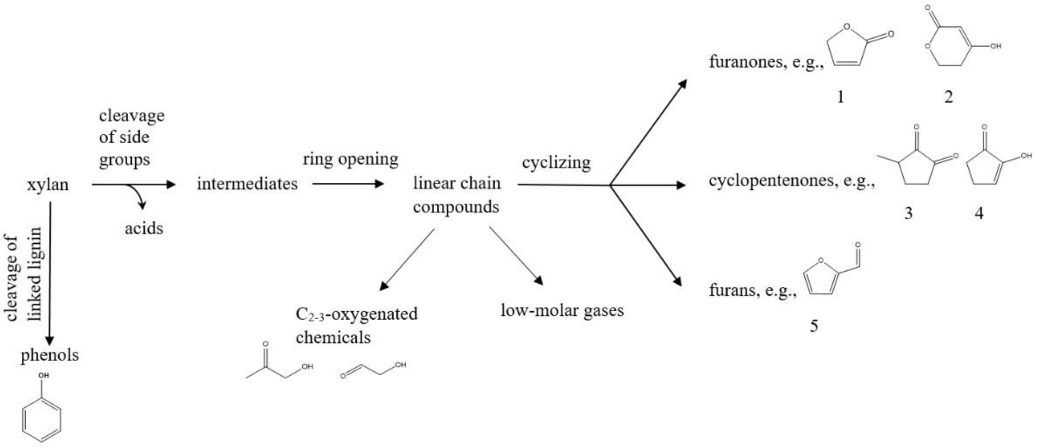


FIGURE 9 A modified decomposition pathway of hemicelluloses pyrolysis [Wang and Luo, 2017]. (1) 5*H*-furan-2-one, (2) 3-hydroxy-2-penteno-1,5-lactone, (3) 3-methylcyclopentane-1,2-dione, (4) 2-hydroxycyclopent-2-en-1-one, and (5) 2-furaldehyde.

5.3.3 Lignin

Lignin pyrolysates are classified into three groups, such as the large-molar oligomers (pyrolytic lignins), the monomeric phenolic compounds (phenols, hydroxylphenols, guaiacols, and syringols), and light compounds (methanol and acetic acid) [Zhu and Lu, 2010]. Devolatilization and char formation are two competing reactions during the pyrolysis of lignin, along with some subsequent secondary reactions. Char formation via crosslinking reactions is favored below 300 ^{o}C, and as the reaction temperature increases, the devolatilization reaction causes the production of pyrolysis oil and gaseous products via cracking the side chains as well as C–C and C–O bonds in the phenylpropane units [Hosoya et al., 2008]. Hence, the yields of guaiacols and syringols first increase due to the breakage of ether bonds between structural units and some C–C bonds; then, as the demethoxylation and demethylation reactions occur, the yields decrease with rising reaction temperature, resulting in the formation of phenols and catechols [Vuori and Bredenberg, 1987].

Various other products, such as aldehydes and ketones, are formed at low reaction temperatures, which can result from the cleavage of glucosidic bonds attached to the lignin structure. Residence time also influences the distribution of lignin pyrolysis products. A too-short residence time results in the insufficient depolymerization of lignin and forms low yields of gas as well as of heterogeneous liquid products due to the random breakage of chemical bonds. A proper residence time affects devolatilization, leading to increasing yields of pyrolysis oil and gas. However, a too-long residence time favors secondary decomposition of the initial pyrolysis products, causing a decrease in pyrolysis oil yield and an increase in gas yield. Some other parameters, such as the pyrolysis atmosphere and heating rate, also affect the behavior of lignin pyrolysis. For example, during pyrolysis under an air atmosphere, the oxidation reaction is favored, but the release of volatiles occurs under an inert gas atmosphere. Increasing the heating rate can decline the residence time in low temperature ranges, resulting in the high conversion of lignin and lower char yield. Variations in feedstock, extraction processes, and the pulping process also influence the pyrolysis behavior of lignin [Alén et al., 1995; Zhao and Liu, 2010; de Wild et al., 2012; Luo et al., 2012]. Therefore, studies of lignin pyrolysis have been conducted mainly on the lignin model compounds as follows [Wang et al., 2014]:

- Milled wood lignin (MWL), which is considered to represent the original lignin that is extracted from finely ball-milled biomass with aqueous dioxane.
- Organosolv lignin, which is obtained from the dissolution of lignin with some solvents, such as ethanol, formic acid, acetic acid, and acetone, under certain temperatures and pressures.
- Kraft lignin, which is isolated from the black liquor produced by kraft pulping.
- Pyrolytic lignin, which is a mixture of incomplete depolymerized products from lignin and can be extracted by using solvents, such as water, ethanol, acid, and alkali, from pyrolysis oil. The pyrolytic lignin is more thermo-instable than natural lignin because it is derived from the partial depolymerization of natural lignin.

The formation of phenolic compounds as the main products of lignin pyrolysis is presented in Figure 10. Some aromatic hydrocarbons and benzyl alcohol are produced in lignin pyrolysis from the removal of the oxygen-containing functional groups and from the rearrangement of aromatics with the methoxyl group, respectively [Alén et al., 1996]. In addition, the cracking of side chains in the phenylpropane units and the removal of the functional groups coupled to the aromatic ring generate low-molar products, such as CO, CO_2, and CH_4 [Collard and Blin, 2014].

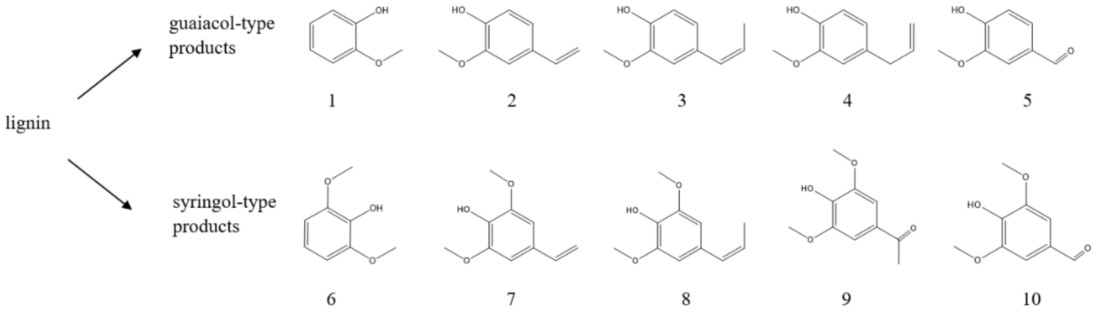


FIGURE 10 Examples of different pyrolysis products from lignin. (1) 2-methoxyphenol (guaiacol), (2) 2-methoxy-4-ethenylphenol (4-vinylguaiacol), (3) 2-methoxy-4-(1-propenyl)phenol (isoeugenol), (4) 2-methoxy-4-(prop-2-en-1-yl)phenol (eugenol), (5) 4-hydroxy-3-methoxybenzaldehyde (vanillin), (6) 2,6-dimethoxyphenol (syringol), (7) 2,6-dimethoxy-4-ethenylphenol (4-vinylsyringol), (8) 2,6-dimethoxy-4-(1-propenyl)phenol (4-propenylsyringol), (9) 4'-hydroxy-3',5'-dimethoxyacetophenone (acetosyringone), and (10) 4-hydroxy-3,5-dimethoxybenzaldehyde (syringylaldehyde).

5.3.4 Extractives

Mechanisms for thermal decomposition of extractives are complex, and there are a multiplicity of possible reaction pathways due to the heterogeneous nature of extractives in different wood species and the wide number of different compounds [Artok and Schobert, 2000; Lappi, 2012]. Hence, influences of heating on extractives have received less attention. Most extractives evaporate at high temperatures, and major pyrolysis products are aliphatic carboxylic acids along with minor amounts of higher-molar-mass, unbranched aliphatic hydrocarbons, and CO_2 [Alén et al., 1996]. In pyrolysis conditions (200-550 ^{o}C), fats are decomposed and free fatty acids are produced while resin acids remain almost unchanged [Pakdel et al., 1993, 1994]. Fatty acids are released from the glyceridic structure during the pyrolysis of fats with further degradation to acrolein or homologic derivatives [Irwin, 1993]. Thus, the rearrangement of the alkyl substituents of fats produces the saturated or unsaturated carboxylic acids, which further form saturated or unsaturated hydrocarbons via rearrangement or decarboxylation.

5.4 Influence of component interaction on product formation

The effect of component interaction on biomass pyrolysis is complex. The primary element influencing the distribution of pyrolytic products is (i) the quantity of each component in the sample, which is based on their abundance in the biomass, as well as (ii) the form of crosslinking structures in the mixed samples [Couhert et al., 2009; Zhang, 2012; Xie et al., 2013]. Hence, the coupling interactions between components should not be ignored.

It can be observed that with the increasing amount of hemicelluloses in the sample mixture of xylan and microcrystalline cellulose, the maximum decomposition rate of hemicelluloses increases while that for cellulose declines. It can be concluded that the hemicelluloses decompose into the melted organics at low temperatures and cover the cellulose surface, resulting in weakening the molar-mass loss strength of cellulose. As a result, formation of hydroxyacetaldehyde increased by the addition of hemicellulose as well as by the secondary decomposition of LG [Liu et al., 2011].

The differences in the mutual attachment of cellulose and lignin result in different pyrolysis behaviors for non-woody biomass. The presence and the form of a crosslinking structure will affect the pyrolysis of the mixture. These effects have been studied by the pyrolysis of herbaceous materials; it was shown that the presence of interaction between lignin and cellulose decreases the formation of LG and increases the yields of low-molar compounds and furans. The cellulose content decreases the lignin mass-loss rates in these types of samples by a slightly shifting impact toward a high temperature region and accelerates the conversion of lignin to phenols [Worasuwannarak et al., 2007; Haensel et al., 2009]. However, these influences cannot be found in woody biomass. It has also been found that a mixture of cellulose and lignin consisting of the natural linking structure reflects obvious interactions in the pyrolysis process [Giudicianni et al., 2013; Zhang et al., 2015].

The interaction between hemicelluloses and lignin is strong. The presence of hemicelluloses decreases the initial lignin decomposition temperature and the mass-loss rate at the second peak of the TG curves, whereas the existence of lignin increases the decomposition rate of hemicelluloses. Hence, it has been clearly found that the formation of furfural as a key product of hemicellulose pyrolysis is prevented by lignin due to the decomposition of lignin at low temperatures. Thus, lignin has a significant impact on hemicellulose pyrolysis at low temperatures.

6 EXPERIMENTAL

6.1 Raw materials and chemicals

In this study, the untreated (Ref) and hot-water-extracted (HWE) feedstocks as well as their soda-AQ-cooked pulps (from untreated (P_{ref}) and HWE (P_{HWE}) materials, respectively) were investigated:

- Silver birch (*Betula pendula*) sawdust (<5 mm) [I]
- Norway spruce (*Picea abies*) sawdust (<5 mm) [II]
- Miscanthus (*Miscanthus* x *giganteus*) stalks [III]
- Okra (*Abelmoschus esculentus*) stalks [III]

Model substances were also used [IV], i.e., α-cellulose (Sigma), glucomannan (MB Med. S. r. L.), and oat spelt xylan (Sigma). The chemicals used in publications [I-IV] were commercially available from supplier Fluka, Merck, and Sigma with a grade >99 %.

6.2 Pretreatment experiments

Pretreatment analyses in publications [I-III] were conducted as follows: hot-water extraction and the soda-AQ cooking conditions as well as the yields of differently-treated feedstocks are presented in Tables 5 and 6 [Lehto and Alén, 2015; Lehto et al., 2016; Ullah et al., 2018a,b]. 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 alkali (NaOH) and AQ charge were determined based on oven-dried (o.d.) feedstock, and the liquor-to-feedstock ratio was 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.

TABLE 5 Treatment conditions of wood and non-wood feedstocks

Treatment conditions	Birch	Spruce[a]	Okra	Miscanthus
Hot-water extraction (°C, min)	170, 38	160, 40 170, 60 180, 180	140, 60	140, 60
Alkali (NaOH) charge (% on the feedstock)	18	20	20	15
AQ charge (% on the feedstock)	0.1	0.1	0.05	0.05
Soda-AQ cooking (°C, min)	170, 90	170, 30	165, 180	165, 60

[a] Hot-water extraction of spruce was conducted in three separate stages.

TABLE 6 Yields of differently-treated wood and non-wood feedstocks

Samples	Birch	Spruce	Okra	Miscanthus
HWE	72.0	72.4	85.6	95.2
P_{ref}	51.6	60.0	40.2	57.5
P_{HWE}[a]	53.5	65.0	37.8	60.3
P_{HWE}[b]	38.5	47.0	32.4	57.4

[a] Refers to cooking yield (% of material charged into reactors).

[b] Refers to total cooking yield (% of original dry feedstock material before pre-treatment).

6.3 Chemical analyses

The differently-treated feedstocks presented in publications [I-III] were analyzed to determine the extractives, monosaccharides, and lignin contents based on the chemical analyses [Chen et al., 2016]. Prior to the analyses, the moisture content was determined according to the 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 untreated, air-dried, 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 they were stored in plastic bags.

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, The Netherlands), and drying was finalized before weighing by means of a gentle nitrogen stream.

Acid hydrolysis of the extractives-free ground samples was performed according to the TAPPI T249 cm-00 standard, and the resulting monosaccharides of wood feedstocks [I and II] were analyzed as their per(trimethylsilyl)ated derivatives using a GC system comprising an HP 5890 Series II Plus GC apparatus (Hewlett Packard Company, Wilmington, NC, USA) equipped with the FID [Alén et al., 1984; Niemelä and Alén, 1999]. 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, Regies Technologies) in pyridine, and the mixture was shaken for 60 min. Xylitol 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 monosaccharides: arabinose, xylose, galactose, glucose, and mannose. It was then possible to perform chromatogram peaks identification and obtain the mass-based response factor between each monosaccharide and the corresponding IS.

The resulting monosaccharides of non-wood feedstocks [III] were analyzed with high performance anion exchange chromatography with pulses amperometric detection (HPAEC-PAD, from the Dionex Corp., Sunnyvale, CA, USA) [Ververis et al., 2004]. A Dionex CarboPac PA-1 column (250 mm × 4 mm inner diameter) was applied for the separation of different monosaccharides at a flow rate of 1.0 mL/min. A post-column alkali (300 Mm NaOH) addition was utilized at a flow rate of 0.2 mL/min to increase the performance of PAD. The peak identification and the mass-based response factors between an internal standard (L-fucose) and each monosaccharide were collected from separate runs with the model monosaccharides. The content of the carbohydrates in acid hydrolysates was determined based on the anhydro forms of the measured monosaccharides; moreover, a decrease in the yield of monosaccharides during acid hydrolysis resulted from a different side reaction (e.g., the formation of furans).

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:

$$c = A/(a \cdot b), \tag{1}$$

where a is the absorptivity (110 L/(gcm)) [Swan, 1965] and b is the length of the light path (cm).

6.4 Elemental analyses

The elemental analysis of model substances used in publication [IV] was performed with a CHNOS elemental analyzer GmbH (Vario EL III) to identify the content of carbon, hydrogen, nitrogen, and oxygen (Table 7). The tests were conducted in duplicates.

TABLE 7 Elemental analysis of cellulose, glucomannan, and xylan. Numbers in parentheses are calculated for "pure substances" without any possible side-groups

Component	C	H	N	O[a]
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)

[a] Calculated by difference.

6.5 Thermogravimetric analyses

The TGA shown in publication [IV] was carried out with a Linseis STA PT1600 instrument. For each test, a sample size of 10-15 mg was used in an alumina crucible. A nitrogen flow of 200 mL/min was used to create an inert environment and to remove the released volatiles. For drying, the furnace temperature was raised from room temperature (≈ 20 °C) to 105 °C at 20 °C/min and maintained at that temperature for 30 min to complete the drying of the sample. Then, the TGA run was continued with the same dried samples for pyrolysis. The pyrolysis temperature was selected as 700 °C. For pyrolysis, the sample temperature was raised from 105 °C to 700 °C at varied heating rates of 10, 15, and 20 °C/min and maintained at that temperature for 40 min to ensure complete pyrolysis. The data generated through TGA experiments were further processed with Microsoft Excel and Matlab®.

6.6 Calibration of GC column

Internal standards could not be applied due to the nature of the experiments, which involved pyrolysis of the samples. The GC column was calibrated [I-IV] using solutions of known concentration of pure compounds as external standards to relatively quantify all the identified peaks from the pyrolysis products (Py-GC/MS) by comparing the products to a set of standard samples of known concentration according to Patwardhan et al. [2009, 2011a,b] and Zhang et al. [2014]. The chromatogram peak identification was also partly confirmed based on the retention times and mass spectra of these pure compounds. In general, several standard methanol or acetone solutions were prepared by diluting stock solutions of each standard. To utilize this, standard solutions for the low concentration range of 0.05-1.0 mg/mL and for the high concentration range of 1.0-8.0 mg/mL were prepared, depending on the standard's chromatographic response (GC/MS). Five series of one µL of prepared solutions as well as their duplicated solutions were injected by the autosampler of GC/MS. The conditions of the GC were set to those of the Py-GC/MS. The calibration response factors were checked once after 10 pyrolysis runs to determine any variation, and, if necessary, the GC-column was re-calibrated. A plot of instrument response (peak area, y-axis) vs. amount of pure compound in standard solution (µg, x-axis) was performed. As an example, the calibration curve for furfural is shown in Figure 11. The coefficients of determination (r^2) values of the linear calibration curves were between 0.96-0.99, and each response factor represented the slope of the line between the response for a given standard and the origin. These 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-methylcyclopent-2-en-1-one, 4-hydroxy-5-methylfuran-3-one, 3-hydroxy-2-methylpyran-4-one, and LG were, respectively, used for 2-hydroxycyclopent-2-en-1-one, 3-hydroxy-2-penteno-1,5-lactone, pyran-type compounds, and anhydrosugars in the absence of commercially available standards for them. Therefore, the relative mass response of a target compound compared to the mass of the corresponding external standard and the weight percent yield for a compound is defined as follows:

$$\%\ \text{yield}_i = \text{mass of compound i in product} / \text{mass of sample} \times 100$$

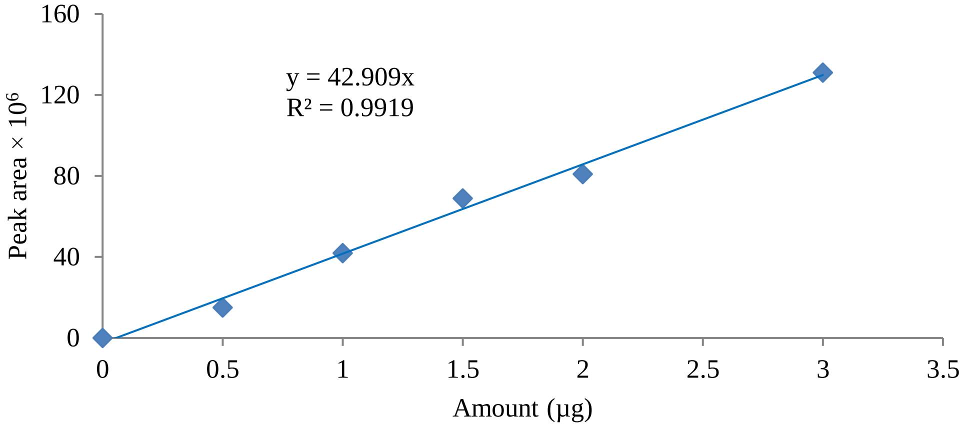


FIGURE 11 Calibration curve for furfural.

The approach of this study pointed out that the simultaneous use of all standards (e.g., 48 [I], 37 [II], 27 [III], and 18 [IV]) was rather complicated in all cases. To make this approach more appropriate and less tedious, the standards were classified into five groups (Table 8) if the average relative standard deviation (RSD) of the response factors was less than or equal to 20 % (Figure 12) [U.S.

Envirornmental Protection Agency, 2003]. Hence, it can be seen that the slopes of the calibration curves for each standard in the group were agreeably close to one another [Patwardhan et al., 2011a]. The classification of pyrolysis products along with peak identification and calibration information is given in Appendix I.

TABLE 8 Group of pure compounds based on average RSD %

Group	Compounds	Average slope	Average SD	Average RSD %
Group I	5-Methylfurfural	62.2	8.6	17.1
	5-Methyl-3*H*-furan-2-one	56.0		
	Cyclohexanone	51.2		
	2-Methylcyclopent-2-en-1-one	65.2		
	Furfural (furan-2-carbaldehyde)	42.9		
	3-Methylcyclopentane-1,2-dione	43.6		
	4-Hydroxy-2,5-dimethylfuran-3-one	41.6		
	4-Hydroxy-5-methylfuran-3-one	35.2		
	Phenol	55.1		
	1,2-Dihydroxybenzene (catechol)	57.3		
	1,6-Anhydro-β-D-glucopyranose (levoglucosan)	67.0		
Group II	5*H*-Furan-2-one	24.8	6.8	8.3
	2,5-Furandicarboxaldehyde	83.0		
	Furanmethanol ((furan-2-yl)methanol)	94.2		
	2-Methylphenol (*o*-cresol)	85.0		
	4-Methylphenol (*p*-cresol)	82.0		
	3,5-Dimethylphenol	87.6		
	2-Methoxyphenol (guaiacol)	79.2		
	2,6-Dimethoxyphenol (syringol)	76.3		
	3-Hydroxy-2-methylpyran-4-one	74.5		
	5-(Hydroxymethyl)furfural	73.0		
Group III	Cyclopent-2-en-1-one	118.4	18.8	13.1
	2,3-Dihydroxybenzaldehyde	119.0		
	2,6-Dimethylphenol	128.6		
	3,4-Dimethylphenol	131.8		
	2-Methoxy-4-(prop-1-en-1-yl)phenol (isoeugenol)	151.0		
	4-Hydroxy-3-methoxybenzoic acid (vanillic acid)	154.7		
	1,2-Dihydroxy-3-methylbenzene	155.0		
	1,2-Dihydroxy-3-methoxybenzene	159.0		
	1,4-Dihydroxybenzene	144.6		
	1,3-Dihydroxybenzene	120.0		
	Naphthalene	178.8		
	1-Benzofuran	160.8		
	Linoleic acid	148.8		

Group IV	2-Methoxy-4-methylphenol	275.0	42.4	16.6
	Toluene	298.5		
	1,2-Dimethylbenzene	230.0		
	Ethenylbenzene	191.7		
	o-Xylene	264.7		
	1*H*-Indene	211.2		
	2,3,6-Trimethylphenol	222.0		
	4-Ethenyl-2-methoxyphenol	251.5		
	2-Methoxy-4-(prop-2-en-1-yl)phenol (eugenol)	331.0		
	4-Allyl-2,6-dimethoxyphenol	274.4		
	4'-Hydroxy-3',5'-dimethoxyacetophenone (acetosyringone)	411.9		
Group V	Acetic acid	4.1	-	-
	Butanal	4.1		

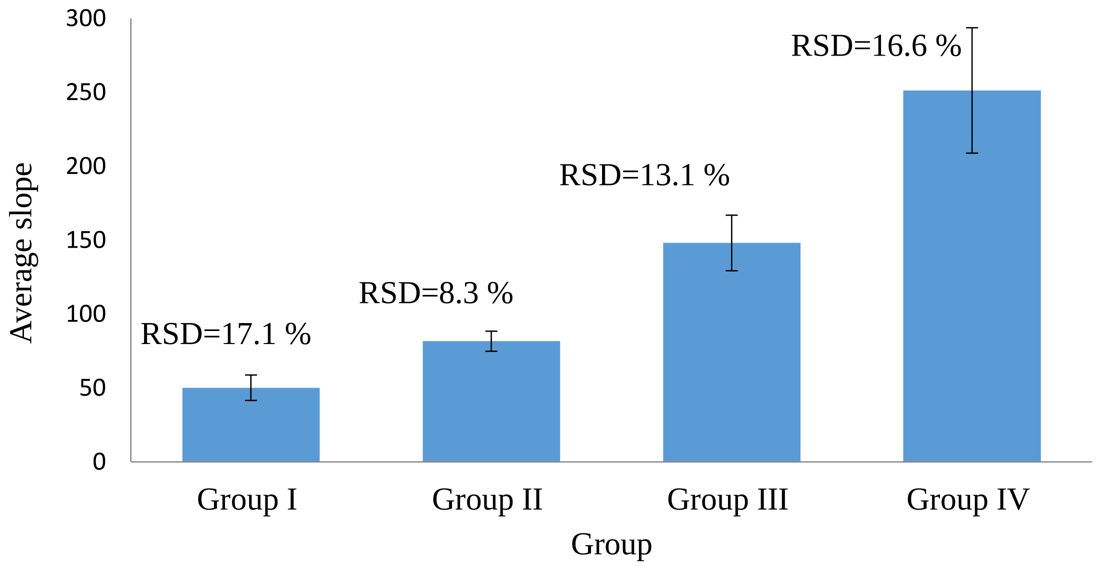


FIGURE 12 Group of pure compounds based on average RSD %.

6.7 Pyrolysis experiments

About 0.5 mg of samples [I-III] and 0.2 mg of samples [IV] were inserted in a quartz tube (3.0 cm x 1.0 mm i.d.) between quartz wool (Figure 13), which was used to keep the solids in the pyrolysis tube. First, a partly filled quartz tube with quartz wool was cleaned at 1000 °C to remove all adsorbed gases and vapors on the surface of the quartz tube. Samples were pyrolyzed at a heating rate of 20 °C/ms to minimize the formation of secondary and tertiary pyrolysis reactions, using a CDS Pyroprobe 1000 resistively heated coil filament pyrolyzer coupled to an HP 5890 II GC (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 MS detector under electron ionization (70 eV) with 2.92 scan/s in the 30-550 m/z interval. For the identification of chromatogram peaks, mass spectra (based on the National Institute of Standards and Technology [NIST] mass spectral library) were used.

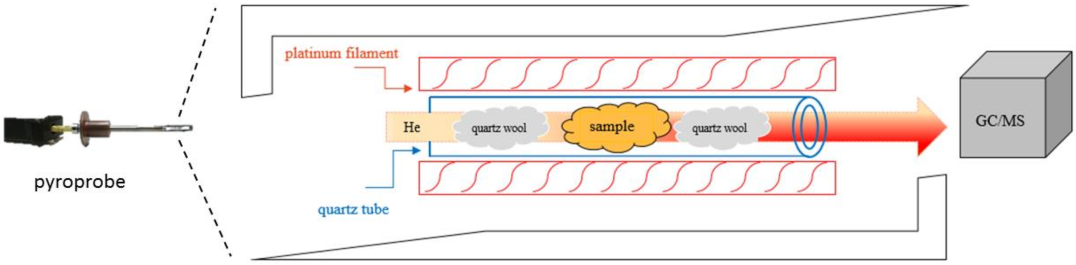


FIGURE 13 Schematic of a pyroprobe filament.

The pyrolysis temperatures were 500 °C and 700 °C in publications [I-III] and 500 °C, 600 °C, and 700 °C in publication [IV], 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 a 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.

7 RESULTS AND DISCUSSION

7.1 Chemical compositions of feedstocks

7.1.1 Birch and spruce sawdust

Chemical compositions of the reference initial and differently-treated (i.e., HWE, delignified, and HWE and delignified) birch [I] and spruce [II] feedstocks are presented in Table 9.

TABLE 9 Chemical composition of the initial and differently-treated birch and spruce sawdust (% of the sample[a] dry solids)

Components	$\mathbf{B_{ref}}$	$\mathbf{B_{HWE}}$	$\mathbf{PB_{ref}}$	$\mathbf{PB_{HWE}}$	$\mathbf{S_{ref}}$	$\mathbf{S_{HWE}}$	$\mathbf{PS_{ref}}$	$\mathbf{PS_{HWE}}$
Carbohydrates[b]	67.5	72.7	91.5	88.7	60.6	59.2	76.1	61.8
Arabinose	0.4	0.1	-	-	1.4	-	0.7	-
Galactose	1.0	0.6	0.8	1.0	1.4	-	1.2	0.6
Glucose	43.4	60.8	66.8	80.6	40.0	55.9	61.3	59.9
Mannose	1.4	1.0	0.4	0.3	11.9	1.0	6.9	0.3
Xylose	21.3	10.2	23.5	6.8	5.9	2.3	6.0	1.0
Lignin	22.1	20.7	2.1	0.8	29.8	36.8	17.8	37.4
Klason	17.6	18.2	1.2	0.2	29.4	36.6	17.3	37.1
Acid-soluble	4.5	2.5	0.9	0.6	0.4	0.2	0.5	0.3
Extractives	2.9	2.8	0.6	0.7	1.2	4.0	0.5	0.8
Others[c]	7.5	3.8	5.8	9.8	8.4	0.0	5.6	-
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

[a] B_{ref} and B_{HWE} refer to untreated and hot-water-extracted birch feedstock, respectively, and PB_{ref} and PB_{HWE} refer to the soda-AQ-delignified pulps of untreated and hot-water-extracted birch feedstock, respectively. S_{ref} and S_{HWE} refer to untreated and hot-water-extracted spruce feedstock, respectively, and PS_{ref} and PS_{HWE} refer to the soda-AQ-delignified pulps of untreated and hot-water-extracted spruce feedstock, respectively.

[b] Monosaccharide units are presented as their anhydro forms.

[c] Includes acetyl groups of xylan, pectins, and inorganics.

It is known that in practice, the soda-AQ process is mainly used for nonwoods and hardwoods due the less-reactive softwood lignin against this sulfur-free process [Feng, 2001; Finell and Nilsson, 2004; Alén, 2011a; Lehto et al., 2016]. On the other hand, it has been shown that the autohydrolysis stage of wood may facilitate lignin removal in the subsequent alkaline delignification, and sulfur-free cooking is possible [Hendriks and Zeeman, 2009; Bajpai, 2012; Lehto et al., 2016]. In the case of spruce, 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).

The results indicated that the cellulose was rather stable during the hot-water treatment. In contrast, 20-25 % of hemicelluloses (as mono-, oligo, and polysaccharides) and 30-35 % of the initial lignin were removed during the treatment in birch feedstocks, while in spruce feedstocks, these removals were 90 % and 10 %, respectively. Due to the hot-water extraction, the mass ratio of carbohydrates to lignin in the hardwood matrix increased from 3.1 to 3.5, and in the softwood matrix, the mass ratio decreased from 2.0 to 1.6. The corresponding mass ratio of aldohexose units (galactose, glucose, and mannose) to aldopentose units (arabinose and xylose) in the fraction of carbohydrates increased in both the hardwood and softwood matrix from 2.1 to 6.1 and 6.1 to 24.7, respectively.

In practice, this also meant that the hydrolyzate primarily contained xylose and mannose moieties from the principal hardwood hemicellulose component, xylan, and the softwood hemicellulose component, glucomannan, respectively. It is possible to utilize this soluble fraction for many purposes. 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 [Ragauskas et al., 2006; Alvira et al., 2010; Cherubini, 2010; Alén, 2011a; Hörhammer et al., 2011]. 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, 2011a].

The approximate carbohydrate and lignin losses were in the case ($B_{HWE} \rightarrow PB_{HWE}$), respectively, 35 % and 98 % and in the case ($S_{HWE} \rightarrow PS_{HWE}$), respectively, 32 % and 34 % of the initial amount. For softwood (due to the higher average molecular mass than that of hardwood lignin), the removal of lignin during autohydrolysis was lower. The mass ratio of carbohydrates to lignin in the hardwood and softwood matrix significantly increased, respectively, from 3.5 to 113.7 and from 1.6 to 1.7. This finding also suggested, probably due to the more open structure of the HWE softwood matrix, slightly higher reactivity of the carbohydrate fraction. On the other hand, highly prolonged hot-water extraction for softwood 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 the hot-water extraction in softwood.

The chemical composition data on pulps indicated that the total removal of carbohydrates in the reference cases ($B_{ref} \rightarrow PB_{ref}$) and ($S_{ref} \rightarrow PS_{ref}$) were, respectively, 30 % and 25 %, and the degree of delignification were 95 % and 64 % of the initial amount. The mass ratio of carbohydrates to lignin in the hardwood and softwood matrix clearly increased, respectively, from 3.1 to 42.9 and from 2.0 to 4.3. This rather low selectivity in the softwood matrix meant that high carbohydrate losses were obtained at the beginning of the cook, and delignification proceeded slowly [Lehto et al., 2016].

7.1.2 Okra and miscanthus stalks

Chemical compositions of the reference initial and differently-treated (i.e., HWE, delignified, and HWE and delignified) okra and miscanthus feedstocks [III] are presented in Table 10. The relative portions of carbohydrates and lignin in the initial raw materials (O_{ref} and M_{ref}) were slightly different. For clarity, only detailed content data on glucose (i.e., the monosaccharide moiety of cellulose) and xylose (i.e., the main monosaccharide moiety of xylan) were included. However, in all these non-wood cases, the number of other substances in varying amounts was also relatively high. It is evident that, depending on the sample, this fraction contained, for example, the acetyl groups of xylan, pectins, proteins, and inorganics, the substance groups that were not determined in detail here. Typically, the contents of inorganics, extractives, and proteins can be higher in non-wood materials than in woods [Alén, 2011b].

TABLE 10 Chemical composition of the initial and differently-treated okra and miscanthus stalk (% of the sample[a] dry solids)

Components	O_{ref}	O_{HWE}	PO_{ref}	PO_{HWE}	M_{ref}	M_{HWE}	PM_{ref}	PM_{HWE}
Carbohydrates[b]	58.3	60.7	86.9	88.5	71.7	63.9	72.4	81.8
Glucose	41.8	44.4	69.9	71.4	48.3	46.7	58.9	65.8
Xylose	12.2	13.8	16.6	16.9	21.3	14.2	13.1	15.6
Others	4.3	2.5	0.4	0.2	2.1	3.0	0.4	0.4
Lignin	20.5	17.7	3.8	2.9	17.8	16.5	1.4	1.1
Klason	17.3	16.1	3.7	2.8	17.7	16.3	1.3	0.9
Acid-soluble	3.2	1.6	0.1	0.1	0.1	0.2	0.1	0.2
Extractives	5.0	3.9	0.4	0.3	1.5	3.5	1.4	0.2
Others[c]	16.2	17.7	8.9	8.3	9.0	16.1	24.8	16.9
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

[a] O_{ref} and O_{HWE} refer to untreated and hot-water-extracted okra feedstock, respectively, and PO_{ref} and PO_{HWE} refer to the soda-AQ-delignified pulps of untreated and hot-water-extracted okra feedstock, respectively. M_{ref} and M_{HWE} refer to untreated and hot-water-extracted miscanthus feedstock, respectively, and PM_{ref} and PM_{HWE} refer to the soda-AQ-delignified pulps of untreated and hot-water-extracted miscanthus feedstock, respectively.

[b] Monosaccharide units are presented as their anhydro forms.

[c] Includes acetyl groups of xylan, pectins, proteins, and inorganics.

In this study, analysis methods related to wood chemistry were applied. However, it is known that, especially due to the presence of proteins, the Klason method may suffer some inaccuracy when applied to herbaceous plants [Dence, 1992; Brunow et al., 1999]. In contrast to hardwood [I] and softwood [II] feedstocks, hot-water extraction of non-wood feedstocks [III] also removes, besides carbohydrate-derived material, an enhanced amount of lignin-derived material even at a low degree of material dissolution. It is also known that, due to different morphological properties of non-wood fiber plants compared to wood feedstocks, non-wood fiber plants may behave in a slightly different way during alkaline pulping [Feng, 2001; Vu, 2004]. The results indicate that, in the case of hot-water extraction, about 10 % of carbohydrates and 25 % of the initial lignin (okra stalk) were removed and the corresponding, distinctly contrary values for miscanthus stalk were about 15 % and 10 %. According to the data in Table 6, there was a difference in mass loss after hot-water extraction between miscanthus and okra stalks (4.8 % for miscanthus stalk and 14.4 % for okra stalk). This clearly suggests that, probably because of the more porous structure of okra stalk, which could be easily detected by a microscope or even by the naked eye, this material was more sensitive to hot-water extraction than miscanthus stalk. Its behavior during this pretreatment phase also seemed to be closer to hardwood [I] than softwood [II].

In the case of okra stalk pulping (O_{ref} → PO_{ref} and O_{HWE} → PO_{HWE}), the degree of delignification was about 93 % whereas in miscanthus stalk pulping (M_{ref} → PM_{ref} and M_{HWE} → PM_{HWE}), it was about 96 %. In the former okra case, the total removal of carbohydrates was 40-45 % of the charged total carbohydrates (about 35 % for cellulose and about 50 % for hemicelluloses). In the latter miscanthus case, the total removal of carbohydrates was about 40 % of the charged total carbohydrates (M_{ref} → PM_{ref}, for cellulose about 30 % and for xylan about 65 %) and about 25 % (M_{HWE} → PM_{HWE}, for cellulose about 15 % and for xylan about 35 %).

7.2 Pyrolysis–gas chromatographic analyses

7.2.1 General

All these chemical treatments, which were carried out according to the principles of integrated biorefinery concepts (i.e., integrating 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 [I-III].

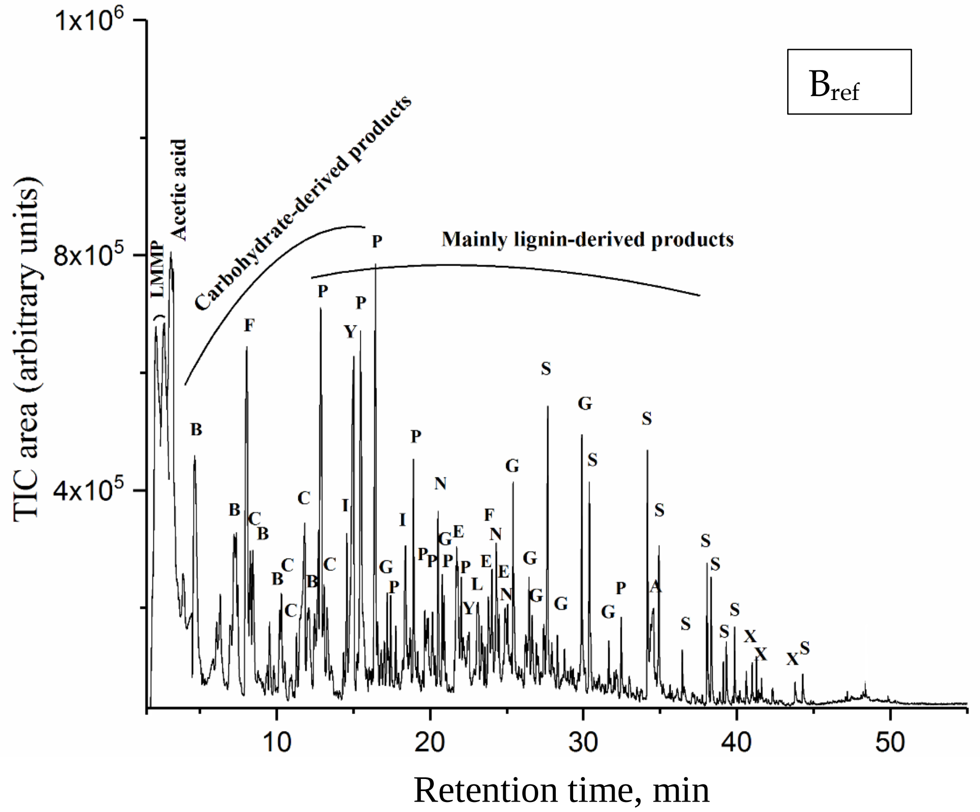
The integrated chromatographic system GC/MS applied was capable of resolving most of the main hydrophilic and lipophilic compounds released from different samples during pyrolysis. In general, pyrolysis tests under the same conditions led to reproducible results, and a typical pyrogram profile for each sample could be obtained. 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 [Lappi, 2012; Custodis et al., 2014; Lehto et al., 2016]. 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 [Shafizadeh, 1985; Alén et al., 1996; Custodis et al., 2014; Wang and Luo, 2017]. 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 deacetylation) more than the xylan backbone degrades itself.

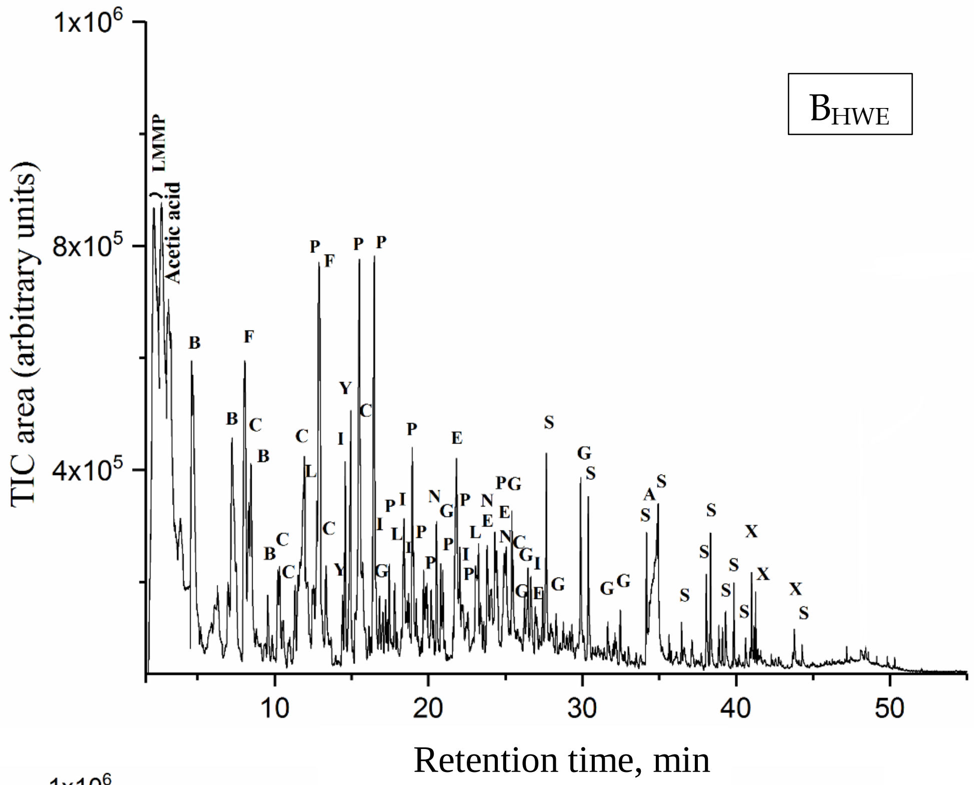
During pyrolysis, the identified compounds (Appendix II) were about 80 of birch sawdust [I], 75 of spruce sawdust [II], 60 of okra and miscanthus stalk [III], and 40 of model compounds [IV]. For simplicity, the dominant GC-amenable pyrolysis products were classified into several compound groups (Appendix I), and the formation of these monomer-related fragments was 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 [Shafizadeh, 1985; Piskorz et al., 1986; Alén et al., 1996; Bridgwater, 2002; Patwardhan, 2010; Lappi, 2012; Lédé, 2012; Custodis et al., 2014; Anca-Couce, 2016; Kawamoto, 2017; Wang and Luo, 2017]. Based on these classification data (Appendix I), it could be roughly concluded that the groups of anhydrosugar (A), cyclopentenone (C), furan (F), indene (I), lactone (L), and pyrone (Y) derivatives originated from carbohydrates, and those of guaiacol (G), phenol (P), and syringol (S) derivatives originated from lignin. The characteristic groups of naphthalene (N) and fatty acid (X) derivatives were obtained from extractives, whereas the groups of other aromatics, benzene (B) and linear ketones (LK) derivatives, were probably formed from all wood and non-wood constituents.

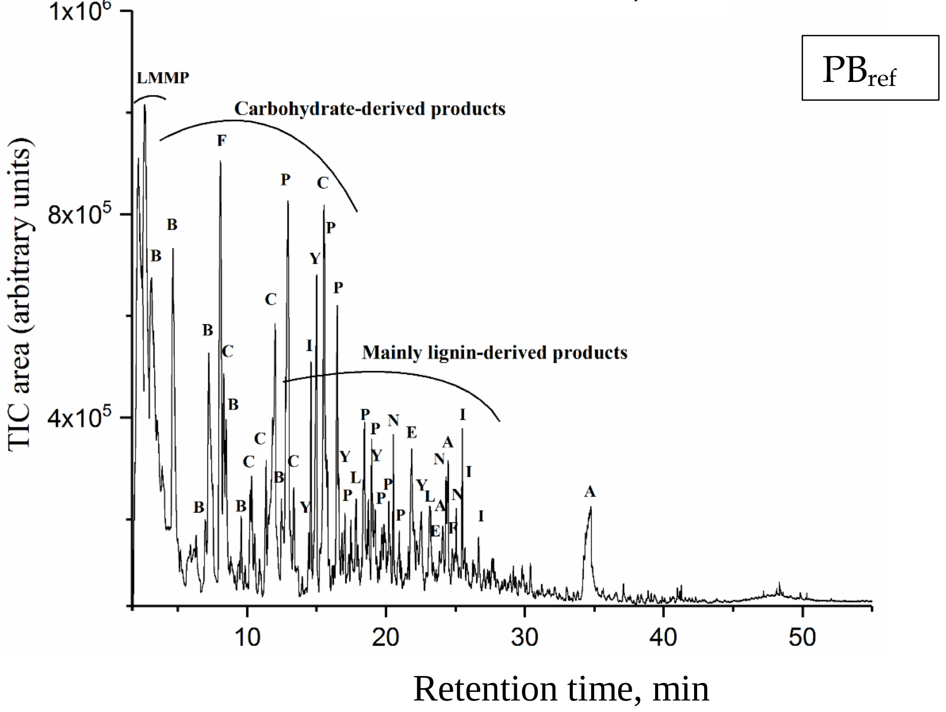
7.2.2 Pyrolysates from wood

Differently-treated birch sawdust

A pyrogram profile for differently-treated birch [I] samples is given in Figure 14.




BHWE
1x10^6
8x10^5
4x10^5
TIC area (arbitrary units)
Retention time, min
10
20
30
40
50
LMMP
Acetic acid
B
F
B
C
B
C
L
P
F
Y
I
C
P
P
C
P
E
S
G
S
A
S
S
S
X
S
X
X
S
G
I
L
I
N
G
P
N
E
PG
N
C
G
I
G
G
G
S
S
S
S


PBref
1x10^6
8x10^5
4x10^5
TIC area (arbitrary units)
Retention time, min
10
20
30
40
50
LMMP
Carbohydrate-derived products
Mainly lignin-derived products
F
B
B
P
C
Y
P
C
P
B
C
I
B
C
C
B
B
C
B
Y
P
P
N
E
I
A
N
Y
I
Y
L
P
P
Y
L
A
N
E
F
I
A

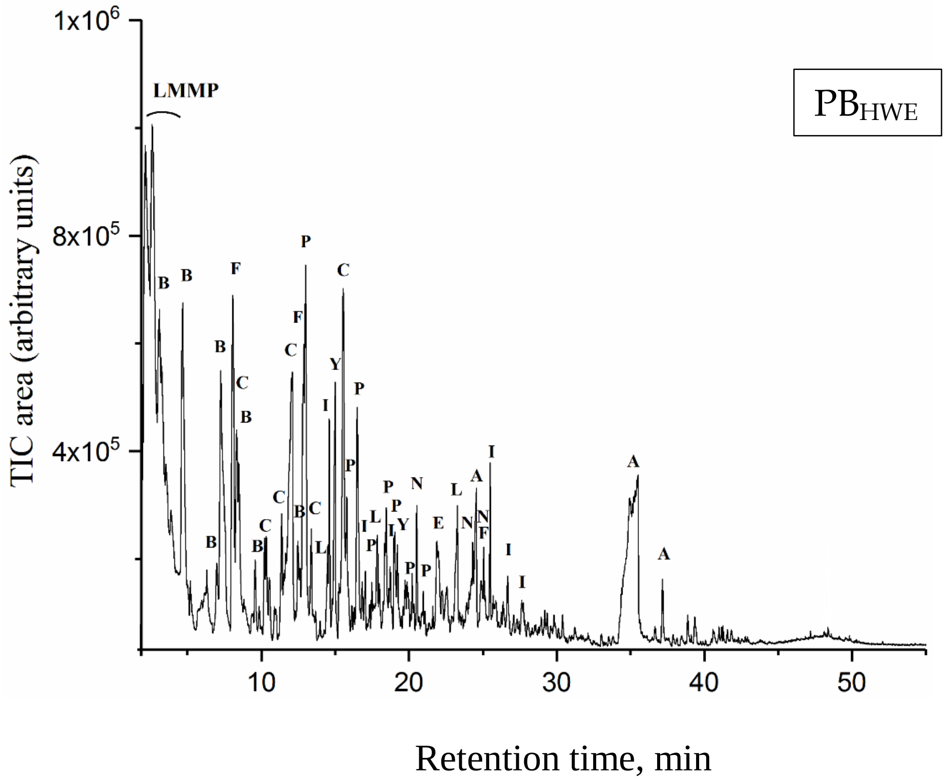
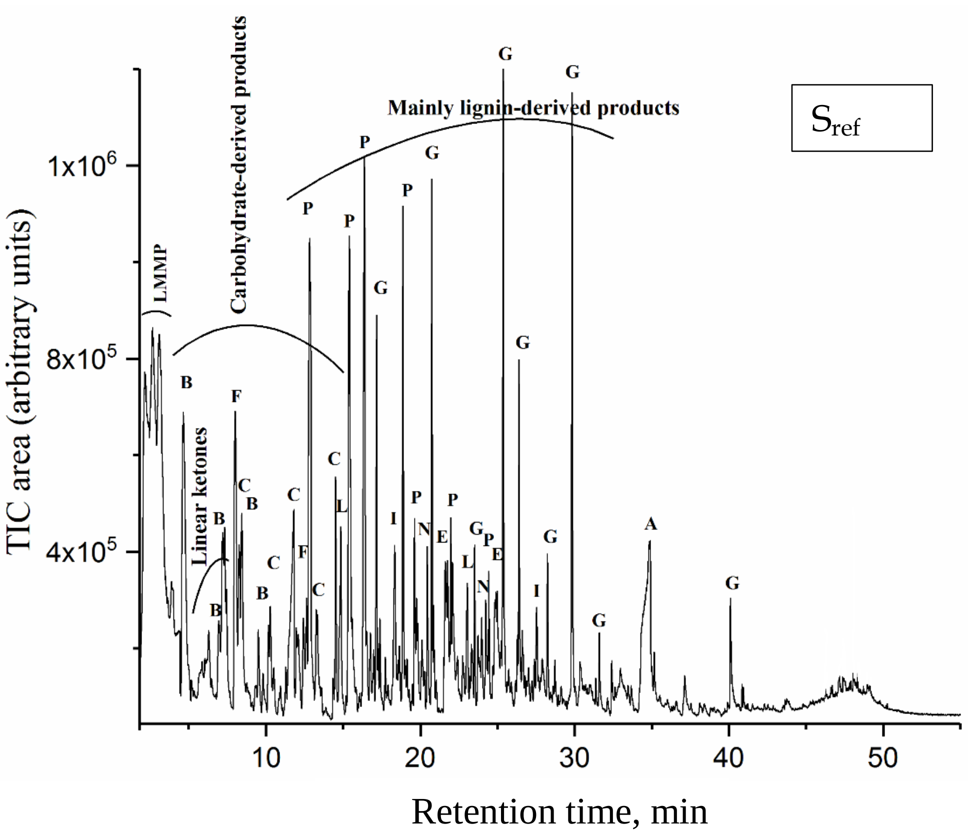
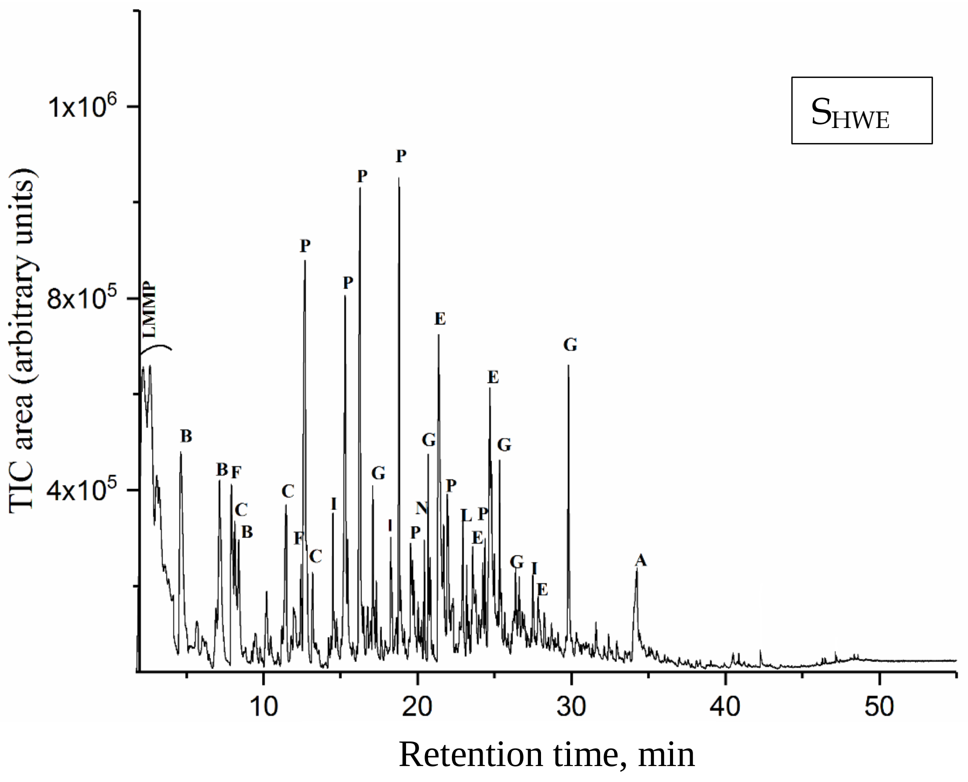


FIGURE 14 The main products formed in the pyrolysis experiments (700 °C and 20 s) from differently-treated birch sawdust. LMMP indicates low-molar-mass products. Letters indicate compound groups to which identified products belong: A (anhydrosugar derivatives), B (benzene derivatives), C (cyclopentenone 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).

Differently-treated spruce sawdust

A pyrogram profile for differently-treated spruce [II] samples is given in Figure 15.





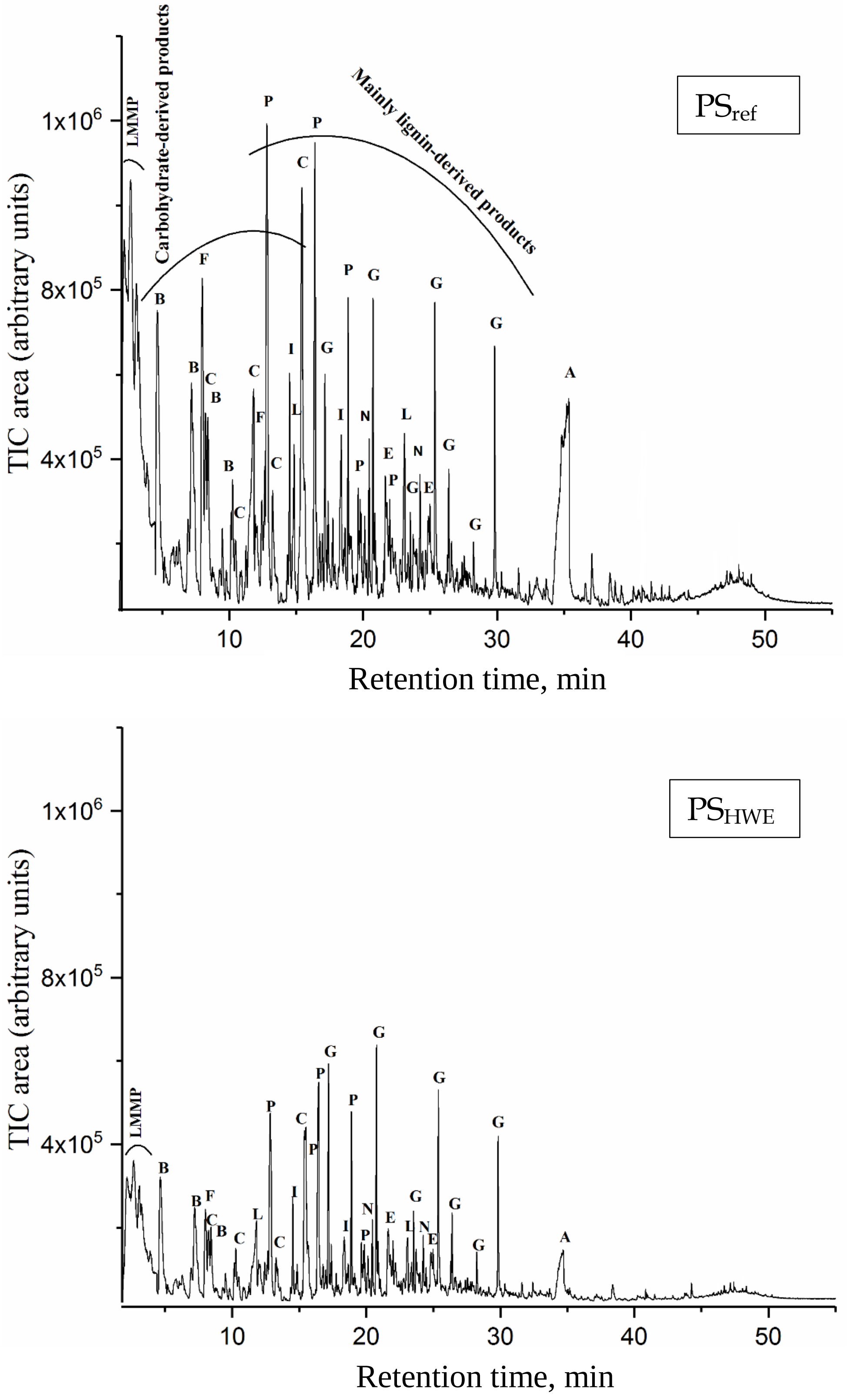


FIGURE 15 The main products formed in the pyrolysis experiments (700 °C and 20 s) from differently-treated spruce sawdust. For the letter symbols, see Figure 14.

Effect of pyrolysis conditions on product groups

In the case of B_{ref}, a pyrolysis time of 5 s at 500 ^{o}C and 700 ^{o}C, resulted in the highest pyrolysis yields similar to those obtained from B_{HWE} and PB_{ref} at 500 ^{o}C for 5 s (Figure 16). In the case of S_{ref}, pyrolysis times of 5 s and 20 s at 500 ^{o}C resulted in the highest pyrolysis yields similar to that obtained from S_{HWE} at 500 ^{o}C for 20 s. Typically, the yield was found to decrease or remain almost similar when the pyrolysis temperature increased from 500 ^{o}C to 700 ^{o}C. As a general trend, the pyrolysis yields were higher for reference samples at both temperatures for undelignified sawdust than for pulps, mainly indicating a higher relative portion of hemicelluloses in these samples (Table 9). This trend was also reflected in the overall treatment yield of the samples (Table 6).

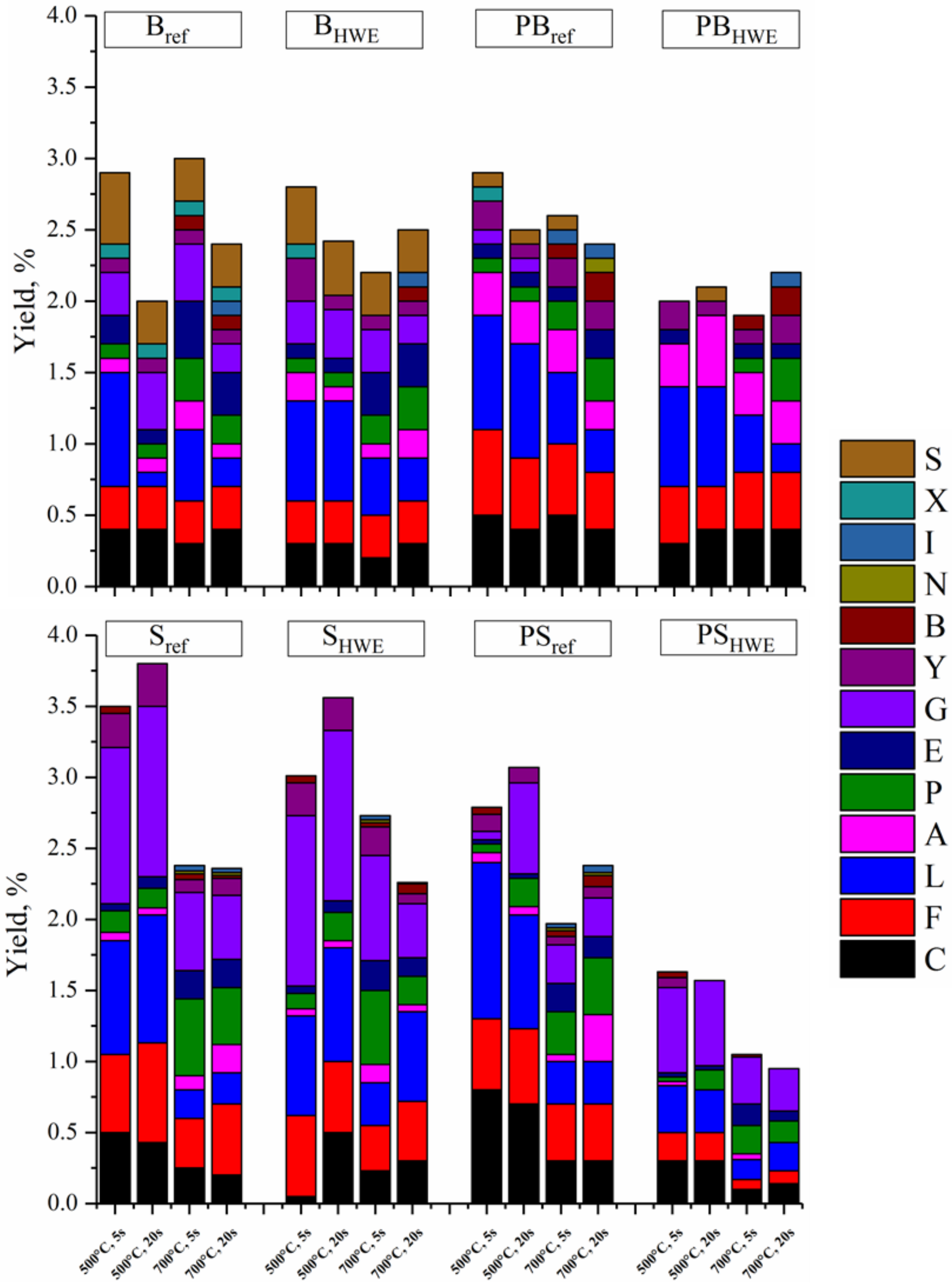


FIGURE 16 Effect of temperature and residence time on yields of various product groups of wood feedstocks. For the letter symbols, see Figure 14.

The main feedstock chemical constituents degrade on heating at different rates [Bridgwater et al., 1999]. Under the pyrolysis conditions of this study, varying amounts of carbohydrate- 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. At 700 °C, a slightly more diverse spectrum of products, including compounds, such as indenes and naphthalenes that are probably formed from certain cyclic aliphatic extractives and fatty acids, was detected (Figure 16).

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 of aliphatic compounds/aromatic compounds in the pyrolysis product fraction. Table 11 shows the ratio of aliphatic products to aromatic products obtained in our experiments. As a typical trend, more aromatic products were formed under harsher conditions: 700 °C/20 s > 700 °C/5 s > 500 °C/20 s > 500 °C/5 s. Thus, as expected from the sample compositions (Table 9), the maximum portion of aliphatic compounds was detected for pulps (PB_{HWE}, and PS_{ref}) at 500 °C/5 s and the minimum one for (B_{ref}, B_{HWE}, and PS_{HWE}) at 700 °C/5 s and 20 s.

TABLE 11 Percentage ratio of aliphatic compounds/aromatic compounds in pyrolysates of wood feedstocks (for abbreviations, see Table 9)

Condition	B_{ref}	B_{HWE}	PB_{ref}	PB_{HWE}	S_{ref}	S_{HWE}	PS_{ref}	PS_{HWE}
500 °C/5 s	63/37	67/33	87/13	95/5	61/39	53/47	93/7	57/43
500 °C/20 s	65/35	62/38	84/16	95/5	63/37	58/42	72/28	51/49
700 °C/5 s	50/50	52/48	81/19	89/11	43/57	44/56	58/42	33/67
700 °C/20 s	56/44	50/50	71/29	73/27	54/46	65/35	61/39	45/55

It could be roughly observed that the compound groups A, C, F, L, and Y (Appendix I) were mainly formed from carbohydrates, F and L from xylan, and G, E, and S from lignin. Based on this assumption, the ratio of carbohydrates to lignin at 500 °C/20 s for birch-derived samples was 1.4 (B_{ref}), 2.1 (B_{HWE}), 10.5 (PB_{ref}), and 20.0 (PB_{HWE}), that was B_{ref}/B_{HWE} 0.7, B_{HWE}/PB_{ref} 0.2, and PB_{ref}/PB_{HWE} 0.5 (estimated values from Table 9 are 0.9, 0.1, and 0.4, respectively). On the other hand, the ratio of xylan to lignin was 0.6 (B_{ref}), 1.2 (B_{HWE}), 6.5 (PB_{ref}), and 10.0 (PB_{HWE}), that was B_{ref}/B_{HWE} 0.5, B_{HWE}/PB_{ref} 0.2 and PB_{ref}/PB_{HWE} 0.7 (estimated values from Table 9 are 0.5, 0.1, and 1.3, respectively). In the case of spruce-derived samples at 500 °C/20 s, the ratio of carbohydrates to lignin was 1.7 (S_{ref}), 1.4 (S_{HWE}), 3.2 (PS_{ref}), and 1.0 (PS_{HWE}), that was S_{ref}/S_{HWE} 1.2, S_{HWE}/PS_{ref} 0.4 and PS_{ref}/PS_{HWE} 3.2 (estimated values from Table 9 are 1.3, 0.4, and 2.5, respectively). Additionally, the ratio of xylan to lignin can be disregarded due to a smaller portion of xylan in the spruce backbone.

Effect of pyrolysis conditions on prominent products

It was evident that hot-water extraction, as well as delignification, caused some chemical changes in the fractions of carbohydrates and lignin in the feedstock matrix, thus also, to some extent, partly reflecting the formation of individual products during pyrolysis. Since a number of significant pyrolysis products could be measured simultaneously, a single pyrolysis run gave fingerprint data for rapid characterization of feedstock materials. Of the main products (Appendix III), 3-hydroxy-2-penteno-1,5-lactone (I), 3-methylcyclopentane-1,2-dione (II), 2-hydroxycyclopent-2-en-1-one (III), furfural (IV), and LG (V) originated from carbohydrates; from lignin, guaiacol (2-methoxyphenol, VI), syringol (2,6-dimethoxyphenol, VII), and isoeugenol (2-methoxy-4-(prop-1-en-1-yl)phenol, VIII) were commonly found in pyrolysates (Figure 17). It was concluded that a correlation exists between the formation of a number of the products and the chemical composition of feedstock. In the case of birch sawdust, for example, at 500 °C/20 s, the GC peak area ratio (I + II + III + IV + V)/(VI + VII + VIII) (i.e., carbohydrates/lignin) for B_{ref}, B_{HWE}, PB_{ref}, and PB_{HWE} was, respectively, 4.0, 4.5, 12.0, and 25.0 (estimated values from Table 9 are 3.1, 3.5, 43.6, and 110.9, respectively). Additionally, at 500 °C/20 s, the GC peak area ratio (I + IV)/(VI + VII + VIII) (i.e., xylan/lignin) for B_{ref}, B_{HWE}, PB_{ref}, and PB_{HWE} was, respectively, 3.0, 2.1, 13.6, and 6.0 (estimated values from Table 9 are 1.0, 0.5, 11.2, and 8.5, respectively). Another example: if 4-allyl-2,6-dimethoxyphenol (IX), from lignin, was included in the calculation at 500 °C/5 s and 700 °C/5 s for B_{ref} and B_{HWE}, the GC peak area ratio (I + II + IV + V)/(IX) (i.e., carbohydrates/lignin) was 9.6 and 14.3 and that of (I + II + IV + V)/(VIII + IX) was 3.2 and 5.7, respectively. At 500 °C/5 s for B_{ref} and B_{HWE}, the corresponding ratio (I + IV)/(VIII + IX) (i.e., xylan/lignin) was 6.2 and 4.2, respectively.

Similarly, in the case of spruce sawdust, for example, at 500 °C/20 s, the GC peak area ratio (I + II + III + IV + V)/(VI + VIII) (i.e., carbohydrates/lignin) for S_{ref}, S_{HWE}, PS_{ref}, and PS_{HWE} was, respectively, 1.4, 1.1, 4.5, and 1.5 (estimated values from Table 9 were 2.0, 1.6, 4.3, and 1.6, respectively). However, it was possible to test many other ratios as well, and representative correlations could be achieved. For example, if *p*-cresol (4-methylphenol, X) from lignin was considered, at 700 °C for 5 s, the straightforward ratio (I + II + III + IV + V)/(VI + VIII + X) (i.e., carbohydrates/lignin) was 1.3 (S_{ref}), 1.3 (S_{HWE}), 4.5 (PS_{ref}), and 1.3 (PS_{HWE}). Another example was when the ratio (I + III + IV + V)/(VI + X) (→ 2.1 (S_{ref}), 1.4 (S_{HWE}), 4.6 (PS_{ref}), and 1.8 (PS_{HWE})) was used. On the other hand, at 500 °C/20 s, the GC peak area ratio (I + IV)/(VI + VIII) (i.e., xylan/lignin) for S_{ref} and S_{HWE} was, respectively, 0.6 and 0.5 (estimated values from Table 9 are 0.2 and 0.1, respectively).

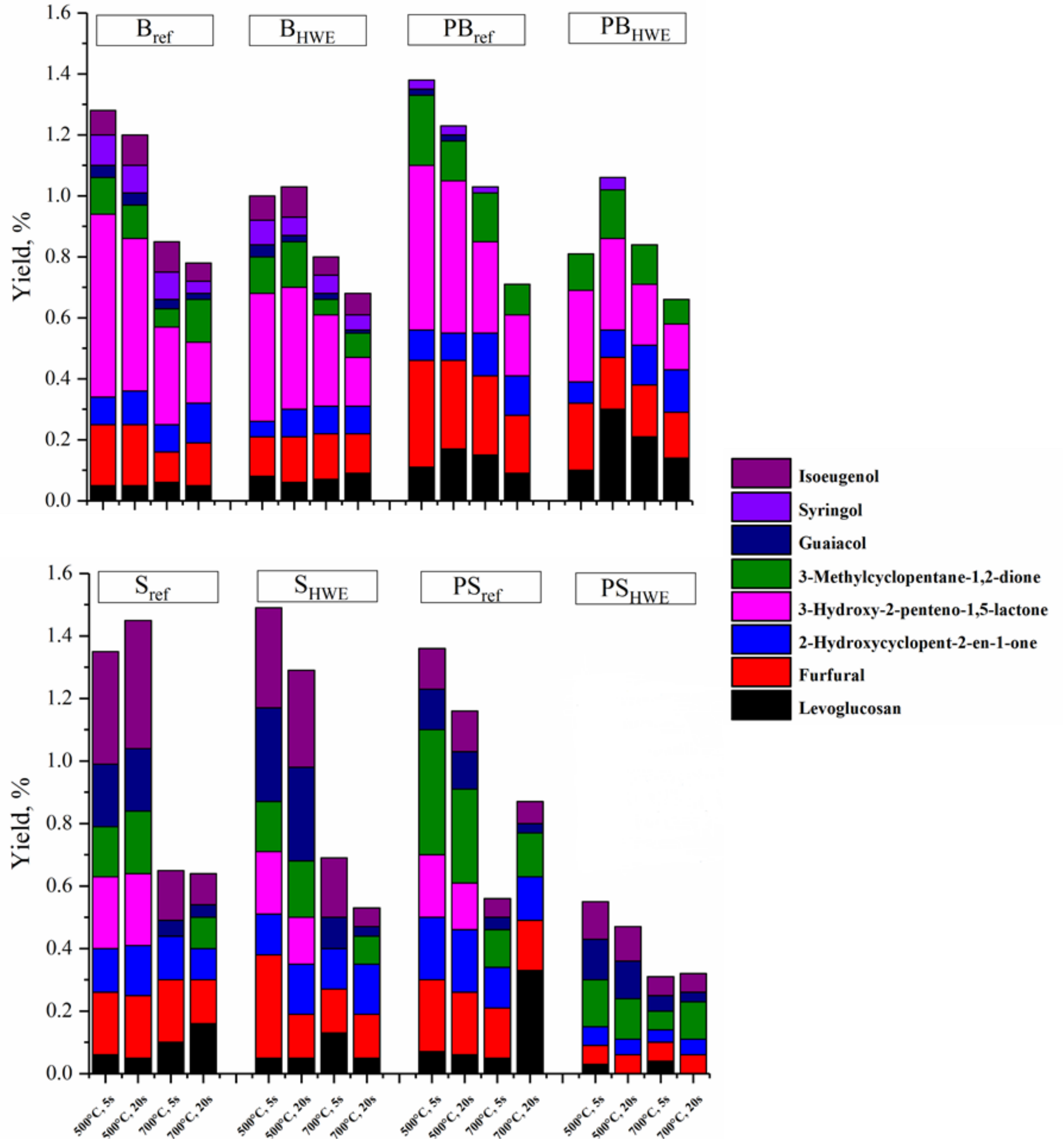


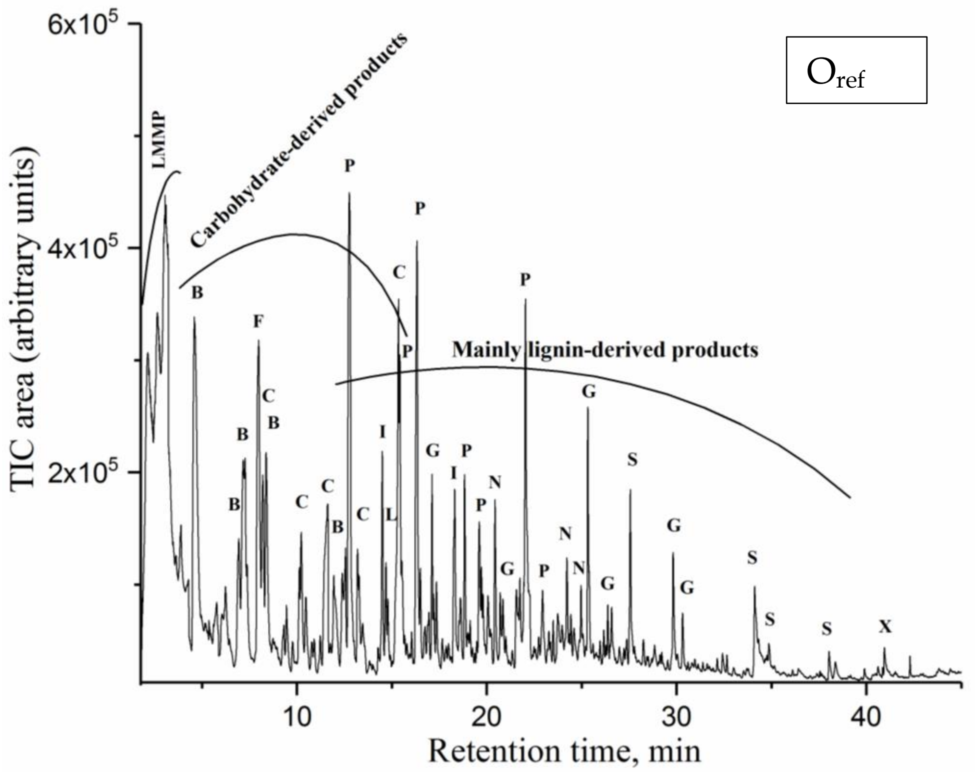
FIGURE 17 Effects of temperature and residence time on yields of prominent pyrolysis products.

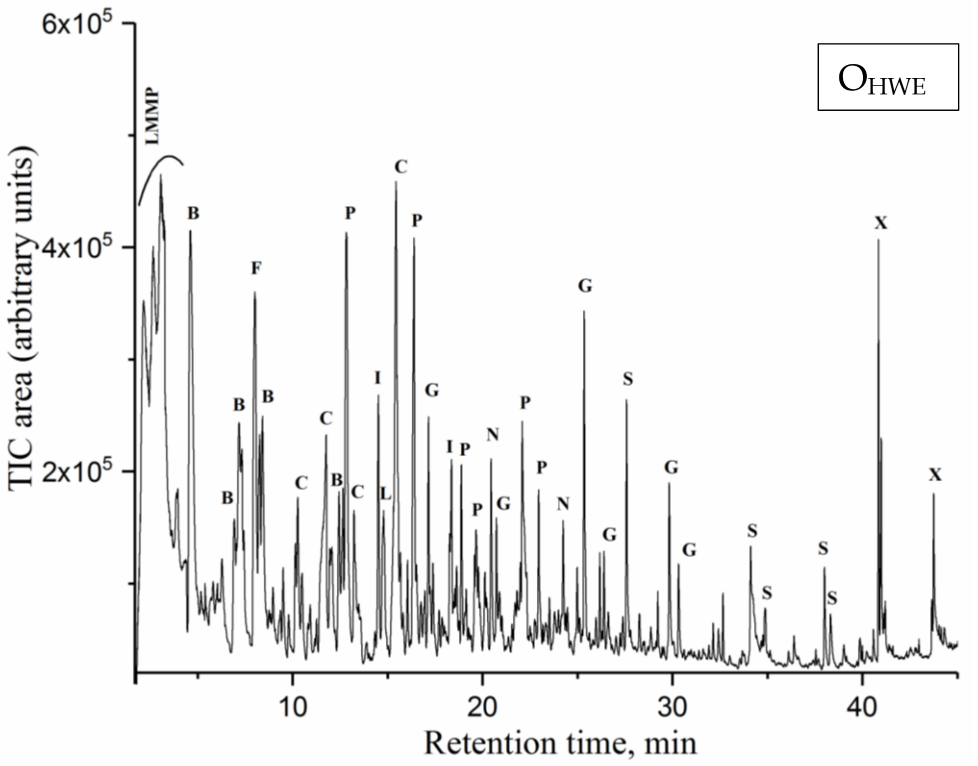
Softwoods generally contain fewer hemicelluloses than hardwoods. However, they differ not only in the content of total hemicelluloses but also in the percentages of individual hemicellulose constituents—in softwoods, primarily glucomannan (containing glucose and mannose units); in hardwoods, mainly xylan (containing xylose units). In comparison with birch [I], these chemical compositions also had some influence on the distribution of pyrolysis products. For example, typically, three times more xylan-derived 3-hydroxy-2-penteno-1,5-lactone was formed from hardwood than from softwood; the percentual amount of xylose in birch sawdust (i.e., in B_{ref}) was 21.3 and 5.9 in S_{ref} (Table 9). Furthermore, anhydrosugars (e.g., LG), detected only in the pyrolysis of hexoses (i.e., D-glucose, D-mannose, and D-galactose), were 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 were principally formed from *trans*-coniferyl alcohol-type units (i.e., guaiacyl lignin) whereas hardwood lignins principally 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.

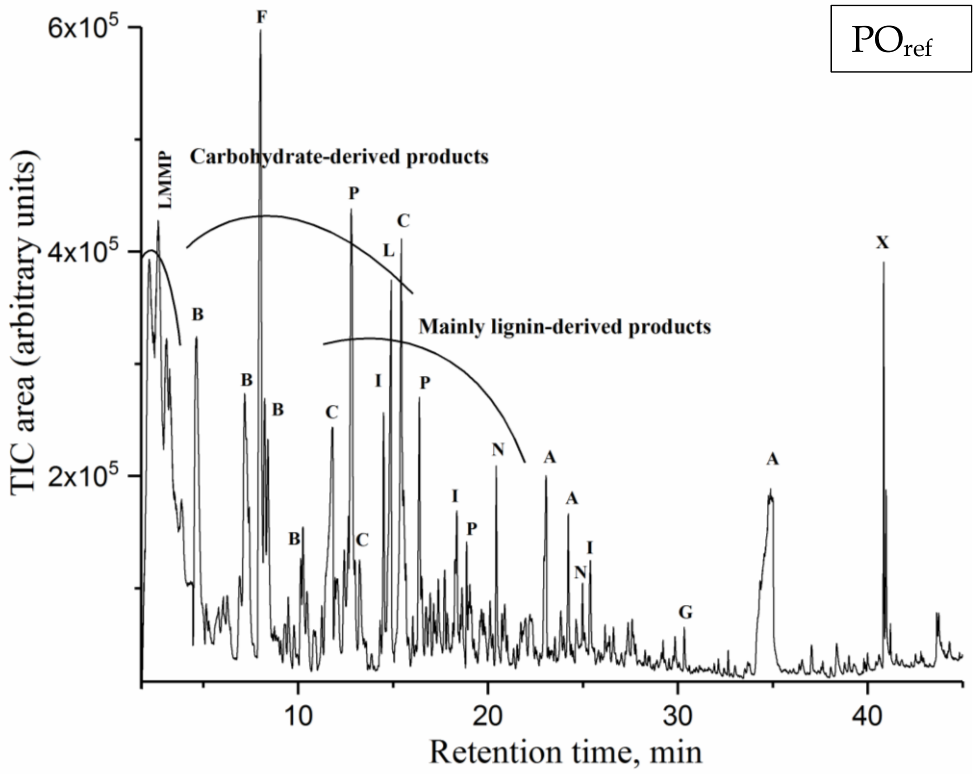
7.2.3 Pyrolysates from non-wood

Differently-treated okra stalk

A pyrogram profile for differently-treated okra stalks samples [III] is given in Figure 18.




O_{HWE}
6x10⁵
4x10⁵
2x10⁵
TIC area (arbitrary units)
10
20
30
40
Retention time, min
LMMP
B
B
B
F
B
C
B
C
P
C
I
L
C
P
G
I
P
P
N
G
P
P
N
G
G
S
G
G
S
S
S
S
X
X


PO_{ref}
6x10⁵
4x10⁵
2x10⁵
TIC area (arbitrary units)
10
20
30
40
Retention time, min
LMMP
Carbohydrate-derived products
Mainly lignin-derived products
F
B
B
B
B
C
C
P
I
L
C
P
I
P
N
A
A
N
I
G
A
X

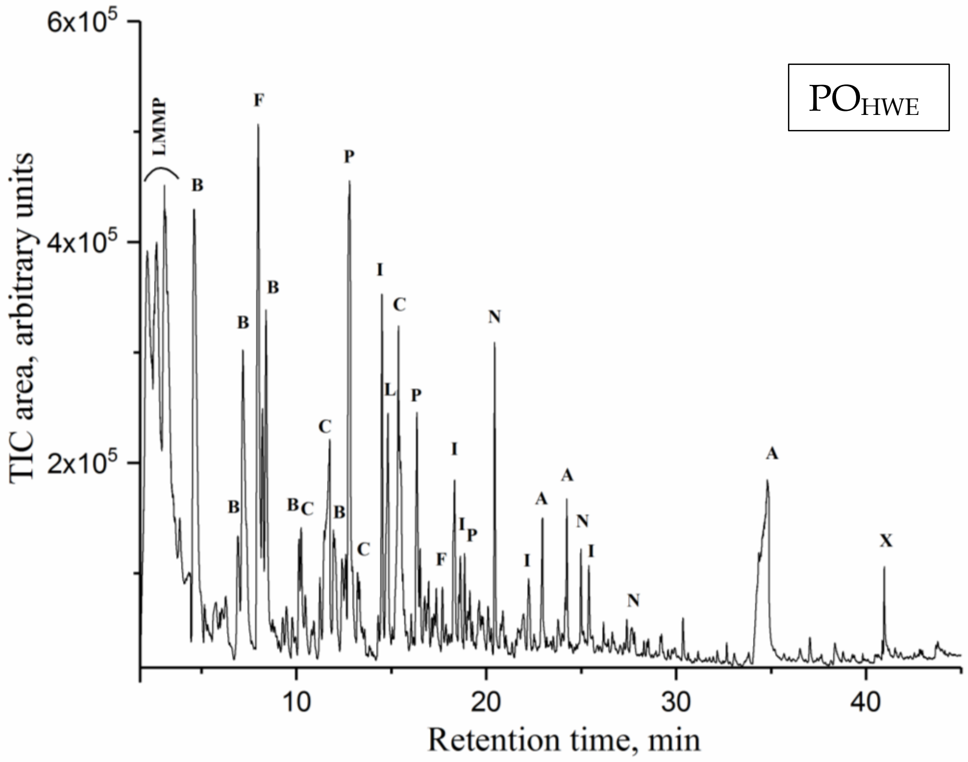
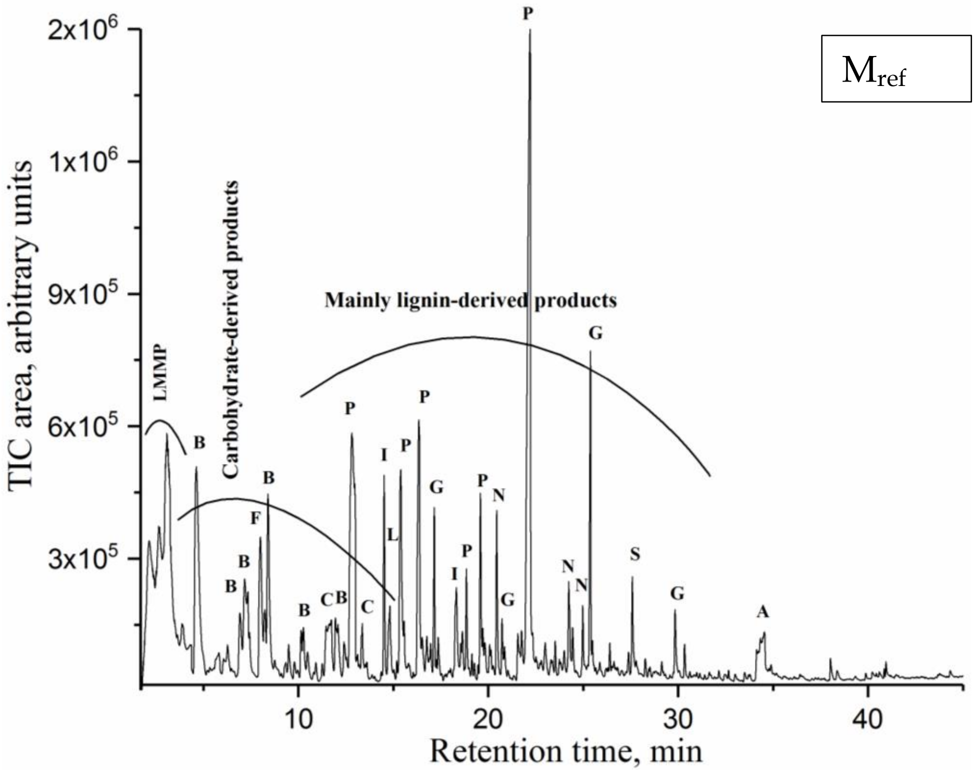
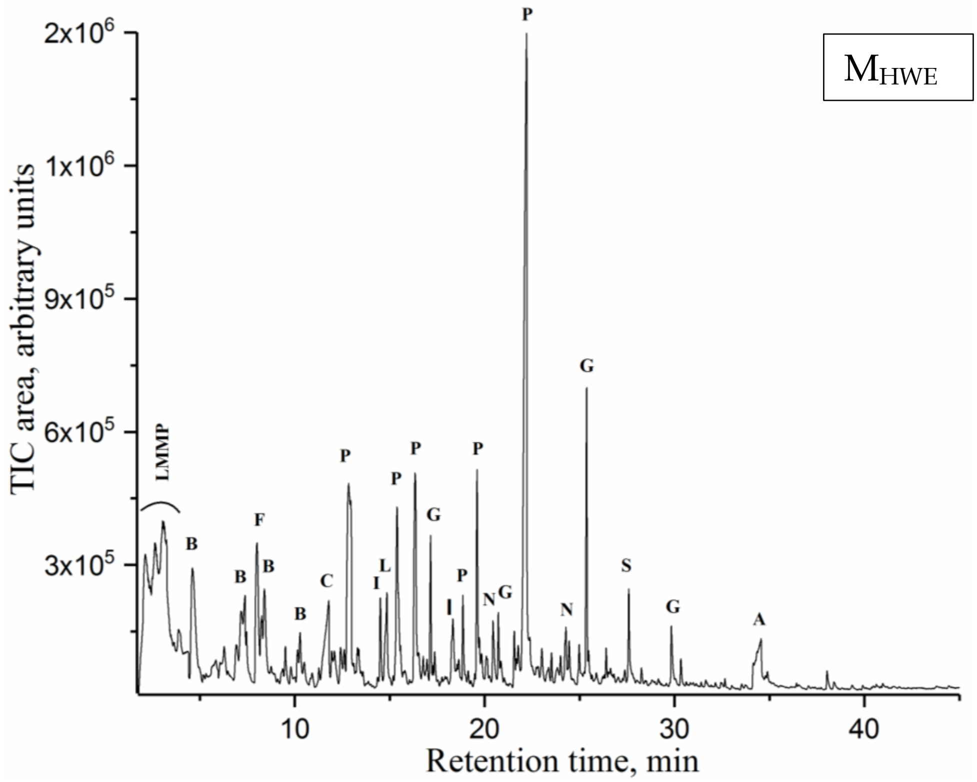


FIGURE 18 The main products formed in the pyrolysis experiments (700 °C and 20 s) from differently-treated okra stalks. For the letter symbols, see Figure 14.

Differently-treated miscanthus stalk

A pyrogram profile for differently-treated miscanthus stalks samples [III] is given in Figure 19. Additionally, results agree well with the data on the thermochemical conversion of miscanthus by pyrolysis [Hodgson et al., 2011; Butler et al., 2013].


M$_{ref}$
TIC area, arbitrary units
2x10^6
1x10^6
9x10^5
6x10^5
3x10^5
Retention time, min
10
20
30
40
LMMP
Carbohydrate-derived products
Mainly lignin-derived products
B
B
B
F
B
B
C
B
C
P
I
L
P
P
G
I
P
P
N
G
P
G
N
N
S
G
A


M$_{HWE}$
TIC area, arbitrary units
2x10^6
1x10^6
9x10^5
6x10^5
3x10^5
Retention time, min
10
20
30
40
LMMP
B
B
F
B
B
C
P
I
L
P
P
G
I
P
P
N
G
P
G
N
S
G
A

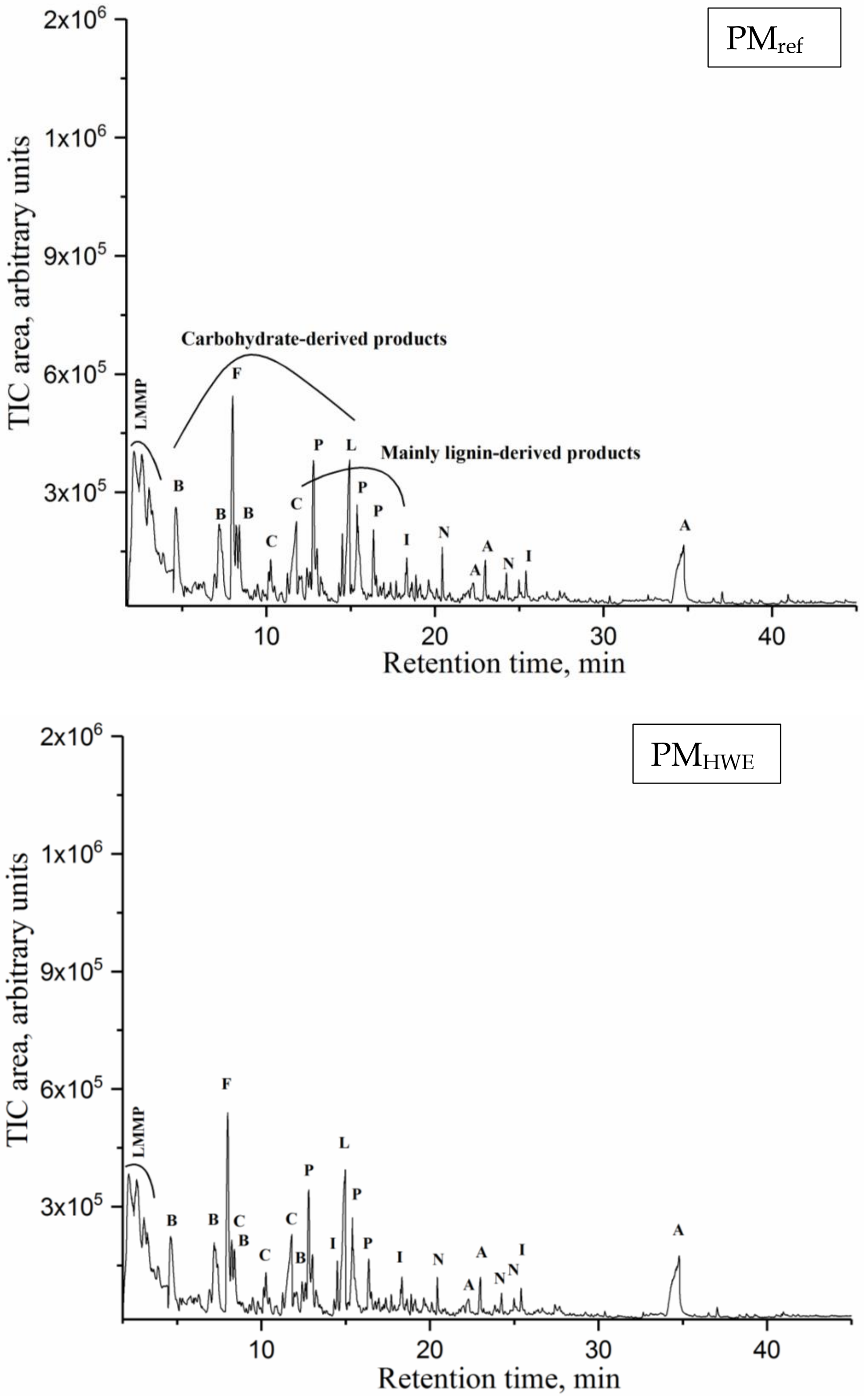


FIGURE 19 The main products formed in the pyrolysis experiments (700 °C and 20 s) from differently-treated miscanthus stalks. For the letter symbols, see Figure 14.

Effect of pyrolysis conditions on product groups

The pyrolysis yields at 500 ^{o}C/5 s and 500 ^{o}C/20 s were slightly higher for reference samples (i.e., $O_{ref} > O_{HWE}$ and $M_{ref} > M_{HWE}$). However, it was difficult to explain these findings straightforwardly based only on the chemical composition of the samples (Table 10). In the case of okra pulps, the highest pyrolysis yield was obtained at 500 ^{o}C/5 s and 500 ^{o}C/20 s from PO_{HWE}, whereas for miscanthus pulps, the yield order was $PM_{ref} > PM_{HWE}$ (Figure 20). Furthermore, it was found that the overall treatment yield of okra-derived samples (Table 6) was also directly reflected in the pyrolysis yields that decreased at 500 ^{o}C/5 s in order $O_{ref} > O_{HWE} > PO_{ref} \approx PO_{HWE}$. On the other hand, the overall treatment yield of miscanthus-derived samples (Table 6) revealed a similar trend of decreasing the pyrolysis yields at 500 ^{o}C/20 s in order $M_{ref} > M_{HWE} > PM_{ref} \approx PM_{HWE}$.

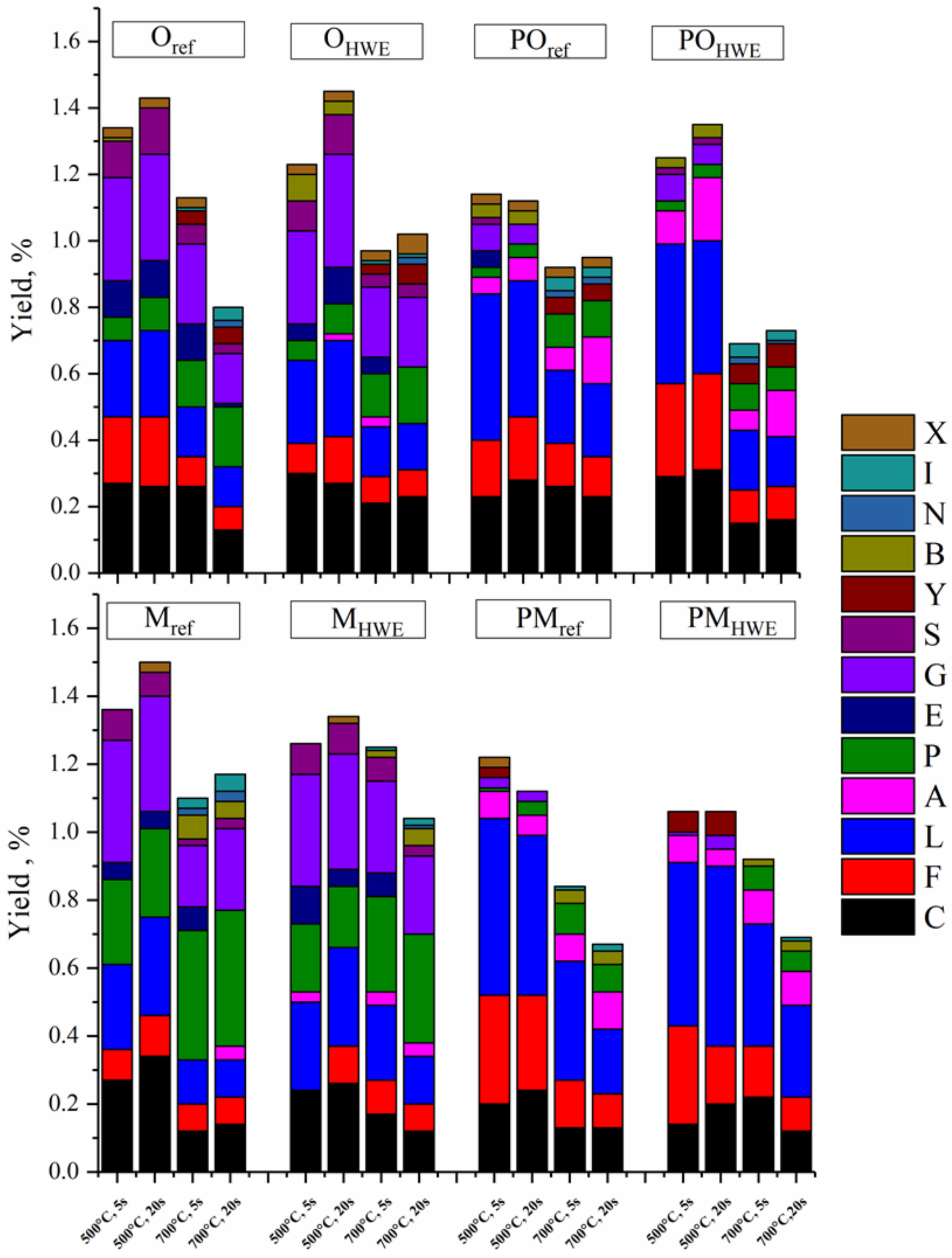


FIGURE 20 Effect of temperature and residence time on yields of various product groups obtained from the pyrolysis of untreated and differently-treated okra and miscanthus stalk. For the letter symbols, see Figure 14.

The main feedstock chemical constituents degrade on heating at different rates [Atsushi et al., 1984]. The results, for example, clearly indicate that in the case of reference and HWE samples, the formation of lignin-derived products (guaiacol, syringol, and phenol derivatives) together with hemicellulose-derived products (lactone, furan, and cyclopentenone derivatives) was particularly enhanced at 500 °C, whereas in the case of pulp samples, as expected from the sample compositions (Table 10), hemicellulose-derived products prevailed (Figure 20). Typically, at 700 °C, a slightly more diverse spectrum of product groups was detected. Table 12 shows the ratio of aliphatic pyrolysis products to aromatic pyrolysis products detected in our experiments under varying pyrolysis conditions. As a characteristic trend, more aromatic products were formed under harsher conditions. Thus, the significant portion of aromatic products, 47-67 %, was obtained from the reference and HWE samples at 700 °C/5 s and 700 °C/20 s whereas the maximum portion of the aliphatic products, 90-99 %, was found in pulp samples at 500 °C/5 s and 500 °C/20 s.

TABLE 12 Percentage ratio of aliphatic compounds/aromatic compounds in pyrolysates (for abbreviations, see Table 10)

Condition	**O$_{\mathrm{ref}}$**	**OHWE**	**PO$_{\mathrm{ref}}$**	**POHWE**	**M$_{\mathrm{ref}}$**	**MHWE**	**PM$_{\mathrm{ref}}$**	**PMHWE**
500 °C/5 s	55/45	61/39	84/16	90/10	45/55	42/58	97/3	99/1
500 °C/20 s	53/47	54/46	91/9	90/10	52/48	51/49	94/6	96/4
700 °C/5 s	48/52	53/47	91/9	73/27	33/67	43/57	85/15	90/10
700 °C/20 s	45/55	51/49	81/19	73/27	36/64	38/62	82/18	76/24

As shown above, the compound groups A, C, F, L, and Y primarily originated from carbohydrates; F and L typically originated from xylan; and G, P, and S originated from lignin (Appendix I). Based on this simple assumption, the ratio of carbohydrates to lignin, at 500 °C/20 s for okra-derived samples, was 1.1 (O$_{\mathrm{ref}}$), 1.1 (OHWE), 9.9 (PO$_{\mathrm{ref}}$), and 10.4 (POHWE), that was O$_{\mathrm{ref}}$/OHWE 1.00, OHWE/PO$_{\mathrm{ref}}$ 0.11, and PO$_{\mathrm{ref}}$/POHWE 0.95 (estimated values from Table 10 are 0.8, 0.1, and 0.8, respectively). On the other hand, the ratio of xylan to lignin was 0.7 (O$_{\mathrm{ref}}$), 0.7 (OHWE), 6.0 (PO$_{\mathrm{ref}}$), and 5.8 (POHWE), that was O$_{\mathrm{ref}}$/OHWE 1.00, OHWE/PO$_{\mathrm{ref}}$ 0.12, and PO$_{\mathrm{ref}}$/POHWE 1.03 (estimated values from Table 10 are 0.8, 0.2, and 0.8, respectively). In the case of miscanthus-derived samples at 500 °C/20 s, the ratio of carbohydrates to lignin was 1.0 (M$_{\mathrm{ref}}$), 1.2 (MHWE), 15.0 (PM$_{\mathrm{ref}}$), and 25.5 (PMHWE), that was M$_{\mathrm{ref}}$/MHWE 0.83, MHWE/PM$_{\mathrm{ref}}$ 0.08, and PM$_{\mathrm{ref}}$/PMHWE 0.59 (estimated values from Table 10 are 1.0, 0.1, and 0.7, respectively). Additionally, the ratio of xylan to lignin indicated the values 0.6 (M$_{\mathrm{ref}}$), 0.8 (MHWE), 10.7 (PM$_{\mathrm{ref}}$), and 17.5 (PMHWE), that was M$_{\mathrm{ref}}$/MHWE 0.75, MHWE/PM$_{\mathrm{ref}}$ 0.07, and PM$_{\mathrm{ref}}$/PMHWE 0.61 (estimated values from Table 10 are 1.3, 0.1, and 0.6, respectively).

Effect of pyrolysis conditions on prominent products

Of the main products (Appendix III), 3-hydroxy-2-penteno-1,5-lactone (I), 3-methylcyclopentane-1,2-dione (II), 2-hydroxycyclopent-2-en-1-one (III), furfural (IV), which originated from carbohydrates, and guaiacol (V), syringol (VI), and isoeugenol (VII), which originated from lignin, were commonly found in pyrolysates (Figure 21).

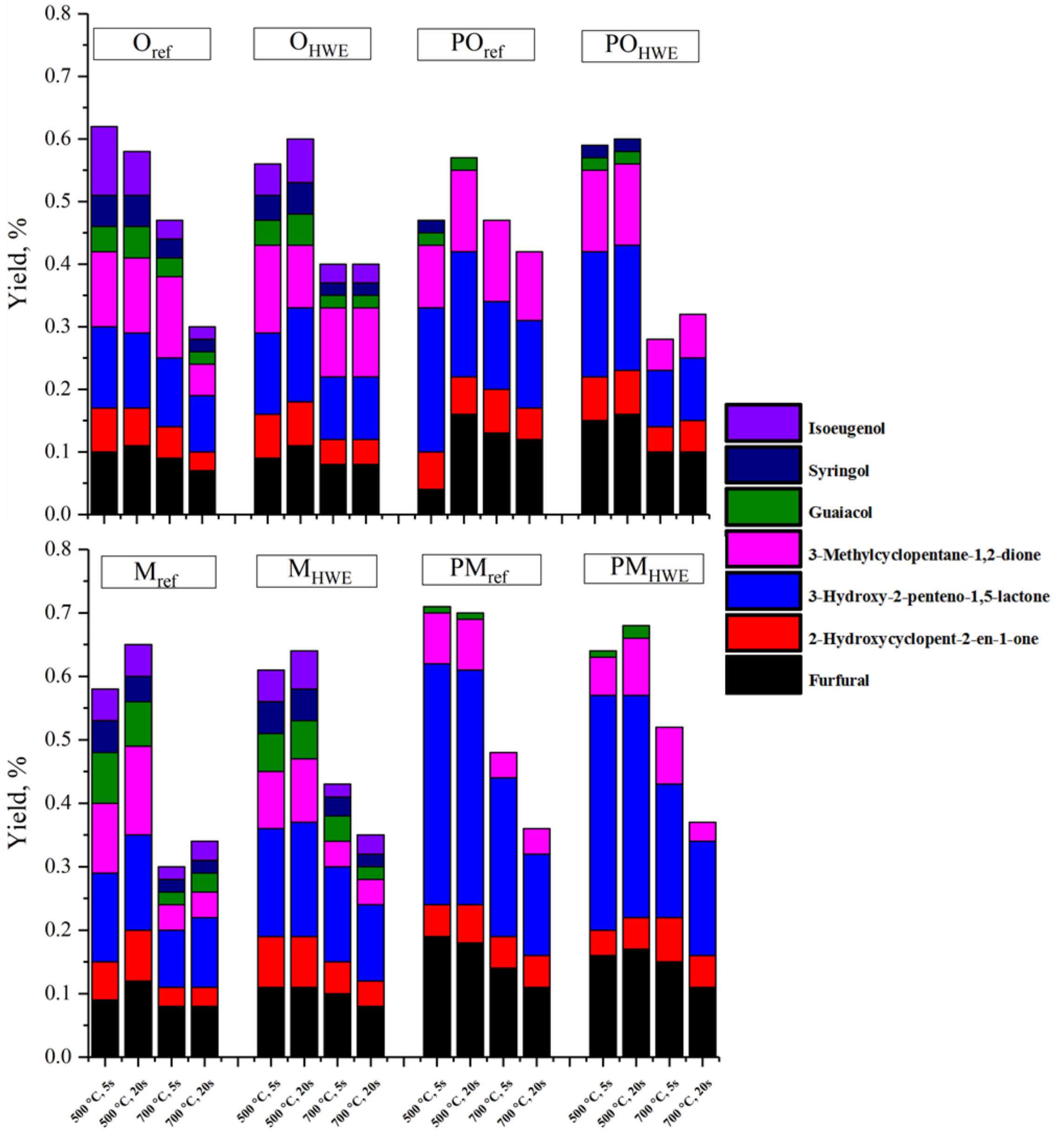


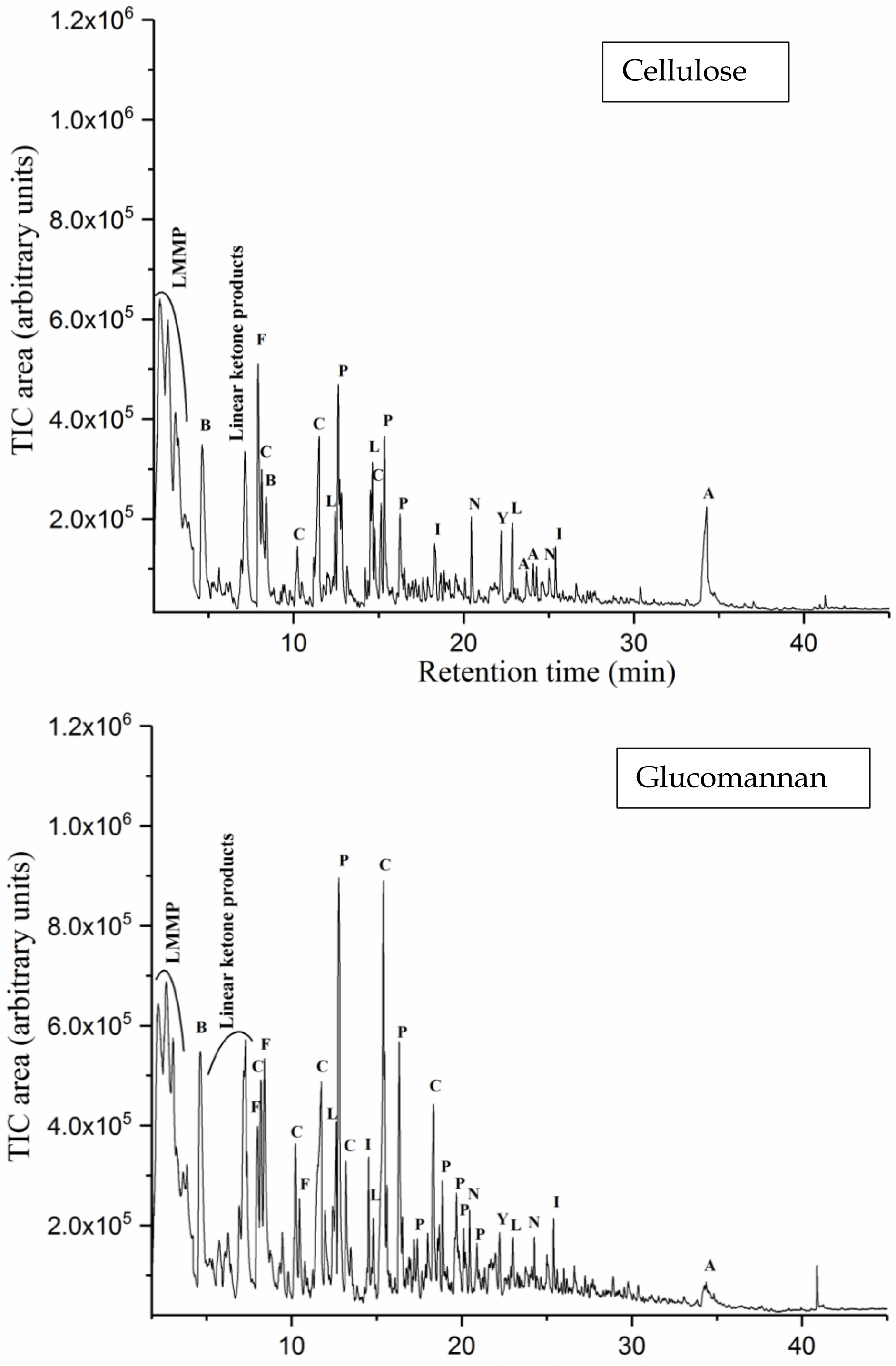
FIGURE 21 Effect of temperature and residence time on yields of prominent pyrolysis products obtained from the pyrolysis of untreated and differently-treated okra and miscanthus stalk.

The relevant correlation between the formation of a number of the pyrolysis products and the chemical composition of feedstock were shown that in the case of okra stalk, for example, at 500 °C/20 s, the GC peak area ratio (I + II + III + IV)/(V + VI + VII) (i.e., carbohydrates/lignin) for O$_{ref}$ and O$_{HWE}$ was, respectively, 2.4 and 2.5 (estimated values from Table 10 are 2.8 and 3.4, respectively). Another example: if at 500 °C/20 s, 5*H*-furan-2-one (VIII, from carbohydrates) and 4-ethenyl-2-methoxyphenol (X, from lignin) were considered, the ratio (I + II + III + IV + VIII)/(V + VII + X) for O$_{ref}$ and O$_{HWE}$ was 3.2 (O$_{ref}$) and 3.1 (O$_{HWE}$). Furthermore, at 500 °C/5 s, the ratio (I + II + III + IV + VIII)/(V + VI + VII) resulted in the values 3.1 and 3.9, respectively. Additionally, at 500 °C/20 s, the GC peak area ratio (I + IV)/(V + VI + VII) (i.e., xylan/lignin) for O_{ref} and O_{HWE} was, respectively, 1.1 and 1.3 (estimated values from Table 10 are 0.6 and 0.8, respectively). Another example: if at 500 °C/20 s, 4-ethenylphenol (IX, from lignin) was considered in the calculation, the GC peak area ratio (III + IV + VIII)/(V + VI + VII + IX + X) for O_{ref} and O_{HWE} was 0.7 and 0.9, respectively.

Similarly, in the case of miscanthus stalk, for example, at 500 °C/20 s, the GC peak area ratio (I + II + III + IV)/(V + VI + VII) (i.e., carbohydrates/lignin) for M_{ref} and M_{HWE} was 3.1 and 2.5 (estimated values from Table 10 are 4.0 and 3.9, respectively). Additionally, the GC peak area ratio (I + II + III + IV + VIII)/(V + VI + VII) for M_{ref} and M_{HWE} was 3.9 and 3.4, respectively. On the other hand, at 500 °C/20 s, the GC peak area ratio (I + IV)/(V + VI + VII) (i.e., xylan/lignin) for M_{ref} and M_{HWE} was 1.7 and 1.5 (estimated values from Table 10 are 1.2 and 0.9, respectively). Another example revealed that the GC peak area ratio (III + IV)/(V + VI + VII) for M_{ref} and M_{HWE} was 1.3 and 1.1, respectively.

7.2.4 Pyrolysates from model substances

The thermochemical behavior of differently-treated wood [I and II] and non-wood [III] materials has been investigated. In each case, the prominent GC-amenable condensable products were determined and classified into several characteristic compound groups. In this comparative section with model substances, the aim was to further clarify the formation of these compound groups under the same pyrolysis conditions as those applied to wood and non-wood materials. Since carbohydrates are the main components of various biorefinery fractions, cellulose and hemicelluloses (glucomannan and xylan) were selected for the Py-GC and TGA experiments [IV]. Examples of a typical pyrogram profile for each sample are presented in Figure 22.


Cellulose
TIC area (arbitrary units)
1.2x10^6
1.0x10^6
8.0x10^5
6.0x10^5
4.0x10^5
2.0x10^5
LMMP
Linear ketone products
B
F
C
B
C
C
L
P
L
C
P
P
I
N
Y
L
A
A
N
I
A
10
20
30
40
Retention time (min)
Glucomannan
TIC area (arbitrary units)
1.2x10^6
1.0x10^6
8.0x10^5
6.0x10^5
4.0x10^5
2.0x10^5
LMMP
Linear ketone products
B
F
C
F
C
C
F
L
P
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C
I
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Retention time (min)

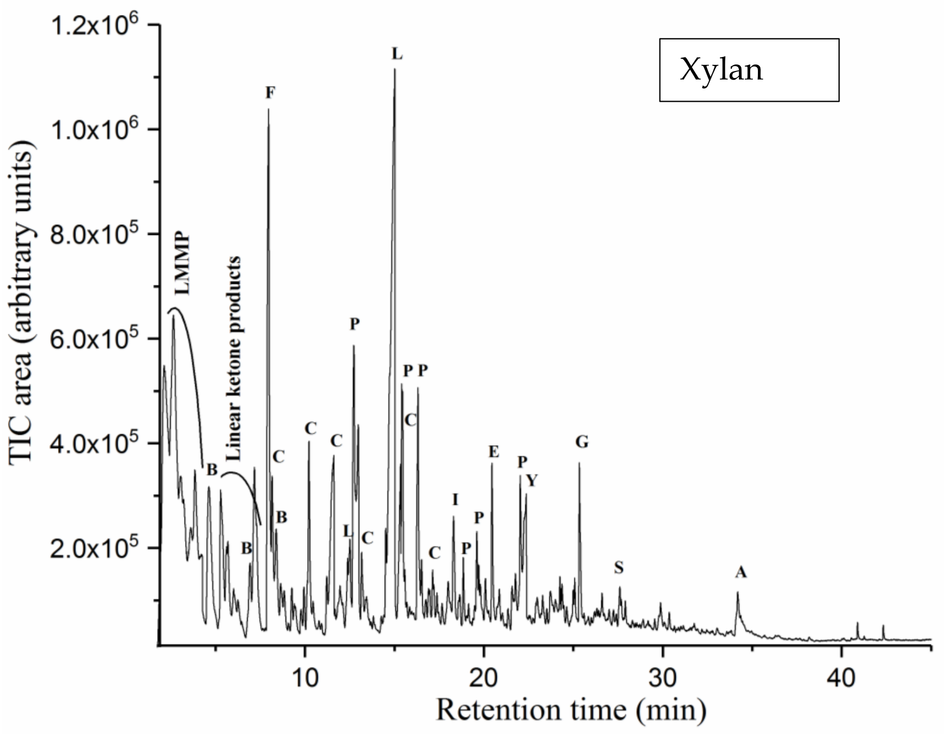

FIGURE 22 The main products formed in the pyrolysis experiments (700 °C and 20 s) with cellulose, glucomannan, and xylan. For the letter symbols, see Figure 14.

Effect of pyrolysis conditions on product groups

During the pyrolysis of model substances, all the compound groups, which were reported for wood and non-wood materials with different relative formation rates, were also found in this case within the temperature range studied, except anhydrosugar derivatives (mainly LG and LGO), which were prominently obtained only from cellulose. Additionally, guaiacol and syringyl derivatives were detected only for xylan, indicating that the xylan preparation used contained some minor guaiacyl-syringyl-type lignin impurities. As a typical trend, in each case, the pyrolysis yield decreased steadily toward harsher pyrolysis conditions (Figure 23).

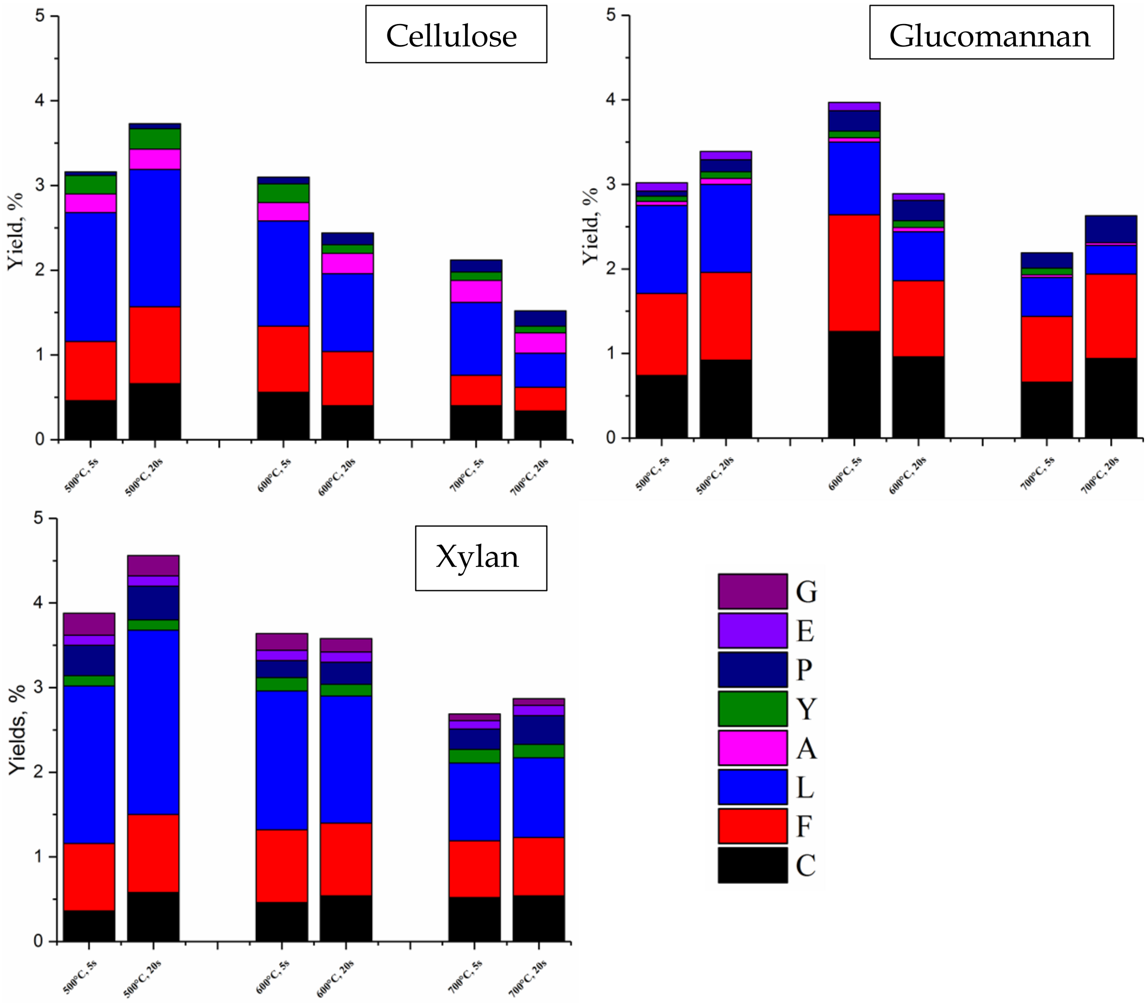

FIGURE 23 Effects of temperature and residence time on yields of main product groups from cellulose, glucomannan, and xylan. For the letter symbols, see Figure 14.

Effect of pyrolysis conditions on prominent products

The formation examples of the selected main pyrolysis products from model substances is shown in Figure 24 and Appendix III. It could be noted that, for example, 3-hydroxy-2-penteno-1,5-lactone (lactone) was primarily formed from xylan (also partly from cellulose), 5*H*-furan-2-one (lactone) from glucomannan (also partly from cellulose), 3-methylcyclopentane-1,2-dione (cyclopentenone) from glucomannan, furfural (furan) from cellulose and xylan, and 5-HMF (furan) from cellulose. Based on the our previous studies [I-III], of these major pyrolysis products, especially 3-hydroxy-2-penteno-1,5-lactone was formed by a factor of three from hardwood [I] than from softwood [II] stating the presence of a higher portion of xylan in hardwood. However, its yield from hardwood was still less than that from xylan, probably due to the impact of its integration with cellulose and lignin. In the case of 5*H*-furan-2-one, its formation was less in spruce than pure glucomannan due to their interaction. On the other hand, its yield droped in hot-water-extracted delignified softwood (PS_{HWE}) sample even by a factor of six, and it could be claimed that this compound produced from glucomannan more readily than from cellulose. A decreasing trend of LG formation in untreated and treated softwood samples revealed that it was produced from both glucomannan and cellulose, but more from cellulose. Also 3-methylcyclopentane-1,2-dione and furfural, are prominent products from birch wood and spruce wood as well as non-wood [IV].

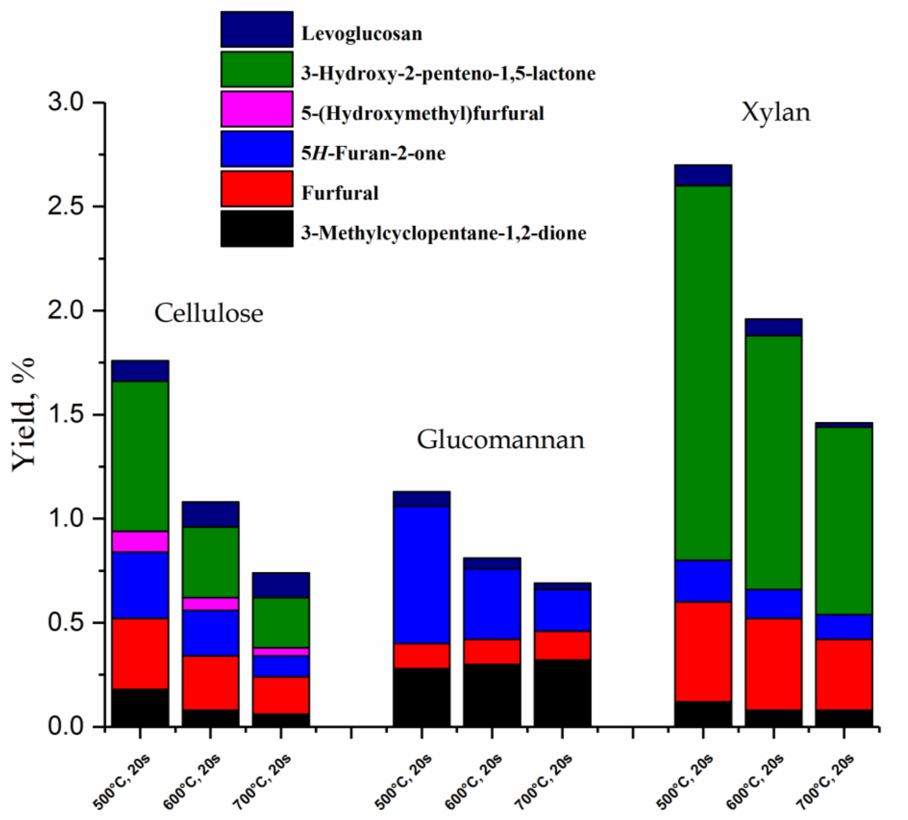

FIGURE 24 Effects of temperature and residence time on yields of some prominent pyrolysis products.

A comprehensive clarification of the multiple pyrolysis reaction routes for cellulose and hemicelluloses was beyond the scope of this study and considered as shown in literatures. Instead, the practical aim was to clarify the chemical composition of condensable liquids obtained from these feedstocks at varying temperatures for evaluating the chemical usefulness of the corresponding fractions. Table 13 illustrates the relative formation of the major product groups (lactone, furan, and cyclopentenone derivatives) from cellulose, glucomannan, and xylan, under varying pyrolysis conditions, whereas the corresponding formation of the minor product groups (phenolic, pyrone, and anhydrosugar derivatives) is shown in Table 14.

TABLE 13 Relative proportions (%) of major product groups obtained from cellulose, glucomannan, and xylan under varying pyrolysis conditions. The values given in parentheses refer to yields (% of the initial feedstock dry matter)[a]

Product group[b]	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)

[a] Data from Figure 23, calculated average values for heating times of 5 and 20 s.
[b] For the letter symbols, see Figure 14.

TABLE 14 Relative proportions (%) of minor product groups obtained from cellulose, glucomannan, and xylan under varying pyrolysis conditions [a]

Product group[b]	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	-

[a] Data from Figure 23, calculated average values for heating times of 5 and 20 s.
[b] For the letter symbols, see Figure 14.

Tables 13 and 14 indicate that no distinct compound group was selectively formed at certain temperatures, and the major product groups (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. In practice, this finding means that if a mixture of cellulose, glucomannan, and xylan with equal proportions would be pyrolyzed at 500 °C, about half of the condensable liquids will consist of lactone derivatives. In the case of cellulose, the proportion of lactone derivatives decreased and that of anhydrosugar derivatives increased steadily as the temperature increased.

For glucomannan and xylan, the proportion of lactone derivatives also decreased and the proportion of cyclopentenone derivatives was slightly depressed toward the maximum temperature. However, for all model substances, no significant changes in the proportion of furan derivatives could be detected.

Thermogravimetric considerations

The TGA and DTG curves of cellulose, glucomannan, and xylan are presented in Figure 25. The average active pyrolysis ranges of 290-410 ºC and 230-340 ºC were observed for cellulose and hemicelluloses, respectively. This also confirmed that within the temperature range studied, cellulose was thermally more stable than the heterogeneous hemicelluloses. The pyrolysis char yield determined was 9, 27, and 25 % of the initial mass for cellulose, glucomannan, and xylan, respectively. This finding agreed well with the earlier data [Alén et al., 1995; Patwardhan et al., 2011a] and suggested more multiple reactions of heterogeneous hemicelluloses and their monosaccharide moieties. According to Patwardhan et al. [2011a], the differences in the char yield between cellulose and hemicelluloses are clearly due to the somewhat different pyrolysis reaction mechanisms. The DTG peak heights (wt%/s) were as follows: cellulose 0.48 at 382 ºC, glucomannan 0.25 at 316 ºC, and xylan 0.57 at 304 ºC.

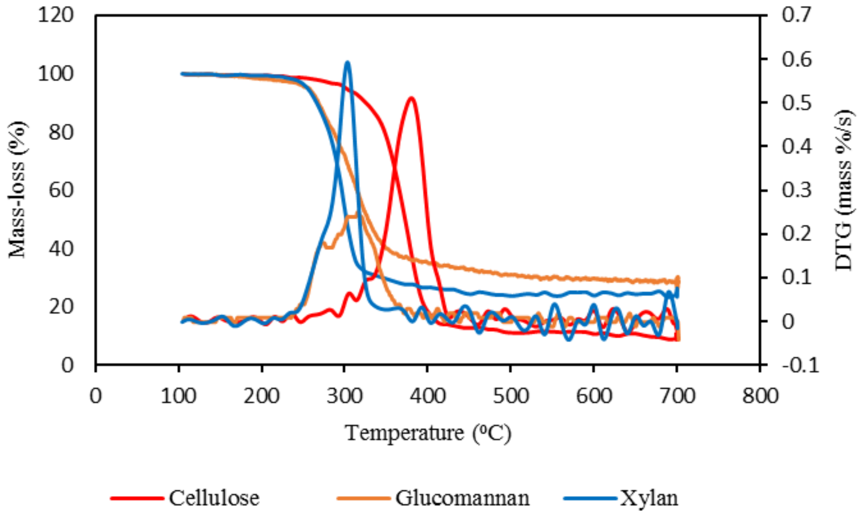

FIGURE 25 TGA and DTG curves of cellulose, glucomannan, and xylan at 20 ºC/min.

The calculated [Doddapaneni et al., 2016] activation energy (E_a) value as a function of fractional conversion (α) for cellulose, glucomannan, and xylan is presented in Figure 26. It could be noted that the variation in E_a was slightly lower for cellulose (142-162 kJ/mol) than for glucomannan and xylan, and an average value of 109.4 kJ/mol [Wang et al., 2016] for cellulose was reported. The E_a value for glucomannan varied between 111 and 301 kJ/mol, and it gradually increased in the progress of pyrolysis. However, at the end of pyrolysis (α > 0.7), a rapid rise (i.e., from 160 to 300 kJ/mol) was observed. This phenomenon has also been reported by Moriana et al. [2014]. They further reported the E_a values between 181 and 206 kJ/mol for glucomannan in the α range 0.1-0.75. In the case of xylan, the E_a value (168-200 kJ/mol) increased until α = 0.6, and, after this point, it started to decrease. The E_a values for xylan between 150 and 250 kJ/mol in the temperature range 185-215 °C was reported [Jin et al., 2013].

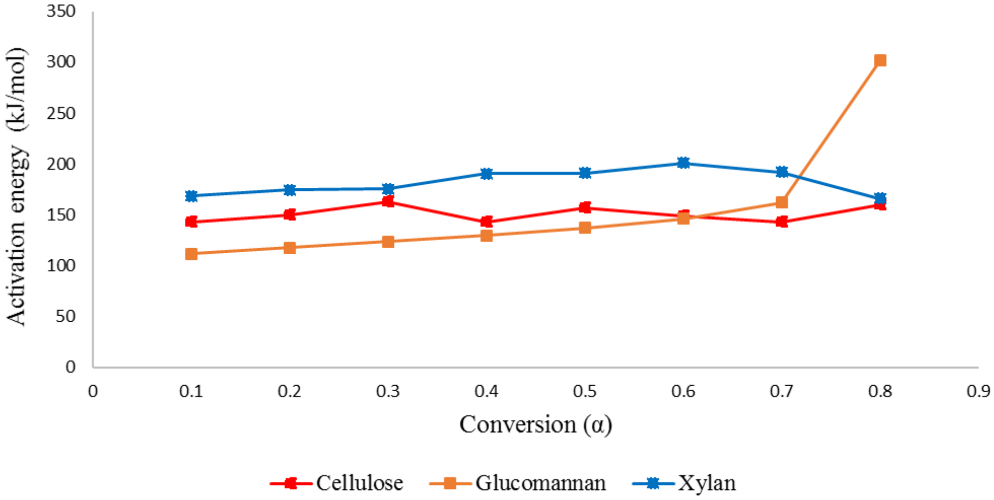

FIGURE 26 Activation energy (E_a) as a function of fractional conversion (α) for cellulose, glucomannan, and xylan.

It has been reported [Janković et al., 2007] that the significant variations in the E_a value with respect to α indicates a multistep reaction mechanism. Practically, the present data suggested that cellulose degradation during pyrolysis proceeded via reasonably simple and straightforward mechanisms without any significant secondary reactions. In contrast, it could be concluded that, due to greater variation in the E_a values for hemicelluloses, their degradation during pyrolysis took place by somewhat more complicated reaction mechanisms as already indicated by the high-char yields. The thermal degradation of the polysaccharides studied occurred by versatile parallel reaction paths that were not characteristically specific for certain temperature ranges. Hence, in this respect, TGA, without any definite detention possibilities, could not suggest distinct differences in their thermochemical degradation behavior.

8 CONCLUDING REMARKS

8.1 Summary of results

Integration of the chemical pretreatment of biomass and the fast pyrolysis of solid organic fractions formed was assessed. The chemical treatments, such as hot-water extraction and delignification carried out according to the principles of common integrated biorefinery concepts (i.e., integrating 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 samples, due to an "enhanced" removal of lignin, were also very suitable as raw material samples for the present pyrolysis investigation (e.g., the formation of lower amount of aromatics).

Fast pyrolysis was applied to solid fractions from hot-water extraction, delignification, and hot-water extraction followed by delignification of selected wood and non-wood feedstocks. The compositions of untreated and differently-treated feedstocks, as well as pyrolysis conditions, had a characteristic effect on the formation of condensable pyrolysis products. It is generally known that the total amount of pyrolysis products recovered from laboratory-scale pyrolyzers is low, but this fraction is still representative of all condensable products. For example, it was apparent that a broad spectrum of non-wood pyrolysis products was somewhat similar to that especially obtained from fast pyrolysis of the analogous hardwood samples. However, similar to the spruce results, the highest pyrolysis yields of the reference and HWE samples were obtained from O_{ref} and M_{ref} as well as from O_{HWE} and M_{HWE} with a pyrolysis time of 20 s at 500 ^{o}C followed by a pyrolysis time of 5 s at 500 ^{o}C. In the case of birch sawdust, the highest yields were detected at 500 ^{o}C/5 s or 700 ^{o}C/5 s. Typically, the yields were found to decrease when the pyrolysis temperature increased from 500 ^{o}C to 700 ^{o}C with both residence times at 5 s and 20 s.

The GC-amenable condensable liquid pyrolysis products could be characteristically classified into about 10 compound groups. The main compound groups were aliphatic compounds (e.g., lactone, furan, and cyclopentenone derivatives) from carbohydrates (principally hemicelluloses), and aromatic compounds (e.g., guaiacol, phenol, and syringol derivatives) from lignin. Prominent products from birch wood and spruce wood, as well as okra and miscanthus, were also among the major pyrolysis products, especially 3-hydroxy-2-penteno-1,5-lactone (lactone), 3-methylcyclopentane-1,2-dione (cyclopentenone), and furfural (furan). Additionally, no syringols could be obtained from softwood pyrolysis, whereas both guaiacols and syringols were formed from hardwood pyrolysis. The results from the model substances pyrolysis revealed that the pyrolytic degradation routes took place as indicated in the earlier literature. The experiments made in this study with model substances led to the same pyrolysis products that could be detected for lignocellulosic feedstocks, and were dominated by the behavior of its structural carbohydrate components, cellulose and hemicelluloses. Hence, 70-90 % of the product groups of carbohydrates pyrolysis were lactone, furan, and cyclopentenone derivatives. The results with model substances also manifested that 3-hydroxy-2-penteno-1,5-lactone was produced from hardwood than from softwood indicating the presence of a higher portion of xylan in hardwood. The 5*H*-furan-2-one was originated from glucomannan more readily than from cellulose. The levoglucosan was formed from both glucomannan and cellulose, but more from cellulose.

The ratio of aliphatic pyrolysis compounds to aromatic pyrolysis compounds was found to be characteristically dependent on feedstock composition and pyrolysis conditions. The aromatics originated from lignin-containing materials (untreated and HWE materials) under harsher pyrolysis conditions, whereas aliphatic products could be principally obtained under milder pyrolysis conditions from carbohydrate-containing materials (especially those after delignification). For example, at the temperature of 500 ^{o}C (for 5 s and 20 s), more primary products were formed without further degradation (whereas, for instance, at 700 ^{o}C, more aromatics were obtained).

Eventually, a simultaneous gas-chromatographic determination of the main compound groups and the selected fingerprint pyrolysis products offered rapid and useful information about the chemical composition of different samples. This finding provides a good basis for further development of a feasible characterization method for wood and non-wood feedstocks. On the other hand, an adequate characterization of pyrolysis products should be conducted before selecting the optimum methods for upgrading or for extracting the valuable compounds. Hence, these kinds of data are of practical importance with respect to efforts to develop new biorefinery possibilities for renewable resources.

8.2 Suggestions for future research

The aim of this study was to tentatively clarify possibilities for developing a rapid characterization method for wood and non-wood feedstocks. It is clearly evident that when developing a proper method (i.e., the accurate determination of response factors between chemical components and pyrolysis products), more relevant data (i.e., based on a great number of samples with varying chemical compositions determined by wet chemical methods) are needed. In the following research phase, this topic will be studied in more detail. However, it should also be pointed out that instead of using absolute amounts, it was shown to be practical to use the concentration ratios of respective pyrolysis products (i.e., use only the corresponding GC peak areas). This is a clear advantage when developing useful instruments. In contrast, another approach would be to use only a specific single compound for this purpose; however, in this case, to obtain repeatable results, knowledge about its absolute concentration is required.

It is also evident that all these chemical treatments with wood and non-wood samples led to various sulfur-free samples. The chemical compositions of formed hydrolysates and black liquors will be also studied in forthcoming studies. For instance, the hydrolysates from hot-water extraction of birch sawdust contained significant amounts of acetic acid, xylose (together with xylose oligomers), and low-molar-mass lignin. In the case of spruce, during the 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 general, 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 dicarboxylic acids. The recovery and utilization of these hydroxy acids from hydrolysates will be separately studied. Therefore, in the soda-AQ delignification stage with the removal of lignin, the black liquors contained fractions of degraded lignin and aliphatic carboxylic acids from carbohydrates. Hence, their recovery and utilization for many purposes are possible. In practice, characteristically, the non-wood-derived cellulose is less stable against alkali than the wood-derived cellulose, and more hemicellulose residues can be found in non-wood black liquors. Thus, recovered black liquors are also attractive materials for the mentioned purposes. Additionally, with respect to the chemical utilization of these liquids (i.e., hydrolyzates from hot-water extraction and black liquors from delignification), one of the most critical factors is that both of them are sulfur-free, which facilitates their further conversion aiming at value-added products (i.e., low-molar-mass phenols) by pyrolysis.

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APPENDIXES

APPENDIX I: Classification of pyrolysis products including peak identification and calibration information.

APPENDIX II: *Y*ields (%) of pyrolysis products of differently-treated silver birch and Norway spruce sawdust as well as okra and miscanthus stalk.
Also yields (%) of cellulose, glucomannan, and xylan pyrolysis products.

APPENDIX III: The main products formed in the pyrolysis experiments with differently-treated feedstocks and model substances.

APPENDIX I

Classification of pyrolysis products including peak identification and calibration information

Compound	RT[a] (min)	Major ion(s) (*m/z*)	Quantification[b]	r^2 Value[c]	Slope
Linear ketones, acids, esters derivatives (<C5) **Group symbol Lk**					
Acetic acid	3.7	43, 60	Standard	0.96	4.1
Butanal	3.9	57, 72	Standard	0.99	4.1
(2*E*)-Penta-2,4-dienal	5.2	53, 82	Butanal		
Methylprop-2-enoate	5.3	55, 86	Acetic acid		
1-Hydroxybutan-2-one	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		
Benzene derivatives **Group symbol B**					
Toluene	4.6	51, 65, 91	Standard	0.99	298.5
1,2-Dimethylbenzene	7.3	91, 106	Standard	0.99	230.0
Ethenylbenzene	8.4	78, 104	Standard	0.96	191.7
4-Ethyltoluene	10.1	77, 91, 105, 120	1,2-Dimethylbenzene		
2-Methylethenylbenzene	12.1	91, 103, 118	Ethenylbenzene		
2,3-Dimethoxytoluene	22.5	91, 109, 137, 152	1,2-Dihydroxy-3-methylbenzene		
Furan derivatives **Group symbol F**					
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
5-Acetoxymethyl-2-furaldehyde	26.7	79, 97, 109, 126	5-(Hydroxymethyl)furfural		
Lactone derivatives **Group symbol L**					
5-Methyl-3*H*-furan-2-one	9.1	55, 70, 98	Standard	0.99	56.0
5*H*-Furan-2-one	12.7	39, 55, 84	Standard	0.99	24.8
3-Methyl-5*H*-furan-2-one	14.5	69, 98	5-Methyl-3*H*-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*H*-furan-2-one	17.9	69, 98	5-Methyl-3*H*-furan-2-one		
4-Hydroxy-6-methyl-2*H*-pyran-2-one	18.3	43, 69, 98, 126	3-Hydroxy-2-methylpyran-4-one		
(1*R*,5*S*)-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		
Cyclic ketones derivatives (mainly cyclopentenone derivatives) **Group symbol C**					

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		
Hydroxy benzene derivatives (phenol derivatives) **Group symbol P**					
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
2,3,5-Trimethylphenol	20.9	77, 91, 121, 136	2,3,6-TrimethylPhenol		
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		
4-Hydroxy-2-methylacetophenone	22.7	77, 107, 135, 150	2-Methoxy-4-methylphenol		
4-(Prop-2-en-1-yl)-phenol	24.5	77, 91, 107, 115, 134	3,4-Dimethylphenol		
Pyran derivatives **Group symbol Y**					
Pyran-2-one	14.3	39, 68, 96	3-Hydroxy-2-methylpyran-4-one		
2*H*-Pyran-2,6(3*H*)-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		
6-Methyldihydro-2*H*-pyran-3(4*H*)-one	22.4	56, 84, 114	3-Hydroxy-2-methylpyran-4-one		
Indene derivatives **Group symbol I**					
1*H*-Indene	14.5	63, 89, 116	Standard	0.99	211.2
2-Methylbenzofuran	16.8	51, 77, 103, 131	1-Benzofuran	0.97	160.7
1-Methyl-1*H*-indene	18.4	115, 130	1*H*-Indene		
2,3- Dihydrobenzofuran	22.1	65, 91, 120	1-Benzofuran	0.97	160.7

2,3-Dihydro-1*H*-indene-1-one	25.6	78, 104, 132	1*H*-Indene		
1*H*-Indenosel	27.5	77, 103, 115, 132	1*H*-Indene		
Methoxy phenol derivatives (guaiacol derivatives) **Group symbol G**					
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
2´-Hydroxy-5´-methoxy-acetophenone	25.8	95, 123, 151, 166	2-Methoxy-4-methylphenol		
2-Methoxy-4-ethyl-6-methylphenol	25.9	77, 136, 151, 166	Eugenol		
3-Methoxy-5-methylphenol	26.1	107, 109, 123, 138	2-Methoxy-4-methylphenol		
2-Methoxy-4-(prop-2-en-1-yl)phenol (eugenol)	26.6	77, 131, 149, 164	Standard	0.97	331.0
2-Methoxy-4-(prop-1-en-1-yl)phenol (isoeugenol)	29.8	91, 103, 131, 149, 164	Standard	0.97	151.0
3-Hydroxy-4-methoxybenzoic acid (isovanillic acid)	30.4	125, 153, 168	4-Hydroxy-3-methoxybenzoic acid (vanillic acid)		
2-Methoxy-4-propylphenol	31.6	77, 122, 137, 166	Eugenol		
1-(4-Hydroxy-3-methoxyphenyl)-ethan-1-one (acetovanillone)	32.4	77, 123, 151, 166	Vanillic acid	0.98	154.7
Guaiacylacetone	33.6	122, 137, 180	Vanillic acid		
(2*E*)-3-(4-hydroxy-2-methoxyphenyl)-2-propenal	40.1	77, 107, 135, 161, 178	Vanillic acid		
Anhydrosugar derivatives **Group symbol A**					
(1*S*,5*R*)-6,8-Dioxabicyclo[3.2.1]oct-2-en-4-one (levoglucosenone)	19.8	39, 68, 98	Levoglucosan		
1,4:3,6-Dianhydro-α-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-β-D-glucopyranose (levoglucosan)	34.5	60, 73, 126, 145	Standard	0.99	67.0
Naphthalene derivatives **Group symbol N**					
Naphthalene	20.5	51, 102, 128	Standard	0.99	178.8
1-Methylnaphthalene	24.3	71, 115, 142	Naphthalene		
Dihydroxy benzene derivatives (catechol derivatives) **Group symbol E**					
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-	24.4	97, 125, 140	Standard	0.97	159.0

methoxybenzene					
1,2-Dihydroxy-4-methylbenzene	24.8	39, 78, 107, 124	1,2-Dihydroxy-3-methylbenzene		
1,4-Dihydroxybenzene	25.6	39, 81, 110	Standard	0.97	144.6
1,4-Dihydroxy-2,5-dimethylbenzene	26.9	95, 109, 123, 138	1,4-Dihydroxybenzene		
4-Ethyl-1,3-benzenediol	27.9	128, 138	1,3-benzenediol		
Dimethoxy phenol derivatives (syringyl derivatives) **Group symbol S**					
2,6-Dimethoxyphenol (syringol)	27.6	96, 139, 154	Standard	0.99	76.3
4-Methyl-2,6-dimethoxyphenol	30.3	125, 153, 168	Syringol		
4-Ethenyl-2,6-dimethoxyphenol	34.1	137, 165, 180	4-Allyl-2,6-dimethoxyphenol		
4-Allyl-2,6-dimethoxyphenol (4-allylsyringol)	34.9	150, 179, 194	Standard	0.98	274.4
4-Hydroxy-3,5-dimethoxybenzaldehyde (syringylaldehyde)	38.3	167, 181, 182	Acetosyringone		
1-(4-Hydroxy-3,5-dimethoxyphenyl)ethanal (homosyringaldehyde)	39.3	167, 196	Acetosyringone		
4'-Hydroxy-3',5'-dimethoxyacetophenone (acetosyringone)	39.8	181, 196	Standard	0.99	411.9
(4-Hydroxy-3,5-dimethoxy-phenyl)-acetone (syringylacetone)	40.6	167, 210	Acetosyringone		
3-(4-Hydroxy-3,5-dimethoxyphenyl)-2-propenal	44.3	137, 165, 180, 208	Acetosyringone		
Linear acids, esters derivatives (>C5) (fatty acid derivatives) **Group symbol X**					
Hexadecanoic acid	40.9	129, 213, 256	Linoleic acid	0.99	148.8
1-Methylethyl hexadecanoate	41.2	129, 213, 239, 256, 298	Linoleic acid		
9,12-Octadecadienoic acid	43.8	185, 241, 284	Linoleic acid		

In all cases, the intercept was 0.0.

[a] RT refers to retention time (min).

[b] Quantification is done by pure compounds.

[c] r^2 refers to coefficient values.

APPENDIX II (1/11)

Yields of silver birch sawdust pyrolysis products at 500 °C and 5 s/20 s (%).

Pyrolysis products	**RT^{a} (min)**	**B_{ref}^{b}**	**B_{HWE}^{c}**	**PB_{ref}^{d}**	**PB_{HWE}^{e}**
Benzene	3.1	0.02/-	-	-	-
Acetic acid	3.7	2.63/3.41	2.13/0.31	-	-
Furfural	8.0	0.19/0.19	0.13/0.15	0.35/0.29	0.22/0.17
Cyclopent-2-en-1-one	8.3	0.03/0.04	0.03/0.03	0.05/0.05	0.03/0.03
5-Methyl-3*H*-furan-2-one	9.1	0.05/0.06	0.05/0.05	0.06/0.05	0.06/0.05
Cyclohexanone	9.9	0.09/0.05	0.04/0.06	0.04/0.03	0.05/0.05
2-Methylcyclopent-2-en-1-one	10.3	0.02/-	0.01/-	0.03/0.04	-/0.02
2-Cyclopenten-1,4-dione	11.2	0.01/0.02	0.02/0.01	-	-
2-Hydroxycyclopent-2-en-1-one	11.8	0.09/0.11	0.05/0.09	0.1/0.09	0.07/0.09
5*H*-Furan-2-one	12.7	0.13/0.15	0.1/0.15	0.13/0.13	0.11/0.13
5-Methylfurfural	12.8	0.06/0.06	0.04/0.04	0.05/0.05	0.04/0.05
Phenol	12.9	0.02/0.02	0.02/0.02	0.02/0.02	-/0.01
3-Methylcyclopent-2-en-1-one	13.3	0.03/0.02	0.01/-	0.03/-	0.02/0.02
Pyran-2-one	14.3	0.03/0.03	0.04/0.03	0.04/0.04	0.04/0.04
3-Hydroxy-2-penteno-1,5-lactone	15.0	0.56/0.47	0.42/0.38	0.54/0.48	0.3/0.3
3-Methylcyclopentane-1,2-dione	15.4	0.12/0.11	0.12/0.15	0.23/0.13	0.12/0.16
2-Methylphenol	15.5	-	-	-/0.03	-
4-Methylphenol	16.4	0.04/0.02	0.02/0.02	0.02/0.02	-
2-Methoxyphenol	17.2	0.04/0.04	0.04/0.02	0.02/0.02	-
4-Methyl-5*H*-furan-2-one	17.9	0.04/0.03	0.1/0.1	0.1/0.1	0.1/0.1
4-Hydroxy-2,5-dimethylfuran-3-one	18.1	-/0.03	-/0.05	-/0.1	0.1/0.1
Methylfuran-2-carboxylate	18.1	0.01/-	0.02/-	0.03/0.01	0.01/0.1
3-Hydroxy-2-methylpyran-4-one	19.0	-/-	0.1/0.02	0.1/0.04	0.04/0.1
2,5-Furandicarboxaldehyde	19.1	-	-	0.08/0.07	-/0.07
Levoglucosenone	19.8	-	0.03/-	0.03/0.03	0.03/0.03
2,3-Dihydroxybenzaldehyde	20.5	0.06/0.05	0.05/-	0.05/0.05	0.04/-
2-Methoxy-4-methylphenol	20.7	0.06/0.04	0.04/0.04	-/0.02	-/0.02
3,5-Dihydroxy-2-methylpyran-4-one	21.8	-	0.06/0.03	-	0.03/-
6-Methyldihydro-2*H*-pyran-3(4*H*)-one	22.4	0.06/0.04	0.05/-	0.05/-	0.03/-
(1*R*,5*S*)-1-Hydroxy-3,6-dioxabicyclo[3.2.1]octan-2-one	23.2	0.05/0.03	0.11/0.1	0.1/0.09	0.09/0.09
2′,5′-Dihydroxyacetophenone	23.4	0.05/0.05	-	-	-
2-Methoxy-4-ethylphenol	23.5	0.03/0.02	0.03/0.02	-	-
1,4:3,6-Dianhydro-α-D-glucopyranose	24.0	0.03/0.03	0.02/-	0.06/-	0.03/-
1,2-Dihydroxy-3-methoxybenzene	24.4	0.06/0.05	0.05/0.06	-	-
2,3-Anhydro-D-mannose	24.5	-	-	0.02/-	0.03/-
5-(Hydroxymethyl)furfural	24.7	-	0.08/0.11	0.08/0.08	0.09/0.08
4-Ethenyl-2-methoxyphenol	25.4	0.04/0.03	0.03/0.03	0.02/-	-
2-Methoxy-4-(prop-2-en-1-yl)phenol	26.6	0.03/0.02	0.03/0.03	-	-
2,6-Dimethoxyphenol	27.6	0.1/0.09	0.08/0.06	0.03/0.03	-/0.04
2-Methoxy-4-(1-propenyl)phenol	29.8	0.08/0.1	0.08/0.10	-	-
4-Methyl-2,6-dimethoxyphenol	30.2	0.09/0.03	0.07/0.07	0.01/-	-
2-Methoxy-4-propylphenol	31.6	0.01/0.02	0.01/0.02	-/0.01	-
1-(4-Hydroxy-3-methoxyphenyl)ethan-1-one	32.4	0.09/0.09	0.09/0.09	-	-
4-Ethenyl-2,6-dimethoxyphenol	34.1	0.06/0.03	0.03/0.02	-	-
Levoglucosan	34.5	0.05/0.05	0.08/0.06	0.11/0.17	0.1/0.3
4-Allyl-2,6-dimethoxyphenol	34.9	0.05/0.05	0.05/0.05	-	-
4-Hydroxy-3,5-dimethoxybenzaldehyde	38.3	0.04/0.02	0.04/0.03	-	-
1-(4-Hydroxy-3,5-	39.3	0.03/0.02	0.02/0.02	-	-

dimethoxyphenyl)ethanal					
4'-Hydroxy-3',5'-dimethoxyacetophenone	39.8	0.03/0.02	0.02/0.02	-	-
(4-Hydroxy-3,5-dimethoxyphenyl)-acetone	40.6	0.02/0.01	0.02/0.01	-	-
Hexadecanoic acid	40.9	0.02/0.02	0.02/0.02	0.02/0.01	0.01/0.01
1-Methylethyl hexadecanoate	41.2	-/0.02	-	0.01/-	0.01/-
9,12-Octadecadienoic acid	43.8	0.02/0.02	0.02/0.01	0.01/-	-
3-(4-Hydroxy-3,5-dimethoxyphenyl)-2-propenal	44.3	-/0.01	0.01/-	0.02/-	-

[a] RT refers to retention time (min).

[b] B$_{ref}$ refers to untreated birch sawdust.

[c] B$_{HWE}$ refers to hot-water-extracted birch sawdust.

[d] PB$_{ref}$ refers to soda-AQ cooked pulp of untreated birch sawdust.

[e] PB$_{HWE}$ refers to soda-AQ cooked pulp of hot-water-extracted birch sawdust.

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Yields of silver birch pyrolysis sawdust products at 700 °C and 5 s/ 20 s (%).

Pyrolysis products	**RT[a] (min)**	**$\mathrm{B_{ref}}^{b}$**	**$\mathrm{B_{HWE}}^{c}$**	**$\mathrm{BP_{ref}}^{d}$**	**$\mathrm{BP_{HWE}}^{e}$**
Benzene	3.1	-	-	0.02/0.08	0.03/0.04
Acetic acid	3.7	5.51/5.00	1.80/1.74	-	-
Toluene	4.6	0.02/0.04	0.01/0.05	0.03/0.05	0.02/0.05
1,2-Dimethylbenzene	7.3	0.01/0.04	0.01/0.03	-/0.04	-/0.04
Furfural	8.0	0.2/0.14	0.15/0.13	0.26/0.19	0.17/0.15
Cyclopent-2-en-1-one	8.3	0.02/0.06	0.04/0.05	0.04/0.06	0.05/0.06
Ethenylbenzene	8.4	0.02/0.01	0.01/0.01	0.01/0.02	0.02/0.02
Cyclohexanone	9.9	0.04/-	0.04/-	0.04/-	0.01/-
3-Methyl-1-ethylbenzene	10.2	-/0.01	-/0.01	-/0.01	-/0.01
2-Methylcyclopent-2-en-1-one	10.3	0.02/0.02	0.01/0.02	0.02/0.02	0.02/0.02
2-Cyclopenten-1,4-dione	11.2	0.04/0.03	0.01/0.02	0.02/0.03	0.04/0.03
2-Hydroxycyclopent-2-en-1-one	11.8	0.09/0.13	0.09/0.09	0.14/0.13	0.13/0.14
5*H*-Furan-2-one	12.7	0.09/-	0.07/0.06	0.1/-	0.1/-
5-Methylfurfural	12.8	0.04/-	0.03/0.06	0.04/0.08	0.04/0.07
Phenol	12.9	0.06/0.1	0.04/0.07	0.06/0.14	0.06/0.1
3-Methylcyclopent-2-en-1-one	13.3	-/0.02	0.02/0.01	0.03/0.02	0.02/0.02
Pyran-2-one	14.3	0.03/-	0.03/0.03	0.03/0.03	0.03/0.05
1*H*-Indene	14.5	0.01/0.01	0.01/0.01	0.01/0.01	0.01/0.01
3-Hydroxy-2-penteno-1,5-lactone	15.0	0.32/0.2	0.25/0.16	0.3/0.2	0.18/0.15
3-Methylcyclopentane-1,2-dione	15.4	0.06/0.14	0.05/0.08	0.16/0.1	0.13/0.08
2-Methylphenol	15.5	0.03/0.03	0.02/0.04	0.04/0.05	0.03/0.04
4-Methylphenol	16.4	0.05/0.06	0.04/0.06	0.04/0.05	0.03/0.05
2-Methylbenzofuran	16.8	0.01/-	-/0.01	0.01/0.01	-/0.01
2-Methoxyphenol	17.2	0.03/0.02	0.02/0.01	-	-
2,6-Dimethylphenol	17.4	0.02/0.01	0.01/0.02	0.01/0.01	-/0.01
4-Methyl-5*H*-furan-2-one	17.9	0.01/0.02	0.03/0.02	0.05/0.02	0.06/0.03
4-Hydroxy-2,5-dimethylfuran-3-one	18.1	0.03/0.02	0.03/0.02	0.04/0.03	0.05/0.03
Methylfuran-2-carboxylate	18.1	-/0.08	0.01/0.08	0.02/0.08	0.01/0.08
2-Ethylphenol	18.3	0.02/0.01	0.01/0.01	0.01/0.01	0.01/0.02
1-Methyl-1*H*-indene	18.4	0.01/-	0.01/0.01	0.01/0.01	0.01/0.01
2-Hydroxy-3-ethylcyclopent-2-en-1-one	18.5	-	-	0.02/-	0.02/-
2,4-Dimethylphenol	18.9	0.02/0.03	0.01/0.03	0.01/0.02	-/0.02
3-Hydroxy-2-methylpyran-4-one	19.0	0.03/0.05	0.03/0.03	0.06/0.05	0.04/0.05
2,5-Furandicarboxaldehyde	19.1	-/0.08	0.07/0.08	0.08/0.08	0.08/0.08
3-Ethylphenol	19.6	0.02/0.02	0.01/0.02	-/0.02	-/0.01
3,5-Dimethylphenol	19.8	0.02/0.02	0.01/0.02	-/0.02	-/0.01
Naphthalene	20.4	-/0.01	-/0.01	0.01/0.01	-/0.01
2,3-Dihydroxybenzaldehyde	20.5	0.05/-	0.05/-	-	-
2-Methoxy-4-methylphenol	20.7	0.03/0.03	0.03/0.03	-	-
2,3,5-Trimethylphenol	20.9	-/0.01	-/0.01	-	-
1,2-Dihydroxybenzene	21.7	0.04/0.07	0.04/0.08	0.04/0.06	0.04/0.06
2,3,6-Trimethylphenol*	22.0	0.01/0.01	0.01/0.01	-	-
4-Ethenylphenol	22.1	-/0.01	-/0.01	-/0.01	-/0.01
6-Methyldihydro-2*H*-pyran-3(4*H*)-one	22.4	0.06/0.07	0.03/0.03	0.07/0.07	0.04/0.04
(1*R*,5*S*)-1-Hydroxy-3,6-dioxabicyclo[3.2.1]octan-2-one	23.2	0.07/0.07	0.1/0.1	0.09/0.09	0.08/0.08
2′,5′-Dihydroxyacetophenone	23.4	0.04/-	0.05/-	-	-
2-Methoxy-4-ethylphenol	23.5	0.03/0.01	0.03/0.02	-	-
1,2-Dihydroxy-3-methylbenzene	23.7	0.05/0.05	0.04/0.05	0.03/0.04	-
1,4:3,6-Dianhydro-α-D-glucopyranose	24.0	0.03/0.04	-/0.03	-/0.04	0.06/0.03

1-Methylnaphthalene	24.3	0.01/0.01	0.01/0.01	-/0.01	-/0.01
1,2-Dihydroxy-3-methoxybenzene	24.4	0.06/0.05	0.06/0.05	-/0.05	-/0.05
2,3-Anhydro-D-mannose	24.5	-	-	0.03/0.04	-/0.05
4-(Prop-2-en-1-yl)phenol	24.5	0.03/0.02	-/0.02	-/0.01	-
5-(Hydroxymethyl)furfural	24.7	0.06/0.06	0.07/0.07	0.07/0.07	0.07/0.07
1,2-Dihydroxy-4-methylbenzene	24.8	0.04/0.04	0.04/0.04	-/0.04	-
4-Ethenyl-2-methoxyphenol	25.4	0.03/0.02	0.02/0.02	-	-
2,3-Dihydro-1*H*-indene-1-one	25.6	-/0.01	-/0.01	0.01/0.01	0.01/0.01
2-Methoxy-4-(prop-2-en-1-yl)phenol	26.6	0.03/0.02	0.02/0.03	-	-
2,6-Dimethoxyphenol	27.6	0.09/0.04	0.06/0.05	0.02/-	-
2-Methoxy-4-(1-propenyl)phenol	29.8	0.1/0.06	0.06/0.07	-	-
4-Methyl-2,6-dimethoxyphenol	30.2	0.05/0.04	0.04/0.03	-	-
2-Methoxy-4-propylphenol	31.6	0.02/0.02	0.02/0.03	-	-
1-(4-Hydroxy-3-methoxyphenyl)ethan-1-one	32.4	0.09/0.09	0.09/0.09	-	-
4-Ethenyl-2,6-dimethoxyphenol	34.1	0.03/0.02	0.02/0.02	-	-
Levoglucosan	34.5	0.06/0.05	0.07/0.09	0.15/0.09	0.21/0.14
4-Allyl-2,6-dimethoxyphenol	34.9	0.05/0.02	0.04/0.04	-	-
4-Hydroxy-3,5-dimethoxybenzaldehyde	38.3	0.04/0.03	0.04/0.02	-	-
1-(4-Hydroxy-3,5-dimethoxyphenyl)ethanal	39.3	0.02/0.02	0.02/0.02	-	-
4'-Hydroxy-3',5'-dimethoxyacetophenone	39.8	0.02/0.02	0.02/0.02	-	-
(4-Hydroxy-3,5-dimethoxyphenyl)-acetone	40.6	0.02/0.02	-	-	-
Hexadecanoic acid	40.9	0.02/0.02	-/0.01	0.02/-	-
1-Methylethyl hexadecanoate	41.2	-/0.02	-/0.02	-	-
9,12-Octadecadienoic acid	43.8	0.02/0.02	0.02/0.01	-	-
3-(4-Hydroxy-3,5-dimethoxyphenyl)-2-propenal	44.3	0.02/0.04	0.01/0.02	0.02/-	0.02/-

[a] RT refers to retention time (min).

[b] $\mathrm{B_{ref}}$ refers to untreated birch sawdust.

[c] $\mathrm{B_{HWE}}$ refers to hot-water-extracted birch sawdust.

[d] $\mathrm{PB_{ref}}$ refers to soda-AQ cooked pulp of untreated birch sawdust.

[e] $\mathrm{PB_{HWE}}$ refers to soda-AQ cooked pulp of hot-water-extracted birch sawdust.

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Yields of Norway spruce sawdust pyrolysis products at 500 ^{o}C and 5 s/ 20 s (%)

Pyrolysis products	**RT^{a} (min)**	**S_{ref}^{b}**	**S_{HWE}^{c}**	**SP_{ref}^{d}**	**SP_{HWE}^{e}**
Butanal	3.9	0.32/0.22	0.16/0.18	0.22/0.16	0.04/-
(2*E*)-Penta-2,4-dienal	5.2	0.26/-	0.08/-	0.42/0.28	-
Pentanal	7.3	1.04/0.94	0.82/0.94	0.82/0.86	0.32/0.28
Furfural	8.0	0.19/0.2	0.33/0.14	0.23/0.2	0.06/0.06
Cyclopent-2-en-1-one	8.3	0.05/0.04	0.03/0.04	0.05/0.05	0.03/0.03
Furanmethanol	8.6	-/0.03	0.01/0.01	0.03/-	-
5-Methyl-3*H*-furan-2-one	9.1	0.08/0.07	0.06/0.06	0.08/0.06	0.05/-
Cyclohexanone	9.9	0.04/0.02	0.04/0.03	0.03/0.02	0.01/0.02
2-Methylcyclopent-2-en-1-one	10.3	0.04/0.01	0.03/0.02	0.04/0.03	0.01/0.02
1-(2-Furyl)ethanone	10.5	0.03/0.03	0.02/0.02	0.03/0.03	-
2-Cyclopenten-1,4-dione	11.2	0.04/0.05	0.03/0.04	0.06/0.06	0.02/0.01
2-Hydroxycyclopent-2-en-1-one	11.8	0.1/0.11	0.1/0.12	0.13/0.13	0.04/0.04
5*H*-Furan-2-one	12.7	0.25/0.28	0.25/0.31	0.45/0.22	0.09/0.09
5-Methylfurfural	12.8	0.06/0.06	0.06/0.07	0.07/0.08	0.03/0.03
Phenol	12.9	0.04/0.05	0.04/0.06	0.02/0.06	0.01/0.04
3-Methylcyclopent-2-en-1-one	13.3	0.01/0.02	0.01/0.02	0.02/0.02	0.01/0.01
3-Methyl-5*H*-furan-2-one	14.5	0.06/0.07	0.06/0.07	0.05/0.06	0.07/0.05
2*H*-Pyran-2,6(3*H*)-dione	14.8	0.11/0.09	0.1/0.09	0.04/-	0.04/-
3-Hydroxy-2-penteno-1,5-lactone	15.0	0.23/0.23	0.17/0.15	0.16/0.15	-
3-Methylcyclopentane-1,2-dione	15.4	0.16/0.2	0.16/0.18	0.4/0.3	0.15/0.13
2-Methylphenol	15.5	-/0.03	-/0.03	-/0.04	-/0.04
4-Methylphenol	16.4	0.05/0.03	0.03/0.04	0.03/0.04	0.01/0.03
2-Methoxyphenol	17.2	0.19/0.19	0.28/0.3	0.13/0.12	0.13/0.12
4-Methyl-5*H*-furan-2-one	17.9	0.06/0.07	0.06/0.07	0.09/0.08	0.05/0.05
4-Hydroxy-2,5-dimethylfuran-3-one	18.1	0.05/0.05	0.05/0.05	0.09/0.07	0.02/0.02
Methylfuran-2-carboxylate	18.1	0.05/0.05	0.05/0.04	0.03/0.01	-
3-Ethyl-2-hydroxycyclopent-2-en-1-one	18.5	0.03/0.02	0.03/0.03	0.04/0.05	0.01/0.03
2,4-Dimethylphenol	18.9	0.02/0.02	0.02/0.02	0.01/0.02	0.01/0.02
3-Hydroxy-2-methylpyran-4-one	19.0	-/0.04	-/0.05	-/0.05	-
2,5-Furandicarboxaldehyde	19.1	0.08/0.08	0.08/0.08	0.08/0.08	0.07/-
3,5-Dimethylphenol	19.8	0.01/-	0.01/0.01	-/0.01	-/0.01
2,3-Dihydroxybenzaldehyde	20.5	0.05/0.05	0.05/0.05	-	-
2-Methoxy-4-methylphenol	20.7	0.14/0.15	0.18/0.18	0.11/0.1	0.1/0.1
1,2-Dihydroxybenzene	21.7	-/0.03	-/0.03	0.03/0.03	0.03/0.03
3,5-Dihydroxy-2-methylpyran-4-one	21.8	0.04/0.04	0.04/-	-	-
2,3,6-Trimethylphenol	22.0	0.01/0.01	0.01/0.01	-	-
6-Methyldihydro-2*H*-pyran-3(4*H*)-one	22.4	0.05/0.05	0.05/0.05	-	-
2,3-Dimethoxytoluene	22.5	0.05/0.05	0.05/0.05	0.05/0.05	0.04/0.04
(1*R*,5*S*)-1-Hydroxy-3,6-dioxabicyclo[3.2.1]octan-2-one	23.2	0.09/0.09	0.06/0.06	0.16/0.15	0.05/0.05
2′,5′-Dihydroxyacetophenone	23.4	0.06/0.06	0.07/0.07	0.05/0.05	0.05/0.05
2-Methoxy-4-ethylphenol	23.5	0.06/0.04	0.06/0.05	0.03/0.03	0.03/0.03
5-(Hydroxymethyl)furfural	24.7	0.1/0.1	0.11/0.1	-/0.11	-/0.1
4-Ethenyl-2-methoxyphenol	25.4	0.09/0.09	0.08/0.08	0.05/0.05	0.05/0.04
2´-Hydroxy-5´-methoxyacetophenone	25.8	0.02/0.02	0.02/0.02	-/0.02	-/0.02
2-Methoxy-4-ethyl-6-methylphenol	25.9	0.02/0.02	0.02/0.02	0.02/-	0.02/-
5-Acetoxymethyl-2-furaldehyde	26.7	0.11/0.1	-	-	-
2-Methoxy-4-(1-propenyl)phenol	29.8	0.36/0.41	0.32/0.31	0.14/0.13	0.12/0.11
2-Methoxy-4-propylphenol	31.6	0.06/0.06	0.06/0.06	0.05/0.05	0.04/0.05
1-(4-Hydroxy-3-methoxyphenyl)ethan-1-	32.4	0.09/0.09	0.09/0.09	0.09/0.09	0.09/0.02

one (acetovanillone)					
Guaiacylacetone	33.6	0.09/0.09	0.09/0.09	0.09/0.09	0.09/0.02
Levoglucosan	34.5	0.06/0.05	0.05/0.05	0.07/0.06	0.03/-
(2*E*)-3-(4-Hydroxy-2-methoxyphenyl)-2-propenal	40.1	0.1/0.1	0.09/0.09	-	-

[a] RT refers to retention time (min).

[b] S_{ref} refers to untreated spruce sawdust.

[c] S_{HWE} refers to hot-water-extracted spruce sawdust.

[d] PS_{ref} refers to soda-AQ cooked pulp of untreated spruce sawdust.

[e] PS_{HWE} refers to soda-AQ cooked pulp of hot-water-extracted spruce sawdust.

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Yields of Norway spruce sawdust pyrolysis products at 700 °C and 5 s/ 20 s (%)

Pyrolysis products	**RT[a] (min)**	**S_{ref}[b]**	**S_{HWE}[c]**	**SP_{ref}[d]**	**SP_{HWE}[e]**
Butanal	3.9	-/0.24	-/0.18	-/0.16	-
Toluene	4.6	0.02/0.02	0.01/-	0.02/0.04	0.01/-
(2*E*)-Penta-2,4-dienal	5.2	0.1/0.22	-/0.14	0.12/0.16	-
Pentanal	7.3	0.62/0.5	0.62/0.86	0.62/0.72	0.12/0.3
Furfural	8.0	0.17/0.14	0.14/0.14	0.16/0.16	0.06/0.06
Cyclopent-2-en-1-one	8.3	0.05/0.04	0.04/0.03	0.05/0.05	0.03/0.03
Furanmethanol	8.6	-/0.01	-/0.01	-	-
Cyclohexanone	9.9	0.02/0.01	0.02/0.03	0.01/-	-
2-Methylcyclopent-2-en-1-one	10.3	0.01/0.03	0.01/0.03	0.03/0.03	0.01/0.02
1-(2-Furyl)ethanone	10.5	0.02/0.03	0.02/0.02	0.02/0.02	-
2-Hydroxycyclopent-2-en-1-one	11.8	0.14/0.1	0.13/0.16	0.13/0.14	0.04/0.05
2-Methylethenylbenzene	12.1	-	-	0.01/0.02	-
5*H*-Furan-2-one	12.7	0.09/0.15	0.09/0.32	0.07/0.09	0.03/0.09
5-Methylfurfural	12.8	0.03/0.05	0.03/0.07	0.07/0.09	0.01/0.03
Phenol	12.9	0.16/0.06	0.16/0.05	0.06/0.11	0.06/0.04
3-Methylcyclopent-2-en-1-one	13.3	0.03/0.03	0.03/0.02	0.02/0.02	0.01/0.01
Pyran-2-one	14.3	0.03/0.03	0.03/-	0.03/0.04	-
1*H*-Indene	14.5	0.01/0.02	0.01/-	0.01/0.02	-
3-Methylcyclopentane-1,2-dione	15.4	-/0.1	-/0.09	0.12/0.14	0.06/0.12
2-Methylphenol	15.5	0.1/0.05	0.1/0.05	0.06/0.07	0.03/0.02
4-Methylphenol	16.4	0.14/0.11	0.12/0.04	0.07/0.09	0.04/0.04
2-Methylbenzofuran	16.8	0.01/0.01	0.01/-	0.01/0.01	-
2-Methoxyphenol	17.2	0.05/0.04	0.1/0.03	0.04/0.03	0.05/0.03
2,6-Dimethylphenol	17.4	-	-	-/0.02	-/0.01
4-Methyl-5*H*-furan-2-one	17.9	0.05/0.05	0.06/0.07	0.05/0.06	0.05/0.04
4-Hydroxy-2,5-dimethylfuran-3-one	18.1	0.02/0.02	0.08/0.05	0.03/0.03	0.01/0.02
Methylfuran-2-carboxylate	18.1	0.03/-	0.03/0.04	0.04/-	-
2-Ethylphenol	18.3	0.02/-	0.02/-	-	-
1-Methyl-1*H*-indene	18.4	0.01/-	0.01/0.01	0.01/0.02	-
3-Ethyl-2-hydroxycyclopent-2-en-1-one	18.5	-	-	0.03/0.03	0.01/0.03
2,4-Dimethylphenol	18.9	0.04/0.04	0.04/0.02	0.03/0.03	0.02/0.02
3-Hydroxy-2-methylpyran-4-one	19.0	0.03/0.04	0.08/0.04	0.03/0.04	-
2,5-Furandicarboxaldehyde	19.1	0.08/0.08	0.08/0.08	0.08/0.08	-
3,5-Dimethylphenol	19.8	0.02/0.04	0.02/0.01	0.02/0.03	0.02/0.02
Naphthalene	20.4	0.01/0.01	0.01/-	0.01/0.01	-
2,3-Dihydroxybenzaldehyde	20.5	0.04/-	0.05/0.05	-	-
2-Methoxy-4-methylphenol	20.7	0.06/0.06	0.09/0.06	0.03/0.03	0.06/0.06
2,3,5-Trimethylphenol	20.9	0.01/0.01	0.02/-	0.02/0.02	0.01/-
1,2-Dihydroxybenzene	21.7	0.07/0.06	0.15/0.03	0.05/0.05	0.05/0.03
4-Ethenylphenol	22.1	0.03/0.04	0.02/-	-/0.02	-
6-Methyldihydro-2*H*-pyran-3(4*H*)-one	22.4	0.03/-	0.06/-	-	-
2,3-Dimethoxytoluene	22.5	-	-/0.06	-	-
(1*R*,5*S*)-1-Hydroxy-3,6-dioxabicyclo[3.2.1]octan-2-one	23.2	0.09/0.03	0.06/0.03	0.12/0.09	0.05/0.05
2′,5′-Dihydroxyacetophenone	23.4	0.05/-	0.06/-	-	0.05/-
2-Methoxy-4-ethylphenol	23.5	0.03/0.03	0.03/0.04	0.03/0.03	0.03/0.03
1,2-Dihydroxy-3-methylbenzene	23.7	-/0.03	-/0.04	0.04/0.03	0.05/0.03
1-Methylnaphthalene	24.3	0.01/0.01	0.01/-	0.01/0.01	-
4-(Prop-2-en-1-yl)phenol	24.5	0.02/0.02	0.02/-	0.01/0.01	0.01/-
5-(Hydroxymethyl)furfural	24.7	-/0.1	-/0.11	-	-
1,2-Dihydroxy-4-methylbenzene	24.8	0.03/0.05	0.01/-	0.05/0.05	0.05/-

4-Ethenyl-2-methoxyphenol	25.4	0.04/0.04	0.05/0.03	0.04/0.02	0.03/0.01
2-Methoxy-4-(prop-2-en-1-yl)phenol	26.6	0.04/0.03	0.04/0.04	0.03/0.03	0.03/0.03
1*H*-Indenol	27.5	0.01/0.01	-	-	-
4-Ethyl-1,3-benzenediol	27.9	0.05/0.05	-	-	-
2-Methoxy-4-(1-propenyl)phenol	29.8	0.16/0.1	0.19/0.06	0.06/0.07	0.06/0.06
2-Methoxy-4-propylphenol	31.6	0.05/0.04	0.06/0.05	0.04/0.04	0.04/0.04
1-(4-Hydroxy-3-methoxyphenyl)ethan-1-one (acetovanillone)	32.4	0.09/0.09	0.09/0.09	-/0.09	-
Guaiacylacetone	33.6	0.08/0.08	0.09/0.08	-	-
Levoglucosan	34.5	0.1/0.16	0.13/0.05	0.05/0.33	0.04/-
(2*E*)-3-(4-Hydroxy-2-methoxyphenyl)-2-propenal	40.1	0.09/0.09	0.08/-	-	-

[a] RT refers to retention time (min).

[b] S_{ref} refers to untreated spruce sawdust.

[c] S_{HWE} refers to hot-water-extracted spruce sawdust.

[d] PS_{ref} refers to soda-AQ cooked pulp of untreated spruce sawdust.

[e] PS_{HWE} refers to soda-AQ cooked pulp of hot-water-extracted spruce sawdust.

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Yields of okra stalk pyrolysis products at 500 °C and 5 s/ 20 s (%)

Pyrolysis products	**RT[a] (min)**	**O_{ref}[b]**	**O_{HWE}[c]**	**OP_{ref}[d]**	**OP_{HWE}[e]**
Furfural	8.0	0.1/0.11	0.09/0.11	0.04/0.16	0.15/0.16
Cyclopent-2-en-1-one	8.3	0.03/0.03	0.03/0.03	0.03/0.04	0.03/0.04
Cyclohexanone	9.9	-	-	-	0.02/0.02
2-Methylcyclopent-2-en-1-one	10.3	0.02/0.01	0.02/0.02	0.02/0.03	0.02/0.03
2-Hydroxycyclopent-2-en-1-one	11.8	0.07/0.06	0.07/0.07	0.06/0.06	0.07/0.07
5*H*-Furan-2-one	12.7	0.08/0.09	0.08/0.08	0.08/0.09	0.08/0.09
Phenol	12.9	0.02/0.03	0.02/0.02	0.02/0.02	0.02/0.02
3-Methylcyclopent-2-en-1-one	13.3	0.01/0.02	0.02/0.03	0.01/0.02	0.01/0.01
3-Methyl-5*H*-furan-2-one	14.5	-/0.03	-/0.03	0.02/0.04	0.03/0.04
3-Hydroxy-2-penteno-1,5-lactone	15.0	0.13/0.12	0.13/0.15	0.23/0.2	0.2/0.2
3-Methylcyclopentane-1,2-dione	15.4	0.12/0.12	0.14/0.1	0.1/0.13	0.13/0.13
4-Methylphenol	16.4	0.01/0.02	0.02/0.02	0.01/0.01	0.01/0.01
2-Methoxyphenol	17.2	0.04/0.05	0.04/0.05	0.02/0.02	0.02/0.02
4-Methyl-5*H*-furan-2-one	17.9	0.01/0.01	0.02/0.02	0.04/0.05	0.05/0.04
4-Hydroxy-2,5-dimethylfuran-3-one	18.1	0.01/0.01	0.02/0.01	0.03/0.03	0.03/0.03
Methylfuran-2-carboxylate	18.1	-	-/0.03	0.03/0.03	0.03/0.03
4-Hydroxy-6-methyl-2*H*-pyran-2-one	18.2	-	-	-	0.04/0.03
2-Hydroxy-3-ethylcyclopent-2-en-1-one	18.5	0.02/0.02	0.02/0.02	0.01/-	0.01/0.01
2,4-Dimethylphenol	18.9	0.01/0.01	0.01/0.01	-/0.01	-/0.01
3-Hydroxy-2-methylpyran-4-one	19.0	-	-	0.04/0.04	0.04/0.03
3-Ethylphenol	19.6	0.01/0.01	0.01/-	-	-
2,3-Dihydroxybenzaldehyde	20.5	0.05/0.05	0.05/0.05	0.05/-	-
2-Methoxy-4-methylphenol	20.7	0.03/0.03	0.03/0.03	0.02/0.02	0.02/0.02
4-Ethenylphenol	22.1	0.02/0.03	0.01/0.03	-	-
6-Methyldihydro-2*H*-pyran-3(4*H*)-one	22.4	-	0.04/0.04	-	-
2-Methoxy-4-ethylphenol	23.5	0.02/0.02	0.02/0.02	-	-
1,4:3,6-Dianhydro-α-D-glucopyranose	24.0	-	-/0.02	0.05/0.04	0.04/0.04
1,2-Dihydroxy-3-methoxybenzene	24.4	0.06/0.06	-/0.06	-	-
2,3-Anhydro-D-mannose	24.5	-	-	-	0.02/0.02
5-(Hydroxymethyl)furfural	24.7	0.1/0.1	-	0.1/-	0.1/0.1
4-Ethenyl-2-methoxyphenol	25.4	0.04/0.04	0.03/0.04	0.02/0.02	0.02/0.02
2-Methoxy-4-(prop-2-en-1-yl)phenol	26.6	0.02/0.02	0.02/0.02	-	-
2,6-Dimethoxyphenol	27.6	0.05/0.05	0.04/0.05	0.02/-	0.02/0.02
2-Methoxy-4-(1-propenyl)phenol	29.8	0.11/0.07	0.05/0.07	-	-
3-Hydroxy-4-methoxybenzoic acid	30.3	0.09/0.09	0.09/0.09	-	-
4-Ethenyl-2,6-dimethoxyphenol	34.1	0.02/0.02	0.02/0.02	-	-
Levoglucosan	34.5	-	-	-/0.03	0.04/0.13
4-Allyl-2,6-dimethoxyphenol	34.9	0.03/0.03	0.02/0.02	-	-
Hexadecanoic acid	40.9	0.03/0.03	0.03/0.03	0.03/0.03	0.03/0.03

[a] RT refers to retention time (min).

[b] O_{ref} refers to untreated okra stalk.

[c] O_{HWE} refers to hot-water-extracted okra stalk.

[d] PO_{ref} refers to soda-AQ cooked pulp of untreated okra stalk.

[e] PO_{HWE} refers to soda-AQ cooked pulp of hot-water-extracted okra stalk.

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Yields of okra stalk pyrolysis products at 700 °C and 5 s/ 20 s (%)

Pyrolysis products	**RT[a] (min)**	**O_{ref}[b]**	**O_{HWE}[c]**	**OP_{ref}[d]**	**OP_{HWE}[e]**
Toluene	4.6	0.01/0.02	0.01/0.02	0.02/0.01	0.02/0.02
1,2-Dimethylbenzene	7.3	-/0.01	-/0.01	-/0.01	0.01/0.01
Furfural	8.0	0.09/0.07	0.08/0.08	0.13/0.12	0.1/0.1
Cyclopent-2-en-1-one	8.3	0.03/0.03	0.03/0.03	0.03/0.03	0.03/0.03
Ethenylbenzene	8.4	0.01/0.01	0.01/0.01	0.01/0.01	0.01/0.01
4-Ethyltoluene	10.1	0.01/-	-/0.01	0.01/0.01	-/0.01
2-Methylcyclopent-2-en-1-one	10.3	0.02/0.01	0.01/0.02	0.01/0.02	0.01/0.01
2-Hydroxycyclopent-2-en-1-one	11.8	0.05/0.03	0.04/0.04	0.07/0.05	0.04/0.05
2-Methylethenylbenzene	12.1	0.01/0.01	0.01/0.01	0.01/0.01	0.01/0.01
5*H*-Furan-2-one	12.7	0.04/0.03	0.05/0.04	0.08/0.04	0.09/0.03
Phenol	12.9	0.06/0.07	0.05/0.06	0.06/0.07	0.04/0.07
3-Methylcyclopent-2-en-1-one	13.3	0.02/0.01	0.01/0.01	0.01/0.01	0.01/-
1*H*-Indene	14.5	0.01/0.01	0.01/0.01	0.01/0.01	0.01/0.01
3-Hydroxy-2-penteno-1,5-lactone	15.0	0.11/0.09	0.1/0.1	0.14/0.14	0.09/0.1
3-Methylcyclopentane-1,2-dione	15.4	0.13/0.05	0.11/0.11	0.13/0.11	0.05/0.07
4-Methylphenol	16.4	0.02/0.04	0.02/0.04	0.02/0.02	0.02/0.02
2-Methylbenzofuran	16.8	-	-	0.02/0.01	0.02/0.01
2-Methoxyphenol	17.2	0.03/0.02	0.02/0.02	-	-
2,6-Dimethylphenol	17.4	0.01/0.01	0.01/0.01	0.01/0.01	-
4-Methyl-5*H*-furan-2-one	17.9	-	-	-/0.02	-/0.01
4-Hydroxy-2,5-dimethylfuran-3-one	18.1	-	-	-/0.02	-/0.01
1-Methyl-1*H*-indene	18.4	-/0.01	-	0.01/0.01	0.01/0.01
2-Hydroxy-3-ethylcyclopent-2-en-1-one	18.5	0.01/-	0.01/0.02	0.01/-	-
2,4-Dimethylphenol	18.9	0.01/0.01	0.01/0.02	0.01/0.01	0.01/0.01
3-Ethylphenol	19.6	0.02/0.01	0.02/0.02	-	-
Naphthalene	20.4	-/0.01	-/0.01	0.01/0.01	0.01/0.01
2,3-Dihydroxybenzaldehyde	20.5	0.05/-	0.05/-	-	-
2-Methoxy-4-methylphenol	20.7	0.02/0.01	0.02/0.02	-	-
4-Ethenylphenol	22.1	0.02/0.03	0.02/0.02		
6-Methyldihydro-2*H*-pyran-3(4*H*)-one	22.4	-	0.03/-	0.04/-	0.02/0.04
2-Methoxy-4-ethylphenol	23.5	0.02/-	-	-	-
1,4:3,6-Dianhydro-α-D-glucopyranose	24.0	-	0.03/-	0.04/0.04	0.02/0.03
2,3-Anhydro-D-mannose	24.5	-	-	-	-/0.02
1-Methylnaphthalene	24.3	-/0.01	-/0.01	0.01/0.01	0.01/0.01
4-Ethenyl-2-methoxyphenol	25.4	0.03/0.02	0.03/0.03	-	-
2,6-Dimethoxyphenol	27.6	0.03/0.02	0.02/0.02	-	-
2-Methoxy-4-(1-propenyl)phenol	29.8	0.03/0.02	0.03/0.03	-	-
3-Hydroxy-4-methoxybenzoic acid	30.3	0.09/0.09	0.09/0.09	-	-
2-Methoxy-4-propylphenol	31.6	0.02/-	0.02/0.02	-	-
4-Ethenyl-2,6-dimethoxyphenol	34.1	-/0.01	0.01/0.01	-	-
Levoglucosan	34.5	-	-	0.03/0.1	0.04/0.09
4-Allyl-2,6-dimethoxyphenol	34.9	0.01/-	0.01/-	-	-
Hexadecanoic acid	40.9	0.03/0.03	0.03/0.03	0.03/0.03	0.03/0.03

[a] RT refers to retention time (min).

[b] O_{ref} refers to untreated okra stalk.

[c] O_{HWE} refers to hot-water-extracted okra stalk.

[d] PO_{ref} refers to soda-AQ cooked pulp of untreated okra stalk.

[e] PO_{HWE} refers to soda-AQ cooked pulp of hot-water-extracted okra stalk.

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Yields of miscanthus stalk pyrolysis products at 500 °C and 5 s/ 20 s (%)

Pyrolysis products	**RT**[a] **(min)**	**M_{ref}**[b]	**M_{HWE}**[c]	**MP_{ref}**[d]	**MP_{HWE}**[e]
Furfural	8.0	0.09/0.12	0.11/0.11	0.19/0.18	0.16/0.17
Cyclopent-2-en-1-one	8.3	0.03/0.03	0.03/0.03	0.03/0.03	0.03/0.02
2-Methylcyclopent-2-en-1-one	10.3	0.02/0.02	0.01/0.02	0.02/0.01	0.01/0.02
2-Hydroxycyclopent-2-en-1-one	11.8	0.06/0.08	0.08/0.08	0.05/0.06	0.04/0.05
5*H*-Furan-2-one	12.7	0.11/0.14	0.09/0.11	0.1/0.13	0.07/0.1
Phenol	12.9	0.06/0.07	0.06/0.06	0.01/0.02	-
3-Methylcyclopent-2-en-1-one	13.3	0.01/0.02	0.01/0.02	0.01/0.01	-/0.02
3-Hydroxy-2-penteno-1,5-lactone	15.0	0.14/0.15	0.17/0.18	0.38/0.37	0.37/0.35
3-Methylcyclopentane-1,2-dione	15.4	0.11/0.14	0.09/0.1	0.08/0.08	0.06/0.09
4-Methylphenol	16.4	0.03/0.0	0.02/0.02	-	-
2-Methoxyphenol	17.2	0.08/0.07	0.06/0.06	0.01/0.01	0.01/0.02
4-Methyl-5*H*-furan-2-one	17.9	-	-	0.04/0.04	0.04/0.05
4-Hydroxy-2,5-dimethylfuran-3-one	18.1	-	-	0.03/0.03	0.03/0.03
Methyl furan-2-carboxylate	18.1	-	-	0.03/0.03	0.03/0.03
4-Hydroxy-6-methyl-2*H*-pyran-2-one	18.3	-	-	0.03/0.03	0.03/0.03
2-Hydroxy-3-ethylcyclopent-2-en-1-one	18.5	0.04/0.04	0.03/0.01	-/0.01	-/0.01
2,4-Dimethylphenol	18.9	0.02/0.01	-/0.01	-	-
3-Hydroxy-2-methylpyran-4-one	19.0	-	-	-	0.03/0.04
3-Ethylphenol	19.6	0.02/0.02	0.01/0.02	-	-
2,3-Dihydroxybenzaldehyde	20.5	0.05/0.05	0.05/0.05	-	-
2-Methoxy-4-methylphenol	20.7	0.05/0.03	0.03/0.03	-	-
4-Ethenylphenol	22.1	0.12/0.15	0.11/0.09	-/0.01	-
2-Methoxy-4-ethylphenol	23.5	0.03/0.03	0.03/0.03	-	-
1,4:3,6-Dianhydro-α-D-glucopyranose	24.0	-	-	0.04/0.04	0.04/0.04
2,3-Anhydro-D-mannose	24.5	-	-	-/0.02	-/0.02
5-(Hydroxymethyl)furfural	24.7	-	-	0.1/0.1	0.1/-
4-Ethenyl-2-methoxyphenol	25.4	0.05/0.05	0.05/0.05	0.02/0.02	-/0.02
2-Methoxy-4-(prop-2-en-1-yl)phenol	26.6	0.02/0.02	0.02/0.02	-	-
2,6-Dimethoxyphenol	27.6	0.05/0.04	0.05/0.05	-	-
2-Methoxy-4-(1-propenyl)phenol	29.8	0.05/0.05	0.05/0.06	-	-
3-Hydroxy-4-methoxybenzoic acid	30.3	0.09/0.09	0.09/0.09		
4-Ethenyl-2,6-dimethoxyphenol	34.1	0.02/0.01	0.02/0.01	-	-
Levoglucosan	34.5	-	0.03/-	0.04/0.04	0.04/0.03
4-Allyl-2,6-dimethoxyphenol	34.9	0.02/0.02	0.02/0.03	-	-
Hexadecanoic acid	40.9	-/0.03	-/0.02	0.03/-	-

[a] RT refers to retention time (min).

[b] M_{ref} refers to untreated miscanthus stalk.

[c] M_{HWE} refers to hot-water-extracted miscanthus stalk.

[d] PM_{ref} refers to soda-AQ cooked pulp of untreated miscanthus stalk

[e] PM_{HWE} refers to soda-AQ cooked pulp of hot-water-extracted miscanthus stalk.

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Yields of miscanthus stalk pyrolysis products at 700 °C and 5 s/ 20 s (%)

Pyrolysis products	**RT[a] (min)**	**M_{ref}[b]**	**M_{HWE}[c]**	**MP_{ref}[d]**	**MP_{HWE}[e]**
Toluene	4.6	0.02/0.02	0.01/0.01	0.01/0.01	0.01/0.01
1,2-Dimethylbenzene	7.3	0.01/0.01	-/0.01	0.01/0.01	-/0.01
Furfural	8.0	0.08/0.08	0.1/0.08	0.14/0.11	0.15/0.11
Cyclopent-2-en-1-one	8.3	0.03/0.03	0.03/0.03	0.03/0.03	0.03/0.03
Ethenylbenzene	8.4	0.02/0.02	0.01/0.01	0.01/0.01	0.01/0.01
2-Methylcyclopent-2-en-1-one	10.3	0.01/0.03	0.03/0.01	0.01/0.01	0.02/0.01
2-Hydroxycyclopent-2-en-1-one	11.8	0.03/0.03	0.05/0.04	0.05/0.05	0.07/0.05
2-Methylethenylbenzene	12.1	0.01/-	-/0.01	-/0.01	-
5*H*-Furan-2-one	12.7	0.04/-	0.07/0.02	0.07/0.03	0.11/0.09
Phenol	12.9	0.13/0.16	0.08/0.1	0.03/0.04	0.04/0.03
3-Methylcyclopent-2-en-1-one	13.3	0.01/0.01	-	-	0.01/-
1*H*-Indene	14.5	0.01/0.01	0.01/0.01	0.01/0.01	-/0.01
3-Hydroxy-2-penteno-1,5-lactone	15.0	0.09/0.11	0.15/0.12	0.25/0.16	0.21/0.18
3-Methylcyclopentane-1,2-dione	15.4	0.04/0.04	0.04/0.04	0.04/0.04	0.09/0.03
2-Methylphenol	15.5	0.02/0.02	0.02/0.02	0.01/0.01	-/0.01
4-Methylphenol	16.4	0.05/0.06	0.04/0.05	0.02/0.02	0.02/0.01
2-Methylbenzofuran	16.8	0.01/0.02	-	-	-
2-Methoxyphenol	17.2	0.02/0.03	0.04/0.02	-	-
2,6-Dimethylphenol	17.4	0.01/0.01	-/0.01	-	-
4-Methyl-5*H*-furan-2-one	17.9			0.02/-	0.02/-
4-Hydroxy-2,5-dimethylfuran-3-one	18.1			0.01/-	0.01/-
1-Methyl-1*H*-indene	18.4	0.01/0.02	-	-/0.01	-
2-Hydroxy-3-ethylcyclopent-2-en-1-one	18.5	-	0.02/-	-	-
2,4-Dimethylphenol	18.9	0.01/0.02	0.01/0.01	0.02/0.01	0.01/0.01
3-Ethylphenol	19.6	0.03/0.03	0.02/0.02	0.01/-	-
Naphthalene	20.4	0.01/0.01	0.01/-	-	-
2,3-Dihydroxybenzaldehyde	20.5	-	0.05/-	-	-
2-Methoxy-4-methylphenol	20.7	0.02/0.02	0.03/0.02	-	-
4-Ethenylphenol	22.1	0.12/0.11	0.11/0.1	-	-
2-Methoxy-4-ethylphenol	23.5	-/0.02	0.02/0.02	-	-
1,4:3,6-Dianhydro-α-D-glucopyranose	24.0	-	-	0.03/0.03	0.03/0.02
1-Methylnaphthalene	24.3	0.01/0.02	-	-	-
4-(Prop-2-en-1-yl)phenol	24.5	0.01/0.01	-	-	-
4-Ethenyl-2-methoxyphenol	25.4	0.03/0.03	0.04/0.03	-	-
2-Methoxy-4-(prop-2-en-1-yl)phenol	26.6	-/0.02	0.02/0.02	-	-
2,6-Dimethoxyphenol	27.6	0.02/0.02	0.03/0.02	-	-
2-Methoxy-4-(1-propenyl)phenol	29.8	0.02/0.03	0.02/0.03		
3-Hydroxy-4-methoxybenzoic acid	30.3	0.09/0.09	0.1/0.09	-	-
4-Ethenyl-2,6-dimethoxyphenol	34.1	-/0.01	0.02/0.01		
Levoglucosan	34.5	-/0.04	0.04/0.04	0.05/0.08	0.07/0.08
4-Allyl-2,6-dimethoxyphenol	34.9	-	0.02/-	-	-

[a] RT refers to retention time (min).

[b] M_{ref} refers to untreated miscanthus stalk.

[c] M_{HWE} refers to hot-water-extracted miscanthus stalk.

[d] PM_{ref} refers to soda-AQ cooked pulp of untreated miscanthus stalk

[e] PM_{HWE} refers to soda-AQ cooked pulp of hot-water-extracted miscanthus stalk.

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Yield of cellulose pyrolysis products (%)

Pyrolysis products	**RT[a] (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*H*-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*H*-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*H*-furan-2-one	14.4	0.06	0.1	0.1	0.1	0.22	-
1*H*-Indene	14.5	-	-	-	-	-	0.02
2*H*-Pyran-2,6(3*H*)-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*H*-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*H*-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	-	-	-	-
6-Methyldihydro-2*H*-pyran-3(4*H*)-one	22.4	0.12	0.14	0.12	0.1	0.1	0.08
(1*R*,5*S*)-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-*a*-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*H*-indene-1-one	25.4	-	-	-	0.02	-	-
Levoglucosan	34.5	0.1	0.1	0.1	0.12	0.14	0.12

[a] RT refers to retention time (min).

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Yield of glucomannan pyrolysis products (%)

Pyrolysis products	**RT[a] (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*H*-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*H*-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*H*-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*H*-furan-2-one	14.4	0.12	-	0.1	0.1	0.1	-
1*H*-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*H*-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*H*-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
6-Methyldihydro-2*H*-pyran-3(4*H*)-one	22.2	0.06	0.08	0.08	0.08	0.08	-
(1*R*,5*S*)-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	-	-	-
Levoglucosan	34.5	0.05	0.07	0.05	0.05	0.03	0.03

[a] RT refers to retention time (min).

(11/11)

Yield of xylan pyrolysis products (%)

Pyrolysis products	**RT[a] (min)**	**500 ^{o}C, 5 s**	**500 ^{o}C, 20 s**	**600 ^{o}C, 5 s**	**600 ^{o}C, 20 s**	**700 ^{o}C, 5 s**	**700 ^{o}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-3*H*-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
5*H*-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-5*H*-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
6-Methyldihydro-2*H*-pyran-3(4*H*)-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	-	-	-	-

[a] RT refers to retention time (min).

APPENDIX III (1/2)

The main products formed in the pyrolysis experiments with differently-treated feedstocks[a]

Product	**Birch**	**Spruce**	**Okra**	**Miscanthus**
Anhydrosugars				
1,4:3,6-Dianhydro-α-D-glucopyranose	+	-	+	+
1,6-Anhydro-β-D-glucopyranose (levoglucosan)	+	+	+	+
Benzene derivatives				
Toluene	+	+	+	+
o-Xylene	+	-	+	+
Cyclopentenone derivatives				
Cyclopent-2-en-1-one	+	+	+	+
2-Methylcyclopent-2-en-1-one	+	+	+	+
2-Cyclopenten-1,4-dione	+	-	-	+
2-Hydroxycyclopent-2-en-1-one	+	+	+	+
3-Methylcyclopentane-1,2-dione	+	+	+	+
Catechol derivatives				
1,2-Dihydroxybenzene (catechol)	+	+	+	-
1,2-Dihydroxy-3-methylbenzene	+	-	-	-
1,2-Dihydroxy-3-methoxybenzene	+	-	-	+
1,2-Dihydroxy-4-methylbenzene	+	+	-	-
1,4-Dihydroxy-2,5-dimethylbenzene	+	-	-	-
Furan derivatives				
Furfural (furan-2-carbaldehyde)	+	+	+	+
5-Methylfurfural	+	+	+	-
2,5-Furandicarboxaldehyde	+	+	-	-
5-(Hydroxymethyl)furfural	+	+	+	+
Guaiacol derivatives				
2-Methoxyphenol (guaiacol)	+	+	+	+
2-Methoxy-4-methylphenol	+	+	+	+
4-Ethenyl-2-methoxyphenol	+	+	+	+
2-Methoxy-4-propylphenol	+	+	-	-
2-Methoxy-4-(prop-2-en-1-yl)phenol (eugenol)	+	+	+	+
2-Methoxy-4-(prop-1-en-1-yl)phenol (isoeugenol)	+	+	+	+
Indene derivatives				
1*H*-Indene	+	+	+	+
1-Methyl-1*H*-indene	+	+	+	+
2,3-Dihydro-1*H*-inden-1-one	+	-	-	-
Lactone derivatives				
5*H*-Furan-2-one	+	+	+	+
3-Hydroxy-2-penteno-1,5-lactone	+	+	+	+
4-hydroxy-2,5-dimethylfuran-3-one	+	+	+	+
1-Hydroxy-3,6-dioxabicyclo[3.2.1]octan-2-one	+	+	-	-
Naphthalene derivatives				
Naphthalene	+	+	+	+
1-Methylnaphthalene	+	+	+	+
Phenol derivatives				
Phenol	+	+	+	+
2-Methylphenol	+	+	+	+
4-Methylphenol	+	+	+	+
2,4-Dimethylphenol	+	+	+	+
3,5-Dimethylphenol	+	+	-	-
4-(Prop-2-en-1-yl)phenol	+	+	+	+
Syringol derivatives				
2,6-Dimethoxyphenol (syringol)	+	-	+	+
4-Allyl-4-methyl-2,6-dimethoxyphenol	+	-	-	-

1-(4-Hydroxy-3-methoxyphenyl)ethan-1-one	+	-	-	-
4-Ethenyl-2,6-dimethoxyphenol	+	-	+	+
4-Allyl-2,6-dimethoxyphenol (4-allylsyringol)	+	-	+	+
4-Hydroxy-3,5-dimethoxybenzaldehyde	+	-	-	+
1-(4-Hydroxy-3,5-dimethoxyphenyl)ethanal	+	-	-	-
4´-Hydroxy-3´,5´-dimethoxyacetophenone	+	-	-	-
3-(4-Hydroxy-3,5-dimethoxyphenyl)prop-2-enal	+	-	-	-

[a] + Indicates the presence of this compound.

(2/2)

The main products formed in the pyrolysis experiments with model substances[a]

Product	**Cellulose**	**Glucomannan**	**Xylan**
Anhydrosugars			
1,4:3,6-Dianhydro-α-D-glucopyranose	+	-	-
2,3-Anhydro-D-mannosae	+	-	-
1,6-Anhydro-β-D-glucopyranose (levoglucosan)	+	+	+
Benzene derivatives			
Toluene	+	+	+
Cyclopentenone derivatives			
Cyclopent-2-en-1-one	+	+	+
2-Methylcyclopent-2-en-1-one	-	+	+
2-Cyclopentene-1,4-dione	+	-	+
2-Hydroxycyclopent-2-en-1-one	+	+	+
3-Methylcyclopentane-1,2-dione	+	+	+
Catechol derivatives			
2,3-Dihydroxybenzaldehyde	+	+	+
Furan derivatives			
Furfural (furan-2-carbaldehyde)	+	+	+
5-Methylfurfural	+	+	-
2,5-Furandicarboxaldehyde	+	-	-
5-(Hydroxymethyl)furfural	+	-	-
Guaiacol derivatives			
2-Methoxyphenol (guaiacol)	-	-	+
2-Methoxy-4-methylphenol	-	-	+
Lactone derivatives			
5*H*-Furan-2-one	+	+	+
3-Hydroxy-2-penteno-1,5-lactone	+	-	+
4-Hydroxy-2,5-dimethylfuran-3-one	+	-	+
1-Hydroxy-3,6-dioxabicyclo[3.2.1]octan-2-one	+	+	-
Linear ketone derivatives			
Methyl acrylate	-	-	+
1-Hydroxy-2-butanone	+	-	+
2-Methylbut-2-enal	+	+	-
Valeraldehyde	+	+	-
Phenol derivatives			
Phenol[c]	+	+	+
2-Methylphenol	+	+	+
4-Methylphenol	+	+	+
2,4-Dimethylphenol	+	+	+
4-Ethenylphenol	-	-	+
Syringol derivatives			
2,6-Dimethoxyphenol (syringol)	-	-	+

[a] + Indicates the presence of this compound.

ORIGINAL PAPERS

I

FAST PYROLYSIS OF HOT-WATER-EXTRACTED AND DELIGNIFIED SILVER BIRCH (*BETULA PENDULA*) SAWDUST BY PY-GC/MS

by

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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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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.

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})

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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_{HWE} and P_{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, Regies Technologies) in pyridine and the mixture was shaken for 60 min [26]. Xylitol (Fluka Chemical Corporation, Seeltze, Germany) served as an internal standard (IS). The column was a DP-1701 capillary column (60 m × 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, Seeltze, 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 × 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 × 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 µg, 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

Table 1
Chemical composition of the initial and differently-treated birch sawdust (% of the sample[a] dry solids).

Components	B_{HWE}	B_{ref}	P_{HWE}	P_{ref}
Carbohydrates[b]	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

[a] B_{HWE} and B_{ref} refer to hot-water-extracted and untreated sawdust, respectively, and P_{HWE} and P_{ref} refer to the soda-AQ-delignified pulps of hot-water-extracted and untreated sawdust, respectively.

[b] Monosaccharide units are presented as their anhydro forms.

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. 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.

The chemical composition data on pulps (i.e., $B_{ref} \rightarrow P_{ref}$ and $B_{HWE} \rightarrow P_{HWE}$) are shown in Table 1. In the former reference case ($B_{ref} \rightarrow P_{ref}$), 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 ($B_{HWE} \rightarrow P_{HWE}$), it was noted that under the same delignification conditions as in case of $B_{ref} \rightarrow P_{ref}$, 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].

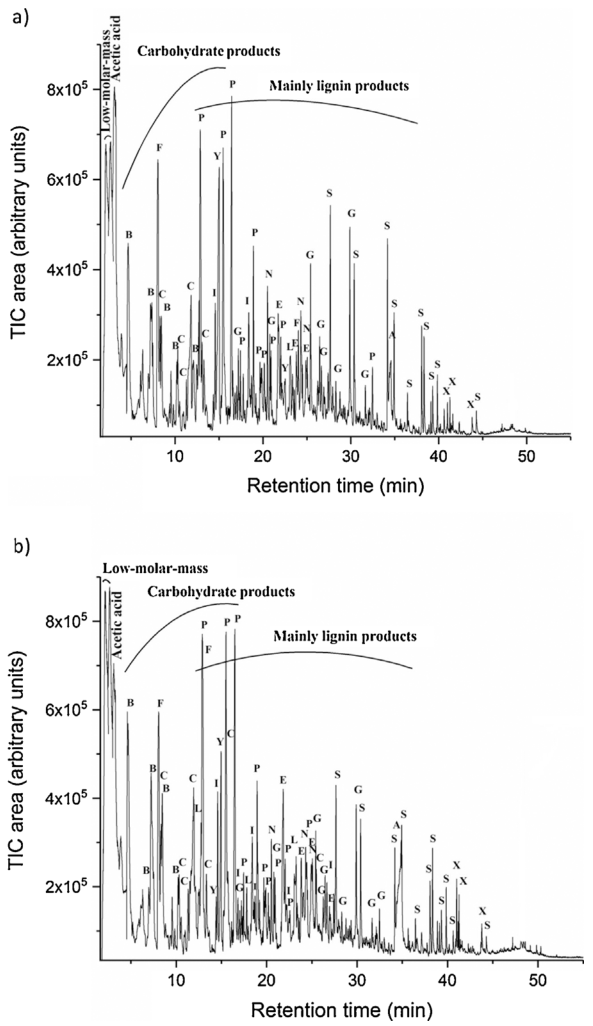

Fig. 1. The main products formed in the pyrolysis experiments (700 °C and 20 s) with untreated (a) and hot-water-extracted (b) birch sawdust. Letters indicate compound groups to which identified products belong: A (anhydrosugar derivatives), B (benzene derivatives), C (cyclopentenone derivatives), E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

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

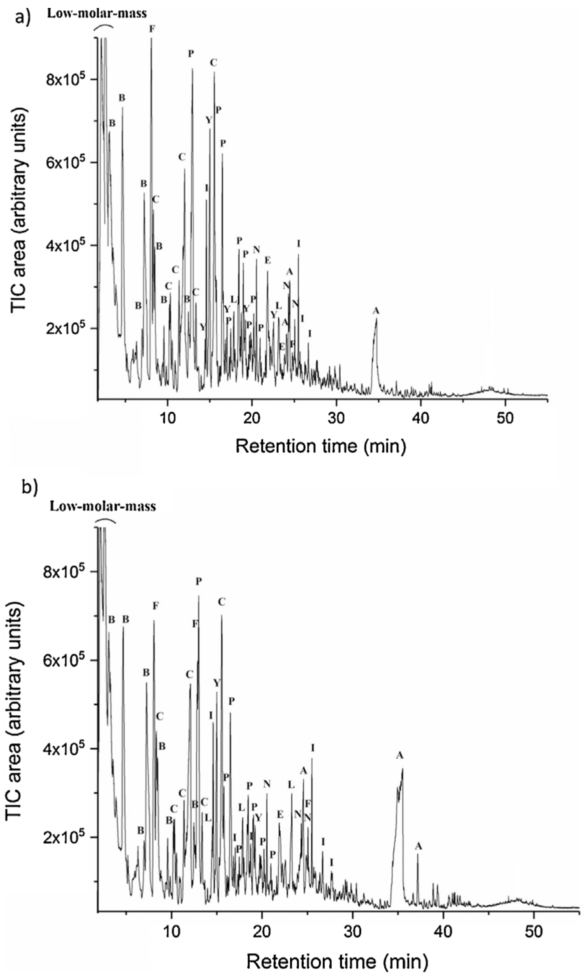

Fig. 2. The main products formed in the pyrolysis experiments (700 °C and 20 s) with soda-AQ-delignified pulps of untreated (a) and of hot-water-extracted (b) birch sawdust. For the letter symbols, see Fig. 1.

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.

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: $B_{ref} > B_{HWE} \approx P_{ref} > P_{HWE}$.

The main feedstock chemical constituents degrade on heating at different rates [32]. Under the pyrolysis conditions of this study,

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-α-D-glucopyranose	24.0	
1,6-Anhydro-β-D-glucopyranose (levoglucosan)[a]	34.5	
Benzene derivatives		B
Toluene[a]	4.6	
o-Xylene[a]	7.3	
Cyclopentenone derivatives		C
Cyclopent-2-en-1-one[a]	8.3	
2-Methylcyclopent – 2-en-1-one[a]	10.3	
2-Cyclopenten-1,4-dione	11.2	
2-Hydroxycyclopent-2-en-1-one	11.8	
3-Methyl – 1,2-cyclopentanedione[a]	15.4	
Catechol derivatives		E
1,2-Dihydroxybenzene (catechol)[a]	21.7	
1,2-Dihydroxy – 3-methylbenzene[a]	23.7	
1,2-Dihydroxy – 3-methoxybenzene[a]	24.3	
1,2-Dihydroxy-4-methylbenzene	24.8	
1,4-Dihydroxy-2,5-dimethylbenzene	26.9	
Furan derivatives		F
Furfural (furan – 2-carbaldehyde)[a]	8.0	
5-Methylfurfural[a]	12.8	
2,5-Furandicarboxaldehyde[a]	19.1	
5-(Hydroxymethyl)furfural[a]	24.7	
Guaiacol derivatives		G
2-Methoxyphenol (guaiacol)[a]	17.2	
2-Methoxy – 4-methylphenol[a]	20.7	
4-Ethenyl-2-methoxyphenol	25.4	
2-Methoxy – 4-(prop-2-en-1-yl)phenol (eugenol)[a]	26.4	
2-Methoxy – 4-(prop-1-en-1-yl)phenol (isoeugenol)[a]	28.3	
Indene derivatives		I
1*H*-Indene[a]	14.6	
1-Methyl-1*H*-indene	18.4	
2,3-Dihydro-1*H*-inden-1-one	25.6	
Lactone derivatives		L
5*H*-Furan-2-one	12.7	
3-Hydroxy-2-penteno-1,5-lactone	15.0	
4-hydroxy – 2,5-dimethylfuran-3-one[a]	17.8	
1-Hydroxy-3,6-dioxabicyclo[3.2.1]octan-2-one	23.2	
Naphthalene derivatives		N
Naphthalene[a]	20.5	
1-Methylnaphthalene	24.3	
Phenol derivatives		P
Phenol[a]	12.9	
2-Methylphenol[a]	15.5	
4-Methylphenol[a]	16.4	
2,4-Dimethylphenol	18.9	
3,5-Dimethylphenol[a]	19.7	
4-(Prop-2-en-1-yl)phenol	24.5	
Syringol derivatives		S
2,6-Dimethoxyphenol (syringol)[a]	27.6	
4-Allyl-4-methyl-2,6-dimethoxyphenol	30.3	
1-(4-Hydroxy – 3-methoxyphenyl)ethan-1-one[a]	32.4	
4-Ethenyl-2,6-dimethoxyphenol	34.1	
4-Allyl – 2,6-dimethoxyphenol (4-allylsyringol)[a]	34.9	
4-Hydroxy-3,5-dimethoxybenzaldehyde	38.3	
1-(4-Hydroxy-3,5-dimethoxyphenyl)ethanal	39.3	
4′-Hydroxy – 3′,5′-dimethoxyacetophenone[a]	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[a]	19.3	
3,4-Dihydro-6-methyl-2*H*-pyran-2-one	22.4	
Fatty acid derivatives		X
Hexadecanoic acid	40.9	
9,12-Octadecadienoic acid	43.8	

[a] Confirmed by the pure standards.

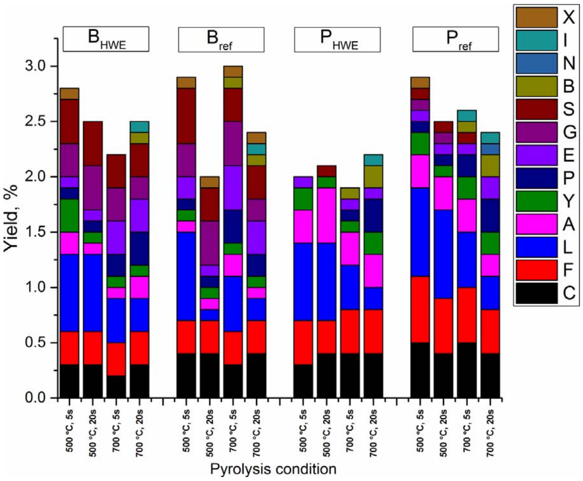

Fig. 3. Effect of pyrolysis temperature and residence time on yields of various product groups. For the letter symbols, see Fig. 1.

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

Condition	B_{HWE}	B_{ref}	P_{HWE}	P_{ref}
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

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 indenes, 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_{ref} and P_{HWE}) at 500 °C/5 s and the minimum one, 50–55%, for delignification feedstocks (B_{ref} and B_{HWE}) at 700 °C/5 s and 20 s.

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_{ref}) and 2.3 (B_{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_{ref}) and 1.4 (B_{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_{ref}) and 2.7 (P_{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/5 s and 700 °C/5 s for B_{ref} and B_{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/5 s for B_{ref} and B_{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.

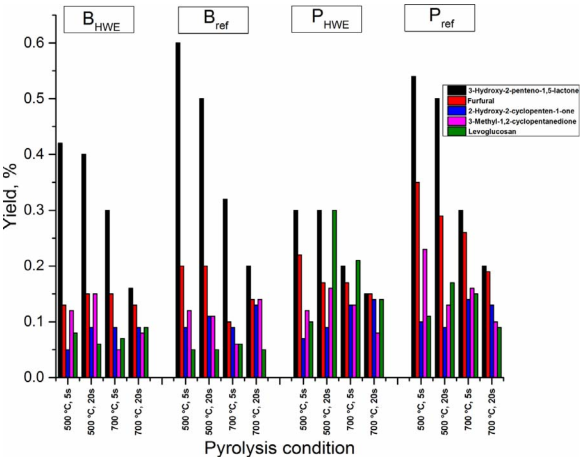

Fig. 4. Effects of pyrolysis temperature and residue time on yields of prominent pyrolysis products.

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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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jaap.2017.09.008.

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Table S1

Peak identification and calibration information of pyrolysis products differently-treated birch sawdust

No.	Compound name	Major ion(s)	RT (min)	Quantification	r^2 Value	Slope
1	Acetic acid	43, 60	3.7	Standard	0.94	4.1
2	Butanal	57, 72	3.9	Standard	0.99	4.1
3	Toluene	51, 65, 91	4.6	Standard	0.99	298.5
4	1,2-Dimethylbenzene	91, 106	7.3	Standard	0.99	230.0
5	Furfural (furan-2-carbaldehyde)	39, 95, 96	8.0	Standard	0.99	42.9
6	Cyclopent-2-en-1-one	39, 82	8.3	Standard	0.98	118.4
7	Furanmethanol ((furan-2-yl)methanol)	53, 69, 81, 98	8.4	Standard	0.99	94.2
8	Ethenylbenzene	78, 104	8.4	Standard	0.96	191.7
9	5-Methyl-2(3*H*)-furanone	55, 70, 98		Standard	0.99	56.0
10	Cyclohexanone	55, 69, 98	9.9	Standard	0.99	51.2
11	2-Methylcyclopent-2-en-1-one	53, 67, 96	10.3	Standard	0.99	65.2
12	2-Cyclopenten-1,4-dione	54, 68, 98	11.2	2-Methylcyclopent-2-en-1-one		
13	2-Hydroxycyclopent-2-en-1-one	55, 69, 98	11.8	2-Methylcyclopent-2-en-1-one		
14	5*H*-Furan-2-one	39, 55, 84	12.7	Standard	0.99	24.8
15	5-Methylfurfural	53, 109, 110	12.8	Standard	0.98	62.2
16	Phenol	66, 94	12.9	Standard	0.98	55.1
17	3-Methylcyclopent-2-en-1-one	53, 67, 96	13.3	2-Methylcyclopent-2-en-1-one		
18	Pyran-2-one	39, 68, 96	14.3	3-Hydroxy-2-methylpyran-4-one		
19	1*H*-Indene	63, 89, 116	14.5	Standard	0.99	211.2
20	3-Hydroxy-2-penteno-1,5-lactone	58, 85, 114	15.0	4-Hydroxy-5-methylfuran-3-one (standard)	0.97	35.2
21	3-Methyl-1,2-cyclopentanedione	69, 83, 112		Standard	0.98	43.6
22	2-Methylphenol	39, 51, 79, 107	15.5	Standard	0.99	85.0
23	4-Methylphenol	39, 51, 79, 108	16.4	Standard	0.99	82.0
24	2-Methylbenzofuran	51, 77, 103, 131	16.8	1-Benzofuran (standard)	0.97	160.7
25	2-Methoxyphenol (guaiacol)	53, 81, 109, 124	17.2	Standard	0.99	79.2
26	2,6-Dimethoxyphenol (syringol)	77, 107, 122	17.4	Standard	0.98	128.6

27	4-Methyl-5*H*-furan-2-one	69, 98	17.9	5*H*-Furan-2-one		
28	4-Hydroxy-2,5-dimethylfuran-3-one	43, 57, 85, 128	18.1	Standard	0.99	41.6
29	Methyl furan-2-carboxylate	39, 95, 126	18.1	Furfural (furan-2-carbaldehyde)		
30	2*H*-Pyran-2-one-4-hydroxy-6-methyl	43, 69, 98, 126	18.3	3-Hydroxy-2-methylpyran-4-one		
31	2-Ethylphenol	63, 77, 107, 122	18.3	2,6-Dimethylphenol		
32	1-Methyl-1*H*-indene	115, 130	18.4	1*H*-Indene		
33	3-Ethyl-2-hydroxycyclopent-2-en-1-one	55, 69, 83, 126	18.5	2-Methylcyclopent-2-en-1-one		
34	2,4-Dimethylphenol	65, 77, 107, 122	18.9	2,6-Dimethylphenol		
35	3-Hydroxy-2-methylpyran-4-one	43, 55, 71, 126	19.0	Standard	0.98	74.5
36	2,5-Furandicarboxaldehyde	53, 67, 95, 124	19.1	Standard	0.99	83.0
37	3-Ethylphenol	77, 107, 122	19.6	3,5-Dimethylphenol		
39	3,5-Dimethylphenol	77, 107, 122	19.8	Standard	0.98	87.6
40	(1*S*,5*R*)-6,8-Dioxabicyclo[3.2.1]oct-2-en-4-one (levoglucosenone)	39, 68, 98	19.8	Levoglucosan		
41	2,3-Dihydroxybenzaldehyde	51, 64, 92, 120, 138	20.5	Standard	0.99	119.0
42	Naphthalene	51, 102, 128	20.5	Standard	0.99	178.8
43	2-Methoxy-4-methylphenol	67, 123, 138	20.7	Standard	0.99	275.0
44	2,3,5-TrimethylPhenol	77, 91, 121, 136	20.9	2,3,6-TrimethylPhenol		
45	1,2-Dihydroxybenzene (catechol)	64, 81, 110	21.7	Standard	0.98	57.3
46	3,5-Dihydroxy-2-methylpyran-4-one	68, 85, 113, 142	21.8	3-Hydroxy-2-methylpyran-4-one		
47	2,3,6-TrimethylPhenol	77, 91, 121, 136	22.0	Standard	0.98	222.0
48	2,3- Dihydrobenzofuran	65, 91, 120	22.1	1-Benzofuran (standard)	0.97	160.7
49	6-Methyldihydro-2*H*-pyran-3(4*H*)-on	56, 84, 114	22.4	3-Hydroxy-2-methylpyran-4-one		
50	(1*R*,5*S*)-1-Hydroxy-3,6-dioxabicyclo[3.2.1]octan-2-one	57, 69, 85, 116, 144	23.2	Levoglucosan		
51	2′,5′-Dihydroxyacetophenone (1-(2,5-dihydroxyphenyl)ethanone)	69, 109, 137, 152	23.4	1,4-Dihydroxybenzene		
52	2-Methoxy-4-ethylphenol	137, 152	23.5	2-Methoxy-4-methylphenol		
53	1,2-Dihydroxy-3-methylbenzene	51, 78, 106, 124	23.7	Standard	0.97	155.0
54	1,4:3,6-Dianhydro-α-D-glucopyranose	69, 86, 98, 144	24.0	Levoglucosan		
55	1-Methylnaphthalene	71, 115, 142	24.3	Naphthalene		
56	1,2-Dihydroxy-3-methoxybenzene	97, 125, 140	24.4	Standard	0.97	159.0

57	2,3-Anhydro-D-mannose	69, 71, 85, 97, 144	24.5	Levoglucosan		
58	4-(Prop-2-en-1-yl)-phenol	77, 91, 107, 115, 134		4-Methylphenol		
59	5-(Hydroxymethyl)furfural	39, 97, 109, 126	24.7	Standard	0.97	73.0
60	1,2-Dihydroxy-4-methylbenzene	39, 78, 107, 124	24.8	1,2-Dihydroxy-3-methylbenzene		
61	4-Ethenyl-2-methoxyphenol	51, 77, 107, 135, 150	25.4	Standard	0.97	251.5
62	2,3-Dihydro-1*H*-indene-1-one	78, 104, 132	25.6	1*H*-Indene		
63	1,4-Dihydroxybenzene	39, 81, 110	25.6	Standard	0.97	144.6
64	2-Methoxy-4-(prop-2-en-1-yl)phenol (eugenol)	77, 131, 149, 164	26.6	2-Methoxy-4-(prop-2-en-1-yl)phenol (eugenol)	0.97	331.0
65	1,4-Dihydroxy-2,5-dimethylbenzene	95, 109, 123, 138	26.9	1,4-Dihydroxybenzene		
66	2,6-Dimethoxyphenol (syringol)	96, 139, 154	27.6	Standard	0.99	76.3
67	2-Methoxy-4-(prop-1-en-1-yl)phenol (isoeugenol)	91, 103, 131, 149, 164	29.8	Standard	0.97	151.0
68	4-Methyl-2,6-dimethoxyphenol	125, 153, 168	30.3	2,6-Dimethoxyphenol (syringol)		
69	2-Methoxy-4-propylphenol	77, 122, 137, 166	31.6	2-Methoxy-4-(prop-2-en-1-yl)phenol (eugenol)		
70	1-(4-Hydroxy-3-methoxyphenyl)-ethan-1-one (acetovanillone)	77, 123, 151, 166	32.4	4-Hydroxy-3-methoxybenzoic acid (vanillic acid) (standard)	0.98	154.7
71	4-Ethenyl-2,6-dimethoxyphenol	137, 165, 180	34.1	4-Allyl-2,6-dimethoxyphenol		
72	1,6-Anhydro-β-D-glucopyranose (levoglucosan)	60, 73, 126, 145	34.5	Standard	0.99	67.0
73	4-Allyl-2,6-dimethoxyphenol (4-allylsyringol)	150, 179, 194	34.9	Standard	0.98	274.4
74	4-Hydroxy-3,5-dimethoxybenzaldehyde (syringylaldehyde)	167, 181, 182	38.3	4'-Hydroxy-3',5'-dimethoxyacetophenone (acetosyringone)		
75	1-(4-Hydroxy-3,5-dimethoxyphenyl)ethanal (homosyringaldehyde)	167, 196	39.3	4'-Hydroxy-3',5'-dimethoxyacetophenone (acetosyringone)		

76	4'-Hydroxy-3',5'-dimethoxyacetophenone (acetosyringone)	181, 196	39.8	Standard	0.99	411.9
77	(4-Hydroxy-3,5-dimethoxy-phenyl)-acetone (syringylacetone)	167, 210	40.6	4'-Hydroxy-3',5'-dimethoxyacetophenone (acetosyringone)		
78	Hexadecanoic acid	129, 213, 256	40.9	Linoleic acid (standard)	0.99	148.8
79	9,12-Octadecadienoic acid	185, 241, 284	43.8	Linoleic acid (standard)		
80	3-(4-Hydroxy-3,5-dimethoxyphenyl)prop-2-enal	137, 165, 180, 208	44.3	4'-Hydroxy-3',5'-dimethoxyacetophenone (acetosyringone)		

In all cases, the intercept was 0.0

Table S2

Group of pure compounds based on average RSD%

Group	Compounds	Average slope	Average SD	Average RSD%
Group I	5-Methylfurfural	62.2	8.6	17.1
	2(3*H*)-Furanone-5-methyl	56.0		
	Cyclohexanone	51.2		
	2-Methylcyclopent-2-en-1-one	65.2		
	Furfural (furan-2-carbaldehyde)	42.9		
	3-Methyl-1,2-cyclopentanedione	43.6		
	4-Hydroxy-2,5-dimethylfuran-3-one	41.6		
	4-Hydroxy-5-methylfuran-3-one	35.2		
	Phenol	55.1		
	1,2-Dihydroxybenzene (catechol)	57.3		
	1,6-Anhydro-β-D-glucopyranose (levoglucosan)	67.0		
	5*H*-Furan-2-one	24.8		
Group II	2,5-Furandicarboxaldehyde	83.0	6.8	8.3
	Furanmethanol ((furan-2-yl)methanol)	94.2		
	2-Methylphenol	85.0		
	4-Methylphenol	82.0		
	3,5-Dimethylphenol	87.6		
	2-Methoxyphenol (guaiacol)	79.2		
	2,6-Dimethoxyphenol (syringol)	76.3		
	3-Hydroxy-2-methylpyran-4-one	74.5		
	5-(Hydroxymethyl)furfural	73.0		
Group III	Cyclopent-2-en-1-one	118.4	18.8	13.1
	2,3-Dihydroxybenzaldehyde	119.0		
	2,6-Dimethylphenol	128.6		
	3,4-Dimethylphenol	131.8		
	2-Methoxy-4-(prop-1-en-1-yl)phenol (isoeugenol)	151.0		
	4-Hydroxy-3-methoxybenzoic acid (vanillic acid)	154.7		
	1,2-Dihydroxy-3-methylbenzene	155.0		
	1,2-Dihydroxy-3-methoxybenzene	159.0		
	1,4-Dihydroxybenzene	144.6		
	1,3-Dihydroxybenzene	120.0		
	Naphthalene	178.8		
	1-Benzofuran	160.8		
	Linoleic acid	148.8		
Group IV	2-Methoxy-4-methylphenol	275.0	42.4	16.6
	Toluene	298.5		
	1,2-Dimethylbenzene	230.0		
	Ethenylbenzene	191.7		
	o-Xylene	264.7		
	1*H*-Indene	211.2		
	2,3,6-Trimethylphenol	222.0		

	4-Ethenyl-2-methoxyphenol	251.5		
	2-Methoxy-4-(prop-2-en-1-yl)phenol (eugenol)	331.0		
	4-Allyl-2,6-dimethoxyphenol	274.4		
	4'-Hydroxy-3',5'-dimethoxyacetophenone (acetosyringone)	411.9		
Group V	Acetic acid	4.1	-	-
	Butanal	4.1		

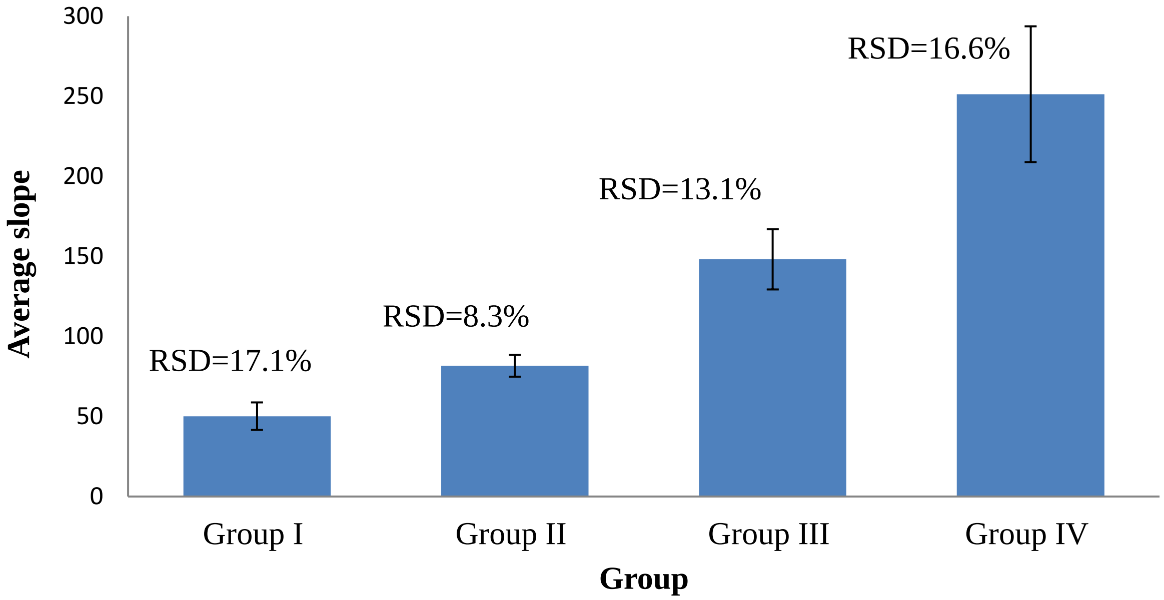

Fig. S1. Group of pure compounds based on average RSD%.

II

FAST PYROLYSIS OF HOT-WATER-EXTRACTED AND DELIGNIFIED NORWAY SPRUCE (*PICEA ABIES*) SAWDUST BY PY-GC/MS

by

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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%).

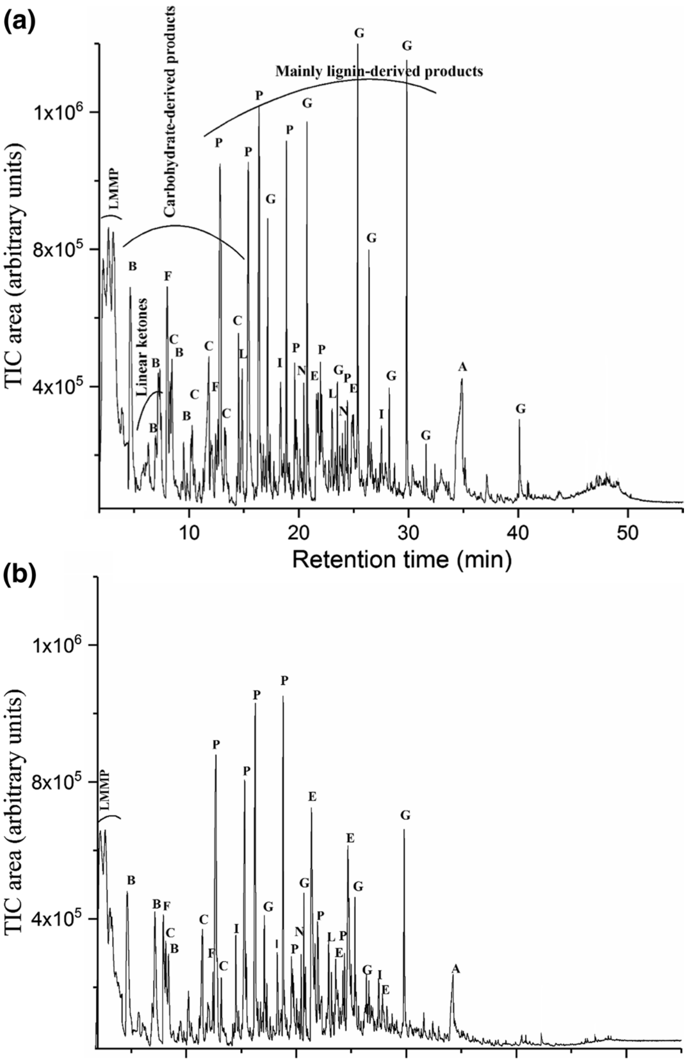

Fig. 1 Main products formed in the pyrolysis experiments (700 °C and 20 s) with untreated (**a**) and HWE (**b**) spruce sawdust. Letters indicate compound groups to which identified products belong: *A* (anhydrosugar derivatives), *B* (benzene derivatives), *C* (cyclopentenone derivatives), *E* (catechol 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,

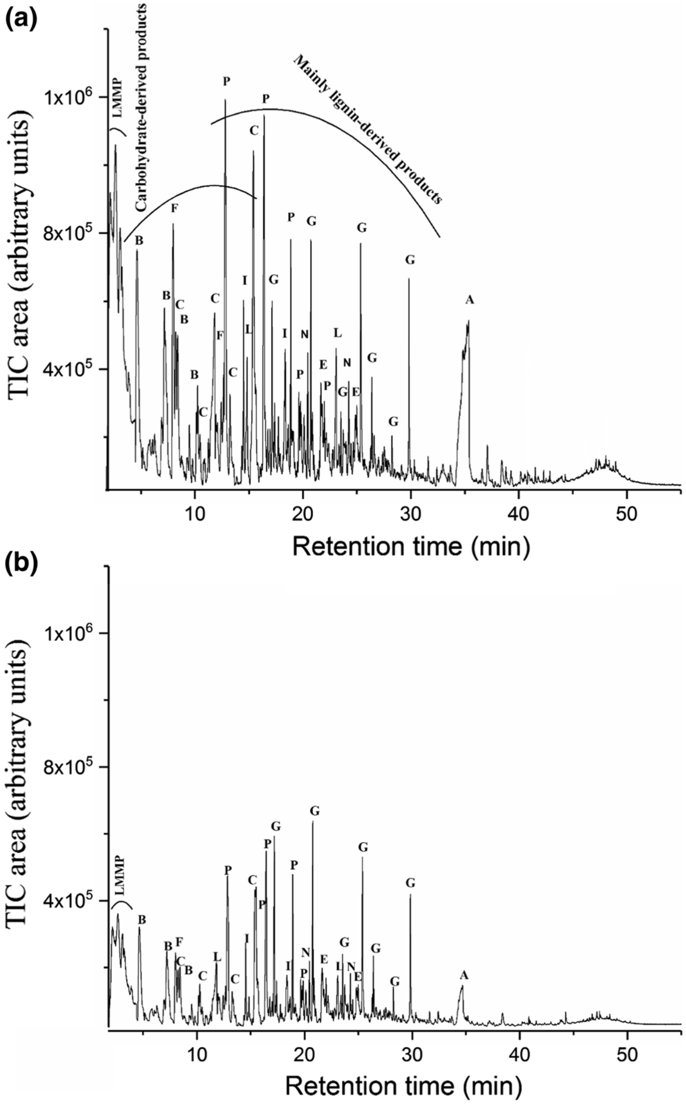

Fig. 2 Main products formed in the pyrolysis experiments (700 °C and 20 s) with the soda-AQ-delignified pulps of untreated (**a**) and of HWE (**b**) spruce feedstocks. For the letter symbols, see Fig. 1

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

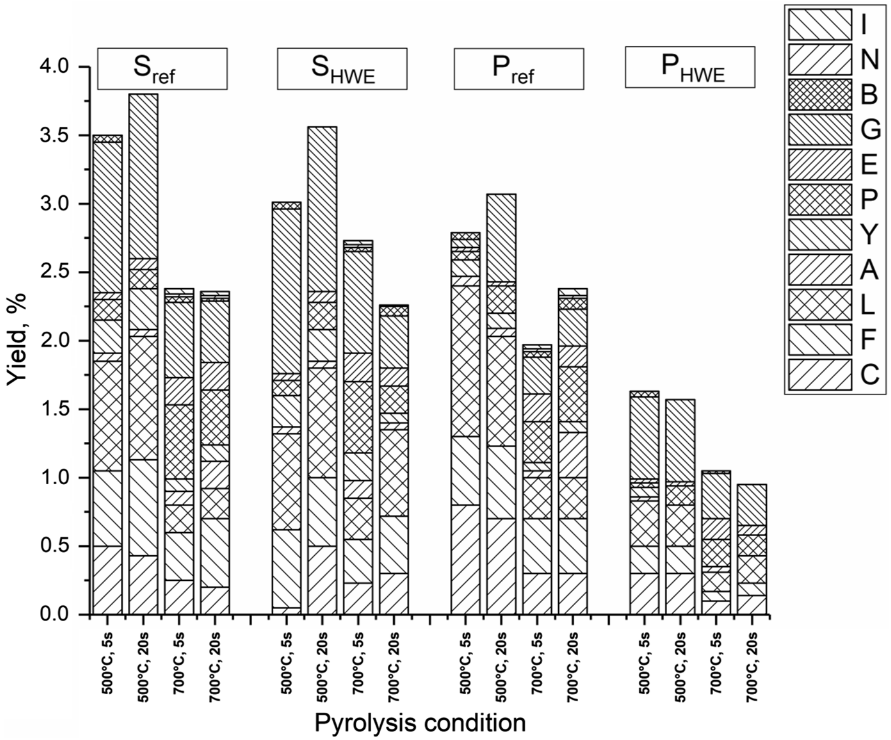

Fig. 3 Effects of temperature and residence time on yields of various product groups. For the letter symbols, see Fig. 1

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

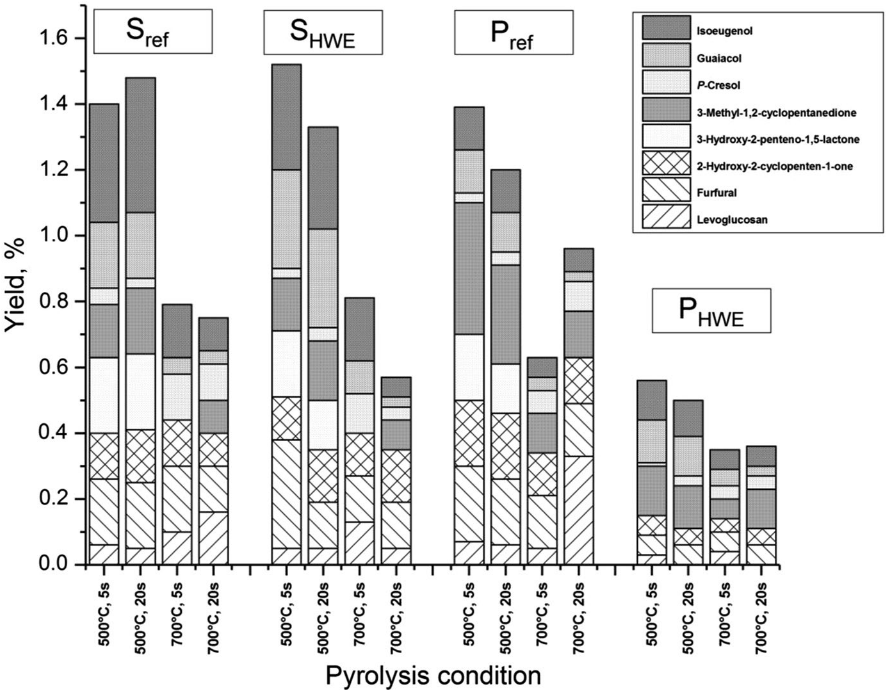

Fig. 4 Effects of temperature and residue time on yields of prominent pyrolysis products

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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Table S1

Peak identification and calibration information of pyrolysis products differently-treated spruce sawdust

No.	Compound name	Major ion(s) *(m/z)*	RT (min)	Quantification	r^2 Value	Slope
1	Toluene	51, 65, 91	4.6	Standard	0.99	298.5
2	(2*E*)-Penta-2,4-dienal	53, 82	5.2	(1*E*)-1-Butene-1,4-diol (standard)	0.98	13.5
3	Pentanal	58, 86	7.3	Butanal (standard)	0.99	4.1
4	Furfural (furan-2-carbaldehyde)	39, 95, 96	8.0	Standard	0.99	42.9
5	Cyclopent-2-en-1-one	39, 82	8.3	Standard	0.98	118.4
6	Ethenylbenzene	78, 104	8.3	Standard	0.96	191.7
7	Furanmethanol ((furan-2-yl)methanol)	53, 69, 81, 98	8.6	Standard	0.99	94.2
8	5-Methyl-2(3*H*)-furanone	55, 70, 98	9.1	Standard	0.99	56.0
9	Cyclohexanone	55, 69, 98	9.9	Standard	0.99	51.2
10	2-Methylcyclopent-2-en-1-one	53, 67, 96	10.3	Standard	0.99	65.2
11	1-(2-Furyl)ethanone	95, 110	10.5	Furanmethanol		
12	2-Cyclopenten-1,4-dione	54, 68, 98	11.2	2-Methylcyclopent-2-en-1-one		
13	2-Hydroxycyclopent-2-en-1-one	55, 69, 98	11.8	2-Methylcyclopent-2-en-1-one		
14	2-Methylethenylbenzene	91, 103, 118	12.1	Ethenylbenzene		
15	5*H*-Furan-2-one	39, 55, 84	12.7	Standard	0.99	24.8
16	5-Methylfurfural	53, 109, 110	12.8	Standard	0.98	62.2
17	Phenol	66, 94	12.9	Standard	0.98	55.1
18	3-Methylcyclopent-2-en-1-one	53, 67, 96	13.3	2-Methylcyclopent-2-en-1-one		
19	Pyran-2-one	39, 68, 96	14.3	3-Hydroxy-2-methylpyran-4-one		
20	1*H*-Indene	63, 89, 116	14.5	Standard	0.99	211.2
21	3-Methyl-2(5*H*)-furanone	69, 98	14.5	5-Methyl-2(3*H*)-furanone		
22	2*H*-Pyran-2,6(3*H*)-dione	55, 84, 112	14.8	3-Hydroxy-2-methylpyran-4-one		
23	3-Hydroxy-2-penteno-1,5-lactone	58, 85, 114	15.0	4-Hydroxy-5-methylfuran-3-one (standard)	0.97	35.2
24	3-Methyl-1,2-cyclopentanedione	69, 83, 112	15.4	Standard	0.98	43.6
25	2-Methylphenol	39, 51, 79, 107	15.5	Standard	0.99	85.0
26	4-Methylphenol	39, 51, 79, 108	16.4	Standard	0.99	82.0
27	2-Methylbenzofuran	51, 77, 103, 131	16.7	1-Benzofuran (standard)	0.97	160.7
28	2-Methoxyphenol (guaiacol)	53, 81, 109, 124	17.2	Standard	0.99	79.2
29	2,6-Dimethylphenol	77, 107, 122	17.3	Standard	0.98	128.6
30	4-Methyl-5*H*-furan-2-one	69, 98	17.9	5*H*-Furan-2-one		
31	4-Hydroxy-2,5-dimethylfuran-3-one	43, 57, 85, 128	18.1	Standard	0.99	41.6
32	Methylfuran-2-carboxylate	39, 95, 126	18.1	Furfural (furan-2-carbaldehyde)		

33	2*H*-Pyran-2-one-4-hydroxy-6-methyl	43, 69, 98, 126	18.3	3-Hydroxy-2-methylpyran-4-one		
34	1-Methyl-1*H*-indene	115, 130	18.3	1*H*-Indene		
35	3-Ethyl-2-hydroxycyclopent-2-en-1-one	55, 69, 83, 126	18.4	2-Methylcyclopent-2-en-1-one		
36	2-Ethylphenol	77, 107, 122	18.4	2,6-Dimethylphenol		
37	2,4-Dimethylphenol	65, 77, 107, 122	18.9	2,6-Dimethylphenol		
38	2,5-Furandicarboxaldehyde	53, 67, 95, 124	19.1	Standard	0.99	83.0
39	3-Hydroxy-2-methylpyran-4-one	43, 55, 71, 126	19.2	Standard	0.98	74.5
40	3,5-Dimethylphenol	77, 91, 107, 122	19.8	Standard	0.98	87.7
41	2-Methoxy-3-methylphenol	77, 95, 123, 138	20.1	2-Methoxy-4-methylphenol		
42	Naphthalene	51, 102, 128	20.4	Standard	0.99	178.8
43	2,3-Dihydroxybenzaldehyde	51, 64, 92, 120, 138	20.5	Standard	0.99	119.0
44	2-Methoxy-4-methylphenol	67, 123, 138	20.7	Standard	0.99	275.0
45	2,3,5-Trimethylphenol	77, 91, 121, 136	20.8	2,3,6-Trimethylphenol		
46	6-Ethyl-*o*-cresol	77, 91, 107, 121, 136	21.5	*o*-Cresol (standard)	0.99	85.0
47	1,2-Dihydroxybenzene (catechol)	64, 81, 110	21.7	Standard	0.98	57.3
48	3,5-Dihydroxy-2-methylpyran-4-one	68, 85, 113, 142	21.8	3-Hydroxy-2-methylpyran-4-one		
49	2,3,6-Trimethylphenol	77, 91, 121, 136	22.0	Standard	0.98	222.0
50	4-Ethenylphenol	65, 91, 120	22.1	3,5-Dimethylphenol		
51	6-Methyldihydro-2*H*-pyran-3(4*H*)-one	56, 84, 114	22.4	3-Hydroxy-2-methylpyran-4-one		
52	2,3-Dimethoxytoluene	91, 109, 137, 152	22.5	1,2-Dihydroxy-3-methylbenzene		
53	4-Hydroxy-2-methylacetophenone	77, 107, 135, 150	22.7	2-Methoxy-4-methylphenol (standard)		
54	(1*R*,5*S*)-1-Hydroxy-3,6-dioxabicyclo[3.2.1]octan-2-one	57, 69, 85, 116, 144	23.2	Levoglucosan		
55	2′,5′-Dihydroxyacetophenone (1-(2,5-dihydroxyphenyl)ethanone)	69, 109, 137, 152	23.4	1,4-Dihydroxybenzene		
56	2-Methoxy-4-ethylphenol	137, 152	23.5	2-Methoxy-4-methylphenol		
57	1,2-Dihydroxy-3-methylbenzene	51, 78, 106, 124	23.7	Standard	0.97	155.0
58	2-Methylnaphthalene		24.2	Naphthalene		
59	4-(Prop-2-en-1-yl)phenol	77, 91, 107, 115, 134	24.5	4-Methylphenol		
60	5-(Hydroxymethyl)furfural	39, 97, 109, 126	24.7	Standard	0.97	73.0
61	1,2-Dihydroxy-4-methylbenzene	39, 78, 107, 124	25.0	1,2-Dihydroxy-3-methylbenzene		
62	4-Ethenyl-2-methoxyphenol	51, 77, 107, 135, 150	25.4	Standard	0.97	251.5
63	2´-Hydroxy-5´-methoxy-acetophenone	95, 123, 151, 166	25.8	2-Methoxy-4-methylphenol (standard)		
64	2-Methoxy-4-ethyl-6-methylphenol	77, 136, 151, 166	25.9	2-Methoxy-4-(prop-2-en-1-yl)phenol (eugenol)	0.97	331.2
65	5-Methyl-3-methoxyphenol	107, 109, 123, 138	26.1	2-Methoxy-4-methylphenol		
66	2-Methoxy-4-(prop-2-en-1-yl)phenol (eugenol)	77, 131, 149, 164	26.4	2-Methoxy-4-(prop-2-en-1-yl)phenol (eugenol)	0.97	331.0
67	5-Acetoxymethyl-2-furaldehyde	79, 97, 109, 126	26.6	5-(Hydroxymethyl)furfural		

68	1*H*-Indenol	77, 103, 115, 132	27.5	1*H*-Indene		
69	4-Ethyl-1,3-benzenediol	128, 138	27.9	1,2-Dihydroxy-3-methylbenzene		
70	2-Methoxy-4-(prop-1-en-1-yl)phenol (isoeugenol)	91, 103, 131, 149, 164	29.8	Standard	0.97	151.0
71	2-Methoxy-4-propylphenol	77, 122, 137, 166	31.6	2-Methoxy-4-(prop-2-en-1-yl)phenol (eugenol)		
72	1-(4-Hydroxy-3-methoxyphenyl)-ethan-1-one	77, 123, 151, 166	32.4	4-Hydroxy-3-methoxybenzoic acid (vanillic acid) (standard)	0.98	154.7
73	Guaiacylacetone	122, 137, 180	33.6	2-Methoxy-4-(prop-2-en-1-yl)phenol (eugenol)		
74	1,6-Anhydro-β-D-glucopyranose (levoglucosan)	60, 73, 126, 145	34.5	Standard	0.99	67.0
75	(2*E*)-3-(4-hydroxy-2-methoxyphenyl)-2-propenal	77, 107, 135, 161, 178	40.1	2-Methoxy-4-(prop-2-en-1-yl)phenol (eugenol)		

In all cases, the intercept was 0.0.

III

FAST PYROLYSIS OF HOT-WATER-EXTRACTED AND SODA-AQ-DELIGNIFIED OKRA (*ABELMOSCHUS ESCULENTUS*) AND MISCANTHUS (*MISCANTHUS X GIGANTEUS*) STALKS BY PY-GC/MS

by

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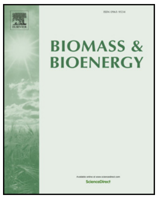

Research paper

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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Condensable products

ABSTRACT

The thermochemical behavior of various samples of okra (*Abelmoschus esculentus*) and miscanthus (*Miscanthus* x *giganteus*) stalks (initial, hot-water-extracted, and those from sulfur-free delignification) were studied by pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS). In all cases, major GC-amenable condensable products were measured semi-quantitatively and classified into several product groups. The formation of these product groups from different feedstock samples with varying mass portions of their structural constituents (carbohydrates and lignin) was investigated at 500 °C and 700 °C with a residence time of 5 s and 20 s. The main product groups were aliphatic compounds, such as lactone, furan, and cyclopentenone derivatives from carbohydrates (mainly hemicelluloses) and aromatic compounds, such as guaiacol, phenol, and syringol derivatives from lignin. Additionally, the formation of aliphatic and aromatic products (e.g., the ratio of aliphatic compounds to aromatic compounds) was found to be characteristically dependent on feedstock composition and pyrolysis conditions. This kind of approach is of practical importance concerning efforts not only to uncover new integrated biorefinery possibilities to manufacture value-added products but also to develop rapid characterization tools for lignocellulosics.

1. Introduction

Due to many reasons, the rapidly increasing utilization of lignocellulosic feedstocks for producing renewable energy and chemicals, especially a variety of various non-wood materials, is in progress [1–7]. At the same time, more effective use of more versatile biomass resources is of great importance. One of the most promising integrated biorefining approaches, mainly utilized for the partial recovery of wood-derived carbohydrates, is based on different pre-treatment processes [8–14], such as hot-water extraction conducted prior to delignification [15–22]. Typically, by such pre-treatments, it is possible to obtain potential by-streams and simultaneously increase the reactivity of feedstock material, resulting in enhanced pulping performance together with spent liquors that have attractive chemical compositions. Hence, by these kinds of integrated biorefinery concepts, the efficient utilization of all major feedstock constituents (cellulose, hemicelluloses, and lignin) can be considered when planning target-oriented economic processes for the manufacture of useful products from fibrous lignocellulosics.

Non-wood based raw materials, such as annual crops, can be applied as an effective fibrous alternative to the decreasing forest wood resources in most developing regions [5,23]. Potential agricultural feedstocks, such as okra (*Abelmoschus esculentus*) and miscanthus (*Miscanthus* x *giganteus*, a hybrid of *M. sinensis* and *M. sacchariflorus*) stalks, may offer interesting raw materials for lignocellulosic biorefineries. Okra is one of the most important vegetables and is widely grown from Asia to Africa, Southern Europe, and America. Its edible green seed pods play an essential role in the human diet by supplying carbohydrates, minerals, and vitamins [24–26]. Post-harvest okra stalk residues have traditionally been an unused fraction of the total harvest, although their utilization for fiber in pulps [27,28], composites [29], and ethanol production [30] has been studied to some extent. In contrast, miscanthus, as a commercial energy crop, is currently of great importance in the sustainable production of biofuel products and chemicals due to its vast production worldwide and its high dry-matter yield [31–36]. Hence, its thermochemical behavior has also been studied [37–40], for example, together with the suitability of its fiber for paper production [41,42]. However, only a limited amount of data on the detailed chemical composition of okra and miscanthus stalk is still available.

Pyrolysis is one of the thermochemical conversion methods of

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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) [43]. In our earlier papers, we studied the thermochemical behavior of silver birch (*Betula pendula*) [44] and Norway spruce (*Picea abies*) [45] sawdust, both untreated and after various chemical treatments (hot-water extraction, delignification, and hot-water extraction followed by delignification), by pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS). In each case, major GC-amenable condensable products were determined and classified into several compound groups, characteristically originated from the main structural constituents (cellulose, hemicelluloses, and lignin) of these wood materials. In this comparative study, the aim was to use the untreated and analogously treated non-wood feedstocks, okra, and miscanthus stalks for the same purpose by utilizing the treatment conditions suitable for these raw materials. Also, in this case, the suitability of this analytical pyrolysis method was investigated under varying pyrolysis conditions as a rapid tool for roughly detecting changes that took place during different treatments in the relative content of each constituent of the feedstock samples.

2. Materials and methods

2.1. Feedstock materials and their analyses

The untreated (okra, O_{ref} and miscanthus, M_{ref}) and hot-water-extracted (HWE) okra and miscanthus stalks (O_{HWE} and M_{HWE}, respectively) (< 5 mm) and the soda-anthraquinone (AQ)-cooked pulps of these feedstocks (PO_{ref}, PO_{HWE}, PM_{ref}, and PM_{HWE}) were investigated.

Hot-water extraction (140 °C for 60 min) and 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 [46–48]. The HWE feedstock obtained was thoroughly washed with tap water, and the amount of the solid residue (“yield”) was calculated on the basis of oven-dried (o.d.) initial and HWE material. The yields of hot-water extraction were 85.6% ($O_{ref} \rightarrow O_{HWE}$) and 95.2% ($M_{ref} \rightarrow M_{HWE}$).

The cooking conditions were as follows: alkali (NaOH) charge 20% (okra) and 15% (miscanthus) on o.d. feedstock, AQ charge 0.05% on o.d. feedstock, cooking temperature 165 °C, cooking time 180 min (okra) and 60 min (miscanthus), and liquor-to-feedstock ratio 5 L kg^{-1}. 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 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. Pulp yields of the material charged into the reactors were 40.2% ($O_{ref} \rightarrow PO_{ref}$), 37.8% ($O_{HWE} \rightarrow PO_{HWE}$), 57.5% ($M_{ref} \rightarrow PM_{ref}$), and 60.3% ($M_{HWE} \rightarrow PM_{HWE}$).

For the chemical analyses, air-dried untreated and HWE 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 before weighing using a gentle nitrogen stream.

Acid hydrolysis of the extractives-free ground samples was performed according to TAPPI T249 cm-00 standard. 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 $(gcm)^{-1}$ [49].

The content of different monosaccharides (i.e., arabinose, galactose, glucose, mannose, and xylose) in the Klason hydrolysates and free monosaccharides in the hot-water-extraction hydrolysates were analyzed with high-performance anion-exchange chromatography with pulsed amperometric detection (HPAEC-PAD, from the Dionex Corp., Sunnyvale, CA, USA) [50]. A Dionex CarboPac PA-1 column (250 mm × 4 mm inner diameter) was applied to the separation of different monosaccharides at a flow rate of 1.0 mL min^{-1}. A post-column alkali (300 Mm NaOH) addition was utilized at a flow rate of 0.2 mL min^{-1} to increase the performance of PAD. The peak identification and the mass-based response factors between an internal standard (L-fucose) and each monosaccharide were collected from separate runs with model monosaccharides. The content of the carbohydrates in acid hydrolysates was determined based on the anhydro forms of the measured monosaccharides. Moreover, a slight decrease (about 5%) in the yield of monosaccharides during acid hydrolysis, which resulted from different side reactions (e.g., the formation of furans), was considered.

2.2. Pyrolysis experiments and product analysis

About 0.5 mg of samples were pyrolyzed in a quartz tube (3.0 cm × 1.0 mm inner diameter, between quartz wool) at a heating rate of 20 °C $(ms)^{-1}$ 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 × 0.25 mm with a film thickness of 0.25 μm). The GC oven temperature program in the analyses of pyrolysis products was as follows: 2 min at 40 °C, 4 °C min^{-1} to 190 °C, 10 °C min^{-1} to 320 °C, and 10 min at 320 °C. Helium was used as carrier gas with a gas flow rate of 1 mL min^{-1} and as an inert atmosphere in the pyrolysis interface. 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. Detection was carried out with an HP 5970 mass spectrometric detector under electron ionization (70 eV). In addition, mass spectra were recorded at a rate of 2.92 scan files per second 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 based on duplicated injections according to our earlier study [44] so that pure compounds (the total number was 27) were used as external standards to relatively quantify all the 60 identified peaks from pyrolysis products (Py-GC/MS) by comparing the products to a set of standard samples of known concentration.

3. Results and discussion

3.1. Raw materials

The main chemical components (and their building blocks) in non-wood feedstocks are basically the same as those in wood feedstocks (resembling primarily hardwoods) and can be found in varying amounts depending on species (genetic differences), growing conditions, and presence of specialized tissues within individual plants [5]. However, it is still possible to detect considerable differences, for example, in both the content and composition of hemicelluloses between

Table 1
Chemical composition of the initial and differently-treated okra and miscanthus stalks (% of the initial sample[a] dry solids).

Components	O_{ref}	O_{HWE}	PO_{ref}	PO_{HWE}	M_{ref}	M_{HWE}	PM_{ref}	PM_{HWE}
Carbohydrates[b]	58.3	51.9	34.9	28.7	71.7	60.8	41.6	47.0
Glucose	41.8	38.0	28.1	23.1	48.3	44.5	33.9	37.8
Xylose	12.2	11.8	6.6	5.5	21.3	13.5	7.5	9.0
Others	4.3	2.1	0.2	0.1	2.1	2.8	0.2	0.2
Lignin	20.5	15.2	1.6	1.0	17.8	15.7	0.8	0.6
Klason	17.3	13.8	1.5	0.9	17.7	15.5	0.7	0.5
Acid-soluble	3.2	1.4	0.1	0.1	0.1	0.2	0.1	0.1
Extractives	5.0	3.3	0.2	0.1	1.5	3.3	0.8	0.1
Others[c]	16.2	15.2	3.5	2.6	9.0	15.4	14.3	9.7
Total	100.0	85.6	40.2	32.4	100.0	95.2	57.5	57.4

[a] O_{ref} and O_{HWE} refer to untreated and hot-water-extracted okra feedstock, respectively, and PO_{ref} and PO_{HME} refer to the soda-AQ-delignified pulps of untreated and hot-water-extracted okra feedstock, respectively. M_{ref} and M_{HWE} refer to untreated and hot-water-extracted miscanthus feedstock, respectively, and PM_{ref} and PM_{HME} refer to the soda-AQ-delignified pulps of untreated and hot-water-extracted miscanthus feedstock, respectively.

[b] Monosaccharide units are presented as their anhydro forms.

[c] Includes acetyl groups of xylan, pectins, proteins, and inorganics.

the different non-wood biomasses but also within the single plant. In practice, it means that among cellulose and common hemicelluloses, there are other miscellaneous hemicelluloses in varying but mainly small amounts. Furthermore, it has been reported that in contrast to wood, the secondary cell wall of grass plants characteristically contains core and non-core lignins [51]. The non-core lignin contains, for example, ferulic acid moieties that are usually esterified to carbohydrates and etherified to lignin, forming "ferulic bridges" [52–56]. The presence of these lignin/phenolic-carbohydrate complexes may also have an effect on the behavior of non-woods during hot-water extraction and the formation of pyrolysis products. However, grass lignins are generally referred to as guaiacyl-syringyl-type lignins, even though they consist of these somewhat unusual aromatic residues in significant amounts as well as a noticeable number of *trans-p*-coumaryl alcohol units [5,57]. Additionally, the morphological properties of non-wood fiber plants differ greatly from those of woods with the compact matrixes, thus affecting both the pulping and papermaking processes and paper properties [58,59].

Chemical compositions of the reference untreated and differently-treated okra and miscanthus stalk are presented in Table 1. The relative portions of carbohydrates and lignin in the initial raw materials (O_{ref} and M_{ref}) were slightly different. For clarity, only detailed content data on glucose (i.e., the monosaccharide moiety of cellulose) and xylose (i.e., the main monosaccharide moiety of xylan) were included. However, in all these non-wood cases, the number of other substances in varying amounts was also relatively high. It is evident that depending on the sample, this fraction contained, for example, acetyl groups of xylan, pectins, proteins, and inorganics, the substance groups that were not determined in detail here. Normally, the contents of inorganics, extractives, and proteins can be higher in non-wood materials than in wood materials [5]. In this study, analytic methods related to wood chemistry were applied. However, it is known that, especially due to the presence of proteins, the Klason method may suffer some inaccuracy when applied to herbaceous plants [60,61].

The results (Table 1) indicate that in the case of hot-water extraction, about 10% of carbohydrates and 25% of the initial lignin (okra stalk) were removed; the corresponding, distinctly contrary values for miscanthus stalk were about 15% and 10%. The difference in mass loss between okra stalk and miscanthus stalk (14.4% for okra stalk and 4.8% for miscanthus stalk) clearly suggest that probably because of the more porous structure of okra stalk, this material is more sensitive to hot-water extraction than miscanthus stalk. Its behavior during this pre-treatment phase also seems to be closer to hardwood [44] than softwood [45]. In this study, however, the essential aim was to perform the first pre-treatment stage under "relatively mild conditions" and only to improve the reactivity of these feedstocks in the second cooking phase. It is obvious that the soluble fractions of carbohydrates (mono-, oligo-, and polysaccharides) and lignin can be utilized for many purposes [5]. Due to the hot-water extraction, the mass ratio of carbohydrates to lignin in the feedstock matrix changed from 2.8 to 3.4 (okra stalk) and 4.0 to 3.9 (miscanthus stalk).

The chemical composition data on pulps are shown in Table 1. It is known that, compared to wood feedstocks, non-wood feedstocks may behave in a slightly different way during alkaline pulping [58,59], although in this case, the main degradation reactions of carbohydrates also include basic peeling and stopping reactions together with alkaline hydrolysis [5,62]. In practice, this means that, characteristically, the non-wood-derived cellulose is less stable against alkali than the wood-derived cellulose, and more hemicellulose residues can be found in non-wood black liquors. The principal aim of the cooking phase was to remove a significant amount of lignin within certain cooking times by using two alkali charge levels: 20% NaOH (okra) and 15% (miscanthus) on o.d. feedstock and by keeping the other cooking conditions constant. The cooking conditions selected were preliminary based on the delignification experiments carried out separately with these feedstocks.

In the case of okra stalk pulping ($O_{ref} \rightarrow PO_{ref}$ and $O_{HWE} \rightarrow PO_{HWE}$), the degree of delignification was about 93%, whereas in miscanthus stalk pulping ($M_{ref} \rightarrow PM_{ref}$ and $M_{HWE} \rightarrow PM_{HWE}$), it was about 96%. In the former okra case, the total removal of carbohydrates was 40–45% of the charged total carbohydrates (about 35% for cellulose and about 50% for hemicelluloses). In the latter miscanthus case, the total removal of carbohydrates was about 40% of the charged total carbohydrates ($M_{ref} \rightarrow PM_{ref}$, for cellulose about 30% and xylan about 65%) and about 25% ($M_{HWE} \rightarrow PM_{HWE}$, for cellulose about 15% and xylan about 35%). The ratio of carbohydrates to lignin was 22.9 (PO_{ref}), 30.5 (PO_{HWE}), 51.7 (PM_{ref}), and 74.4 (PM_{HWE}), whereas the ratio of xylan to lignin was 4.4 (PO_{ref}), 5.8 (PO_{HWE}), 9.4 (PM_{ref}), and 14.2 (PM_{HWE}). The chemical compositions of the sulfur-free black liquors formed were not investigated here in detail, and the recovery and utilization of alkali-catalyzed degradation products of carbohydrates (aliphatic carboxylic acids [62] and hemicellulose residues), and various lignin fragments from these black liquors will be clarified separately in future studies.

3.2. *Pyrolysis experiments*

The integrated chromatographic method GC/MS applied was capable of resolving most of the main hydrophilic and lipophilic compounds formed from feedstock samples during pyrolysis, and about 60 compounds were identified. Pyrolysis tests under the same conditions resulted in reproducible results, and a typical pyrogram profile for each sample could be detected; examples of different pyrograms (at 700 °C for 20 s) are given in Figs. 1 and 2. Based on this general finding, it could be expected that the total amounts of the relative proportions of varying compounds or compound groups were characteristically dependent on the sample preparation and pyrolysis conditions. This finding was also valid, although the total amount of pyrolysis products that are typically recovered from laboratory-scale pyrolyzers is known to be low [63,64]. Furthermore, it is a fact that the characteristic feature for all the pyrolysis products of lignocellulosics is a prominent amount of gases and highly volatile products, such as carbon monoxide, carbon dioxide, methanol, acetaldehyde, acetic acid, glycolaldehyde, acetol, and certain $< C_5$-hydrocarbons and/or their derivatives [63,65,66]. In this study, however, only the higher-molar-mass condensable products that were formed from the individual feedstock constituents were considered.

The postulated mechanisms for the degradation products in the wood-derived components have been shown in many investigations [62–69]. For clarity, in this study, the dominant GC-amenable pyrolysis products were classified into specific compound groups (Table 2), and

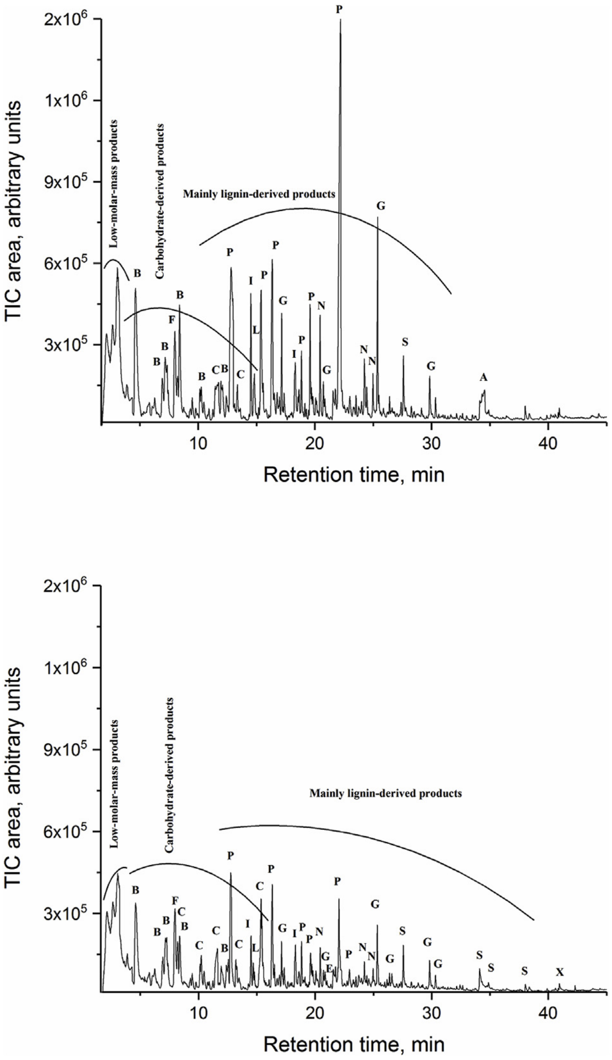

Fig. 1. The main products formed in the pyrolysis experiments (700 °C and 20 s) with the initial okra (O_{ref}, upper) and miscanthus (M_{ref}, lower) samples. Letters indicate compound groups to which identified products belong: A (anhydrosugar derivatives), B (benzene derivatives), C (cyclopentenone derivatives), E (catechol derivatives), F (furan derivatives), G (guaiacol derivatives), I (indene derivatives), L (lactone derivatives), N (naphthalene derivatives), P (phenol derivatives), S (syringol derivatives), and X (fatty acid derivatives).

the formation of these monomer-related fragments was determined in different cases. Based on these classification data, it could be roughly concluded that the groups of anhydrosugar (A), cyclopentenone (C), furan (F), indene (I), lactone (L), and pyrone (Y) derivatives originated from carbohydrates and those of guaiacol (G), phenol (P), and syringol (S) derivatives originated from lignin. The characteristic groups of naphthalene (N) and fatty acid (X) derivatives were obtained from extractives, whereas the group of other aromatics, benzene (B) derivatives, was probably formed from all wood constituents. It was obvious that this wide spectrum of pyrolysis products was somewhat similar to that especially obtained from fast pyrolysis of the analogous hardwood samples [44]. Additionally, results agreed well with the data on the thermochemical conversion of miscanthus by pyrolysis [38,40].

3.3. Practical considerations

Similar to the spruce results [45], the highest pyrolysis yields of reference and HWE samples were obtained from O_{ref} and M_{ref} as well as from O_{HWE} and M_{HWE} with a pyrolysis time of 20 s at 500 °C followed by a pyrolysis time of 5 s at 500 °C (Fig. 3). In the case of birch sawdust [44], the highest yields were detected at 500 °C/5 s or 700 °C/5 s. Typically, the yields were found to decrease when the pyrolysis temperature increased from 500 °C to 700 °C with both residence times 5 s and 20 s. As a general trend, the pyrolysis yields were at 500 °C/5 s and 500 °C/20 s, slightly higher for reference samples (i.e., $O_{ref} > O_{HWE}$ and $M_{ref} > M_{HWE}$). However, it was difficult to explain these findings straightforwardly based only on the chemical composition of the samples (Table 1).

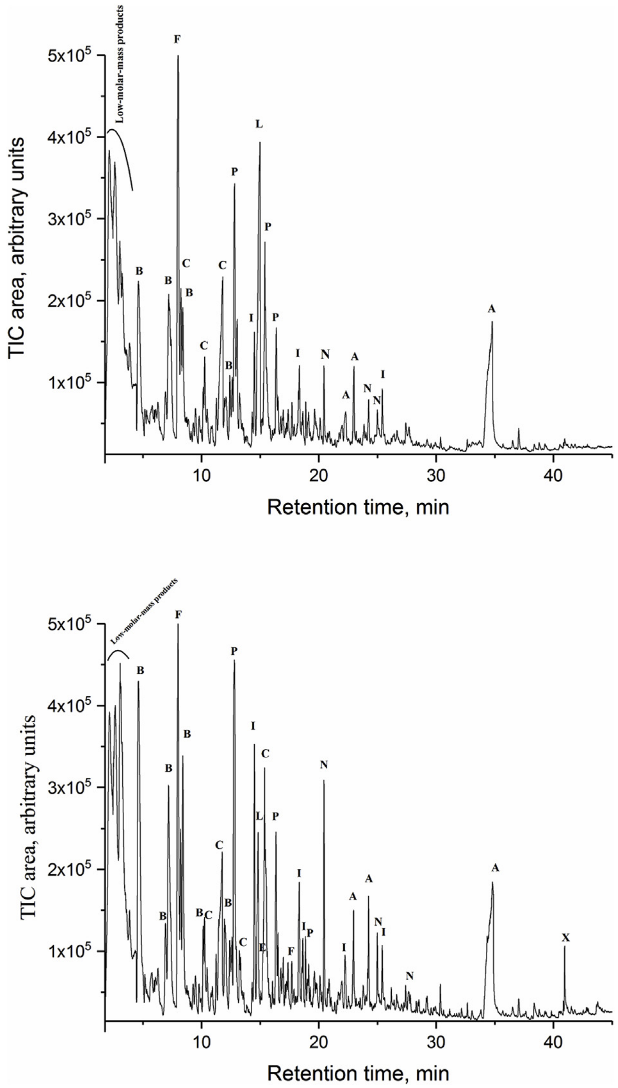

Fig. 2. The main products formed in the pyrolysis experiments (700 °C and 20 s) with the delignified hot-water-extracted okra (PO_{HWE}, upper) and miscanthus (PM_{HWE}, lower) samples. For the letter symbols, see Fig. 1.

In the case of okra pulps, the highest pyrolysis yield was obtained at 500 °C/5 s and 500 °C/20 s from PO_{HWE}, whereas for miscanthus pulps, the yield order was $PM_{ref} > PM_{HWE}$ (Fig. 4). Furthermore, it was found that the overall treatment yield of okra-derived samples was 85.6%, 40.2%, and 32.4% of the initial O_{ref} dry matter for O_{HWE}, PO_{ref}, and PO_{HWE}, respectively. This trend was also reflected in the pyrolysis yields that decreased at 500 °C/5 s in order $O_{ref} > O_{HWE} \approx PO_{HWE} > PO_{ref}$. On the other hand, the overall treatment yield of miscanthus-derived samples was 95.2%, 57.5%, and 57.4% of the initial M_{ref} dry matter for M_{HWE}, PM_{ref}, and PM_{HWE}, respectively; the pyrolysis yields decreased at 500 °C/20 s in order $M_{ref} > M_{HWE} > PM_{ref} \approx PM_{HWE}$.

The main feedstock chemical constituents degrade on heating at

Table 2
The main products formed in the pyrolysis experiments with differently-treated okra and miscanthus stalks.

Product	Retention time (min)	Symbol
Anhydrosugars		A
1,4:3,6-Dianhydro-α-D-glucopyranose	24.0	
1,6-Anhydro-β-D-glucopyranose (levoglucosan)[a]	34.5	
Benzene derivatives		B
Toluene[a]	4.6	
o-Xylene[a]	7.3	
Cyclopentenone derivatives		C
Cyclopent-2-en-1-one[a]	8.3	
2-Methylcyclopent-2-en-1-one[a]	10.3	
2-Cyclopenten-1,4-dione	11.2	
2-Hydroxycyclopent-2-en-1-one	11.8	
3-Methylcyclopentane-1,2-dione[a]	15.4	
Furan derivatives		F
Furfural (furan-2-carbaldehyde)[a]	8.0	
5-(Hydroxymethyl)furfural[a]	24.7	
Guaiacol derivatives		G
2-Methoxyphenol (guaiacol)[a]	17.2	
2-Methoxy-4-methylphenol[a]	20.7	
4-Ethenyl-2-methoxyphenol	25.4	
2-Methoxy-4-(prop-2-en-1-yl)phenol (eugenol)[a]	26.4	
2-Methoxy-4-(prop-1-en-1-yl)phenol (isoeugenol)[a]	28.3	
Indene derivatives		I
1*H*-Indene[a]	14.6	
1-Methyl-1*H*-indene	18.4	
Lactone derivatives		L
5*H*-Furan-2-one	12.7	
3-Hydroxy-2-penteno-1,5-lactone	15.0	
4-Hydroxy-2,5-dimethylfuran-3-one[a]	17.8	
Naphthalene derivatives		N
Naphthalene[a]	20.5	
1-Methylnaphthalene	24.3	
Phenol derivatives		P
Phenol[a]	12.9	
2-Methylphenol[a]	15.5	
4-Methylphenol[a]	16.4	
2,4-Dimethylphenol	18.9	
4-Ethenylphenol	22.1	
4-(Prop-2-en-1-yl)phenol	24.5	
Syringol derivatives		S
2,6-Dimethoxyphenol (syringol)[a]	27.6	
4-Ethenyl-2,6-dimethoxyphenol	34.1	
4-Allyl-2,6-dimethoxyphenol (4-allylsyringol)[a]	34.9	
Fatty acid derivatives		X
Hexadecanoic acid	40.9	
Pyrone derivatives		Y
3-Hydroxy-2-methylpyran-4-one[a]	19.3	

[a] Confirmed by pure standards.

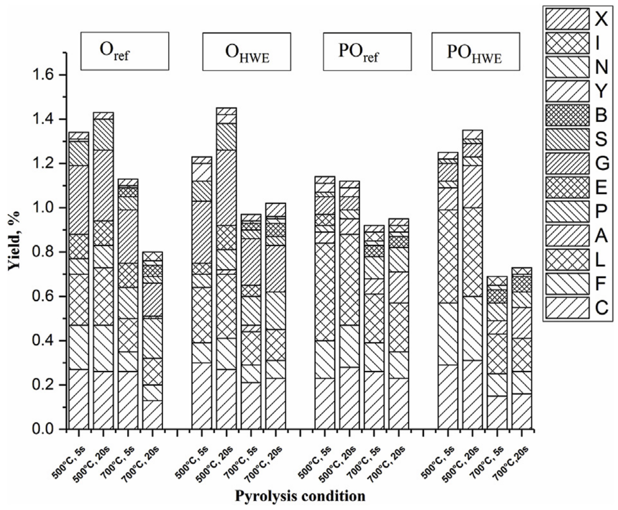

Fig. 3. Effect of temperature and residence time on yields of various product groups obtained from the pyrolysis of untreated and differently-treated okra stalk. For the letter symbols, see Fig. 1.

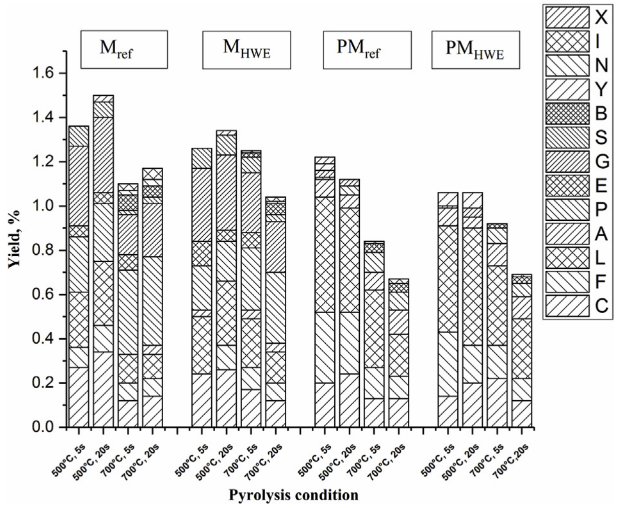

Fig. 4. Effect of temperature and residence time on yields of various product groups obtained from the pyrolysis of pulps from untreated and differently-treated miscanthus stalk. For the letter symbols, see Fig. 1.

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

Condition	O_{ref}	O_{HWE}	PO_{ref}	PO_{HME}	M_{ref}	M_{HWE}	PM_{ref}	PM_{HWE}
500 °C/5 s	55/45	61/39	84/16	90/10	45/55	42/58	97/3	99/1
500 °C/20 s	53/47	54/46	91/9	90/10	52/48	51/49	94/6	96/4
700 °C/5 s	48/52	53/47	91/9	73/27	33/67	43/57	85/15	90/10
700 °C/20 s	45/55	51/49	81/19	73/27	36/64	38/62	82/18	76/24

different rates [52]. In this study, during pyrolysis, a variety of low-molar-mass pyrolysis products were formed from the high-molar-mass initial polymers, carbohydrates, and lignin, and could be partly found in pyrolysates. Additionally, part of the devolatilized products might be selectively condensed before reaching the GC column. The results, for example, clearly indicate that in the case of reference and HWE samples, the formation of lignin-derived products (guaiacol, syringol, and phenol derivatives) together with hemicellulose-derived products (lactone, furan, and cyclopentenone derivatives) was especially enhanced at 500 °C, whereas in the case of pulp samples, as expected from the sample compositions (Table 1), hemicellulose-derived products were prevailing (Figs. 3 and 4). Typically, at 700 °C, a slightly more diverse spectrum of product groups was detected. Table 3 shows the ratio of aliphatic pyrolysis products to aromatic pyrolysis products detected in our experiments under varying pyrolysis conditions. As a characteristic trend, more aromatic products were formed under harsher conditions. Thus, the significant portion of aromatic products, 47–67%, was obtained from reference and HWE samples at 700 °C/5 s and 700 °C/20 s, whereas the maximum portion of aliphatic products, 90–99%, was found in pulp samples at 500 °C/5 s and 500 °C/20 s.

As shown above, it could be roughly considered that the compound groups A, C, F, L, and Y were mainly originated from carbohydrates, F and L typically from xylan, and G, P, and S from lignin (Table 2). Based on this simple assumption, the ratio of carbohydrates to lignin at 500 °C/20 s for okra-derived samples was 1.1 (O_{ref}), 1.1 (O_{HWE}), 9.9 (PO_{ref}), and 10.4 (PO_{HWE}); i.e., O_{ref}/O_{HWE} 1.00, O_{HWE}/PO_{ref} 0.11, and PO_{ref}/PO_{HWE} 0.95 (estimated values from Table 1 are 0.8, 0.1, and 0.8, respectively). On the other hand, the ratio of xylan to lignin was 0.7 (O_{ref}), 0.7 (O_{HWE}), 6.0 (PO_{ref}), and 5.8 (PO_{HWE}); i.e., O_{ref}/O_{HWE} 1.00, O_{HWE}/PO_{ref} 0.12, and PO_{ref}/PO_{HWE} 1.03 (estimated values from Table 1 are 0.8, 0.2, and 0.8, respectively). In the case of miscanthus-derived samples at 500 °C/20 s, the ratio of carbohydrates to lignin was 1.0 (M_{ref}), 1.2 (M_{HWE}), 15.0 (PM_{ref}), and 25.5 (PM_{HWE}); i.e., M_{ref}/M_{HWE} 0.83, M_{HWE}/PM_{ref} 0.08, and PM_{ref}/PM_{HWE} 0.59 (estimated values from Table 1 are 1.0, 0.1, and 0.7, respectively). Additionally, the ratio of xylan to lignin indicated the values 0.6 (M_{ref}), 0.8 (M_{HWE}), 10.7 (PM_{ref}), and 17.5 (PM_{HWE}); i.e., M_{ref}/M_{HWE} 0.75, M_{HWE}/PM_{ref} 0.07, and PM_{ref}/PM_{HWE} 0.61 (estimated values from Table 1 are 1.3, 0.1, and 0.6, respectively).

Since a number of significant pyrolysis products could be measured simultaneously, a single pyrolysis run gave fingerprint data for rapid characterization of feedstock materials. Of the main products, furfural (I, the compound group F from hemicelluloses), 2-hydroxycyclopent-2-en-1-one (II, C from hemicelluloses), 5*H*-furan-2-one (III, L from hemicelluloses), 3-hydroxy-2-penteno-1,4-lactone (IV, L from hemicelluloses), 3-methylcyclopentane-1,2-dione (V, C from hemicelluloses), 2-methoxyphenol (VI, G from lignin), 4-ethenylphenol (VII, P from lignin), 4-ethenyl-2-methoxyphenol (VIII, G from lignin), 2,6-dimethoxyphenol (IX, S from lignin), and 2-methoxy-4-(prop-1-en-1-yl) phenol (X, G from lignin) are commonly found in pyrolysates (Table 2 and Figs. 5 and 6).

It was concluded that a relevant correlation exists between the formation of a number of the pyrolysis products and the chemical composition of feedstock. In the case of okra stalk, for example, at 500 °C/20 s, the GC peak area ratio (I + II + III + IV + V)/(VI + VIII + X) (i.e., carbohydrates/lignin) for O_{ref} and O_{HWE} was 3.2 (O_{ref}) and 3.1 (O_{HWE}) (estimated values from Table 1 are 2.8 and 3.4, respectively), whereas at 500 °C/5 s, the ratio (I + II + III + IV + V)/(VI + IX + X) resulted in the values 3.1 and 3.9, respectively. Additionally, at 500 °C/20 s, the GC peak area ratio (I + II + III)/(VI + VII + VIII + IX + X) (i.e., xylan/lignin) for O_{ref} and O_{HWE} was 0.7 and 0.9 (estimated values from Table 1 are 0.6 and 0.8, respectively). Similarly, in the case of miscanthus, for example, at 500 °C/20 s, the GC peak area ratio (I + II + III + IV + V)/(VI + IX + X) (i.e., carbohydrates/lignin) for M_{ref} and M_{HWE} was 3.9 (M_{ref}) and 3.4 (M_{HWE}) (estimated values from Table 1 are 4.0 and 3.9, respectively). On the other hand, at 500 °C/20 s, the GC peak area ratio (I + II)/(VI + IX + X) (i.e., xylan/lignin) for M_{ref} and M_{HWE} was 1.3 (M_{ref}) and 1.1 (M_{HWE}) (estimated values from Table 1 are 1.2 and 0.9, respectively).

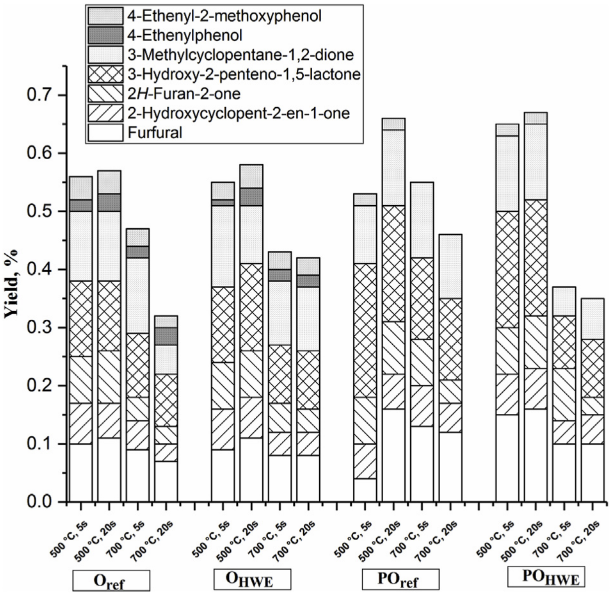

Fig. 5. Effect of temperature and residence time on yields of prominent pyrolysis products obtained from the pyrolysis of untreated and differently-treated okra stalk.

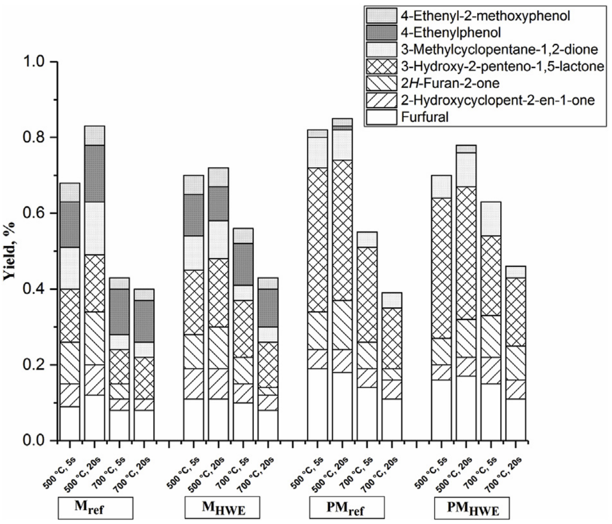

Fig. 6. Effect of temperature and residence time on yields of prominent pyrolysis products obtained from the pyrolysis of pulps from untreated and differently-treated miscanthus stalk.

It is evident that hot-water extraction as well as delignification also caused some chemical changes in the residual fractions of carbohydrates and lignin in the treated feedstock matrix, thus, to some extent, partly reflecting the formation of individual pyrolysis products. However, in spite of this, based on these preliminary results, it seems that the analytical fast pyrolysis method applied offers a potential tool for feedstock characterization. Furthermore, it is evident that to obtain a useful correlation (e.g., the determination of relevant factors) between the pyrolysis and chemical composition data, a wide range of repeatable experiments within the same feedstock type is still needed.

4. Conclusions

Currently, one potential eco-friendly biorefinery concept is based on the hot-water extraction of fibrous non-wood feedstocks prior to sulfur-free alkaline pulping. In our present study, according to this integrated biorefinery approach, various samples of okra and miscanthus stalks (initial and hot-water-extracted, as well as those from their soda-anthraquinone delignification) were pyrolyzed (at 500 °C and 700 °C for 5 s and 20 s) by pyrolysis-gas chromatography/mass spectrometry to (a) create novel data on condensable low-molar-mass pyrolysis products obtained from these feedstocks, and (b) clarify possibilities for developing a rapid characterization method for these lignocellulosics. The most significant findings were as follows:

- In contrast to hardwood (silver birch) and softwood (Norway spruce) feedstocks, hot-water extraction of non-wood feedstocks, okra and miscanthus stalks, removes, besides carbohydrate-derived material, an enhanced amount of lignin-derived material even at a low degree of material dissolution. Additionally, all the samples studied in this connection can be readily delignified. The soluble hot-water-extracted fractions, as well as those dissolved during delignification, offer many attractive utilization possibilities for a wide spectrum of value-added products.
- The compositions of untreated and differently-treated feedstocks, as well as pyrolysis conditions, have characteristic effects on the formation of condensable pyrolysis products. The devolatilized fractions, containing a great number of individual compounds, are similar to those obtained from birch wood. In the case of untreated

and hot-water-extracted samples, at 500 °C, the ratio of aliphatic pyrolysis products to aromatic pyrolysis products is 42–61%/39–58%, whereas at 700 °C, the corresponding ratio is 33–53%/47–67%. In the case of pulp samples, the corresponding ratio is 84–99%/1–16% at 500 °C and 73–91%/9–27% at 700 °C. The main compound groups are aliphatic compounds, such as lactone, furan, and cyclopentenone derivatives from carbohydrates (mainly hemicelluloses), and aromatic compounds, such as guaiacol, phenol, and syringol derivatives from lignin.
- A simultaneous gas-chromatographic determination of the main compound groups and the selected fingerprint pyrolysis products offers fast and useful information about the chemical composition of different samples. This finding provides a sound basis for further development of a feasible characterization method, especially for the non-wood samples studied.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.biombioe.2018.09.001.

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Table S1

Peak identification and calibration information of pyrolysis products differently-treated okra and miscanthus stalks

No.	Compound name	Major ion(s) (*m/z*)	RT (min)	Quantification[a]	r^2 Value	Slope
1	Toluene	51, 65, 91	4.6	Standard	0.99	298.5
2	1,2-Dimethylbenzene	91, 106	7.3	Standard	0.99	230.0
3	Furfural (furan-2-carbaldehyde)	39, 95, 96	8.0	Standard	0.99	42.9
4	Cyclopent-2-en-1-one	39, 82	8.3	Standard	0.98	118.4
5	Ethenylbenzene	78, 104	8.4	Standard	0.96	191.7
6	Benzene-1-ethyl-3-methyl	77, 91, 105, 120	10.1	Toluene		
7	2-Methylcyclopent-2-en-1-one	53, 67, 96	10.3	Standard	0.99	65.2
8	2-Hydroxycyclopent-2-en-1-one	55, 69, 98	11.8	2-Methylcyclopent-2-en-1-one		
9	Benzene-1-ethenyl-4-methyl	77, 91, 103, 118	12.1	Ethenylbenzene		
10	5*H*-Furan-2-one	39, 55, 84	12.7	Standard	0.99	24.8
11	5-Methylfurfural	53, 109, 110	12.8	Standard	0.98	62.2
12	Phenol	66, 94	12.9	Standard	0.98	55.1
13	3-Methylcyclopent-2-en-1-one	53, 67, 96	13.3	2-Methylcyclopent-2-en-1-one		
14	1*H*-Indene	63, 89, 116	14.5	Standard	0.99	211.2
15	3-Hydroxy-2-penteno-1,5-lactone	58, 85, 114	15.0	4-Hydroxy-5-methylfuran-3-one	0.97	35.2
16	3-Methylcyclopentane-1,2-dione	69, 83, 112	15.4	Standard	0.98	43.6
17	2-Methylphenol	39, 51, 79, 107	15.5	Standard	0.99	85.0
18	4-Methylphenol	39, 51, 79, 108	16.4	Standard	0.99	82.0
19	2-Methylbenzofuran	51, 77, 103, 131	16.8	1-Benzofuran	0.97	160.7
20	2-Methoxyphenol (guaiacol)	53, 81, 109, 124	17.2	Standard	0.99	79.2
21	2,6-Dimethylphenol	77, 107, 122	17.4	Standard	0.98	128.6
22	4-Methyl-5*H*-furan-2-one	69, 98	17.9	5*H*-Furan-2-one		
23	4-Hydroxy-2,5-dimethylfuran-3-one	43, 57, 85, 128	18.1	Standard	0.99	41.6
24	Methyl furan-2-carboxylate	39, 95, 126	18.1	Furfural (furan-2-carbaldehyde)		
25	1-Methyl-1*H*-indene	115, 130	18.4	1*H*-Indene		
26	3-Ethyl-2-hydroxycyclopent-2-en-1-one	55, 69, 83, 126	18.5	2-Methylcyclopent-2-en-1-one		
27	2,4-Dimethylphenol	65, 77, 107, 122	18.9	2,6-Dimethylphenol		

28	3-Hydroxy-2-methylpyran-4-one	43, 55, 71, 126	19.0	Standard	0.98	74.5
29	3-Ethylphenol	77, 107, 122	19.6	3,5-Dimethylphenol		
30	2,3-Dihydroxybenzaldehyde	51, 64, 92, 120, 138	20.5	Standard	0.99	119.0
31	Naphthalene	51, 102, 128	20.5	Standard	0.99	178.8
32	2-Methoxy-4-methylphenol	67, 123, 138	20.7	Standard	0.99	275.0
33	4-Ethenylphenol	65, 91, 120	22.1	3,5-Dimethylphenol		
34	6-Methyldihydro-2*H*-pyran-3(4*H*)-on	56, 84, 114	22.4	3-Hydroxy-2-methylpyran-4-one		
35	2-Methoxy-4-ethylphenol	137, 152	23.5	2-Methoxy-4-methylphenol		
36	1,2-Dihydroxy-3-methylbenzene	51, 78, 106, 124	23.7	Standard	0.97	155.0
37	1,4:3,6-Dianhydro-α-D-glucopyranose	69, 86, 98, 144	24.0	Levoglucosan		
38	1-Methylnaphthalene	71, 115, 142	24.3	Naphthalene		
39	1,2-Dihydroxy-3-methoxybenzene	97, 125, 140	24.4	Standard	0.97	159.0
40	2,3-Anhydro-D-mannose	69, 71, 85, 97, 144	24.5	Levoglucosan		
41	4-(Prop-2-en-1-yl)-phenol	77, 91, 107, 115, 134		4-Methylphenol		
42	5-(Hydroxymethyl)furfural	39, 97, 109, 126	24.7	Standard	0.97	73.0
43	4-Ethenyl-2-methoxyphenol	51, 77, 107, 135, 150	25.4	Standard	0.97	251.5
44	2-Methoxy-4-(prop-2-en-1-yl)phenol (eugenol)	77, 131, 149, 164	26.6	Standard	0.97	331.0
45	2,6-Dimethoxyphenol (syringol)	96, 139, 154	27.6	Standard	0.99	76.3
46	2-Methoxy-4-(prop-1-en-1-yl)phenol (isoeugenol)	91, 103, 131, 149, 164	29.8	Standard	0.97	151.0
47	3-Hydroxy-4-methoxybenzoic acid	125, 153, 168	30.3	4-Hydroxy-3-methoxybenzoic acid (vanillic acid)	0.98	154.7
48	2-Methoxy-4-propylphenol	77, 122, 137, 166	31.6	2-Methoxy-4-(prop-2-en-1-yl)phenol (eugenol)		
49	4-Ethenyl-2,6-dimethoxyphenol	137, 165, 180	34.1	4-Allyl-2,6-dimethoxyphenol		
50	1,6-Anhydro-β-D-glucopyranose (levoglucosan)	60, 73, 126, 145	34.5	Standard	0.99	67.0
51	4-Allyl-2,6-dimethoxyphenol (4-allylsyringol)	150, 179, 194	34.9	Standard	0.98	274.4

52	Hexadecanoic acid	129, 213, 256	40.9	Linoleic acid	0.99	148.8

In all cases, the intercept was 0.0

[a] all quantification is done by pure compounds shown.

IV

PYROLYTIC BEHAVIOR OF LIGNOCELLULOSIC-BASED POLYSACCHARIDES

by

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Pyrolytic behavior of lignocellulosic-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 5*H*-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.

Keywords Cellulose · Glucomannan · Xylan · Pyrolysis–gas chromatography · Condensable products · Thermogravimetry

Introduction

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

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

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Thermal analysis can be defined as a set of techniques used to describe the physical or chemical changes associated with substances as a function of temperature [7]. The thermal behavior of lignocellulosic materials and their components can be studied in many alternative ways. Py-GC/MS reveals the composition of products and indicates the mechanisms of degradation reactions; it also provides information about the original structure of the samples being studied. In general, many studies indicated that during pyrolysis under an inert atmosphere, biomass converts into low-degree-polymerized products [8–17]. However, there have still been less attention on pyrolysis of glucomannan and xylan as well as their quantification analyses. The dissimilarities in pyrolysis behavior of the main components in lignocellulosic biomass are due to differences in their molecular structures and chemical natures. Therefore, the study of pyrolysis behavior of the main biomass substituents is essential to understand the overall pyrolysis behavior of biomass. In contrast, thermal gravimetric (TG) analysis (i.e., mass change vs. temperature) and differential scanning calorimetry (DSC) (i.e., heat flux vs. temperature) primarily give information concerning the mass loss of a sample over the whole process, the rate of mass loss, and the endothermic and exothermic temperature ranges upon heating. These methods are widely applied techniques, especially for the study of thermal stability of polymers. In practice, it is useful to record the first derivative of the TG curve (i.e., differential thermogravimetry (DTG)) for more clearly detecting small features/boulders as peaks on the curve. Particularly, successful approaches have also been the simultaneous combination of TG methods and spectroscopic techniques. In general, the mass loss of a sample of the TG curve under a certain heating rate and the peak height of the DTG curve are directly related to the temperature during the process and the reaction rate at the corresponding temperature, respectively. Therefore, investigation of samples by TG and DTG is also important due to fluctuations in available data [18–21].

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

Hemicelluloses (25–35% of the wood dry solids) are linear low-molar-mass heteropolysaccharides with specific side-groups, and their thermal and chemical stability is generally lower than that of cellulose, presumably due to their lack of crystallinity and lower DP (100–200) [33, 34]. Softwoods and hardwoods (and non-woods) differ not only in the content of total hemicelluloses but also in the percentages of individual hemicellulose constituents; in hardwoods and non-woods, primarily xylan (containing xylose units), and in softwoods, mainly glucomannan (containing mannose and glucose units). In hardwoods, the content of xylan and glucomannan is 20–30% and $< 5\%$ of the wood dry solids, respectively, whereas in softwoods, the corresponding contents are 5–10% and 15–20% of the dry wood solids [33]. The thermal degradation reactions of heteropolymeric hemicelluloses are principally similar to those of homopolymeric cellulose, although hemicelluloses reacted more readily than cellulose during heating [13, 18, 34–36]. The differences observed in the degradation rates of various polysaccharides can be explained as being primarily due to the different glycosidic bonds between sugar moieties as well as different DP and crystallinity of cellulose. Of the hemicelluloses, xylan is the least thermally stable because it is more susceptible than glucomannan to degradation of glycosidic bonds and dehydration reactions [37]. In general, the char formation from hemicellulose pyrolysis is slightly higher than that from cellulose [13, 14, 19, 38].

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

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

In our earlier studies, we investigated the thermochemical behavior of differently treated wood and non-wood materials [4–6]. In this comparable study with model substances, firstly, the aim was to further clarify the formation of compound groups under the same pyrolysis conditions as those applied in our previous experiments. Secondly, to verify the formation of main pyrolysis products with respect to their main carbohydrate constituents as well as the effect of the interaction of main carbohydrate constituents in hardwood, softwood, and non-wood on the pyrolysis products. Since carbohydrates are the main components of various biorefinery fractions, we selected for our Py-GC and TG experiments cellulose and hemicelluloses (glucomannan and xylan) and the quantification analyses of GC-detectable pyrolysis products of these samples were reported. The thermochemical behavior of lignin as well as lignin-containing black liquors from alkaline delignification of wood and non-wood fibrous feedstocks will be separately investigated under the analogous conditions in the forthcoming studies.

Experimental

Thermogravimetric analyses

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

Pyrolysis experiments

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

The GC conditions were the same as those applied earlier to the similar purpose [4]. The column was a ZB-35HT (Inferno) capillary GC column (30 m × 0.25 mm with a film thickness of 0.25 μm). The GC oven temperature program in the analyses of pyrolysis products was as follows: 2 min at 40 °C, 4 °C min^{-1} to 190 °C, 10 °C min^{-1} to 320 °C, and 10 min at 320 °C. Helium was used as the carrier gas with a gas flow rate of 1 mL min^{-1} and as an inert atmosphere in the pyrolysis interface. Detection was carried out with an HP 5970 mass spectrometric detector under electron ionization (70 eV) with 2.92 scan per seconds in the 30–550 *m/z* interval.

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

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

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

Component	C	H	N	O[a]
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)

[a] Calculated by difference

Results and discussion

Thermogravimetric considerations

The temperature at which decomposition reactions of wood occur and the changes in specimen mass associated with the reactions can be found by thermogravimetric analysis, which exactly recorded the mass loss of the solid sample versus temperature/time. Traditionally, the chemical kinetic models for the biomass and its components are proposed from the analysis of the different mass loss stages and validated through the correlation between the predicted data and the experimental mass loss curve. According to TG the mass loss of cellulose and hemicelluloses typically starts at about 100 °C (i.e., due to the loss of adsorbed water). At temperatures between 100 and 250 °C, the rate of mass loss is quite slow, but above 250 °C, it increases [19]. For example, cellulose undergoes an extensive endothermic–exothermic sequence immediately above 300 °C [20, 47], and it has been reported that for xylan, displaying clear exothermic behavior [48], the most intensive thermal degradation takes place in the temperature range 200–260 °C [19, 49].

Figure 1 shows TG and DTG curves of cellulose, glucomannan, and xylan. The average active pyrolysis ranges of 290–410 °C and 230–340 °C were observed for cellulose and hemicelluloses, respectively. The higher thermal stability of cellulose (glucan-based polysaccharide), compared to amorphous hemicelluloses with several types of glycosidic bonds and side-groups, was mainly attributed to its unbranched and ordered (i.e., highly crystalline) structure [1, 19, 21, 41, 50]. Among the hemicelluloses, xylan had lower thermal stability than glucomannan. The pyrolysis char yield determined was 9, 27, and 25% of the initial mass for cellulose, glucomannan, and xylan, respectively. This finding agreed well with the earlier data [19, 51] and suggested more multiple reactions of heterogeneous hemicelluloses and their monosaccharide moieties. According to [51], the differences in the char yield between cellulose and hemicelluloses are clearly due to the somewhat different pyrolysis reaction mechanisms. The DTG peak heights (wt % s^{-1}) were as follows: cellulose 0.48 at 382 °C, glucomannan 0.25 at 316 °C, and xylan 0.57 at 304 °C.

The calculated, based on the Flynn–Wall–Ozawa method [52] activation energy (E_a), value as a function of fractional conversion (α) for cellulose, glucomannan, and xylan is presented in Fig. 2. It could be noted that the variation in E_a was slightly lower for cellulose (142–162 kJ mol^{-1}) than for glucomannan and xylan. In the literature, depending on the sample origin, a variety of E_a values for cellulose have been given; for example, an average value of 109.4 kJ mol^{-1} [50]. The E_a value for glucomannan varied between 111 and 301 kJ mol^{-1}, and it gradually increased in the progress of pyrolysis. However, at the end of pyrolysis ($\alpha > 0.7$), a rapid rise (i.e., from 160 to 300 kJ mol^{-1}) was observed. This phenomenon has also been reported earlier by [53]. They also reported the E_a values between 181 and 206 kJ mol^{-1} for glucomannan in the α range 0.1–0.75. In the case of xylan, the E_a value (168–200 kJ mol^{-1}) increased until $\alpha = 0.6$, and, after this point, it started to decrease. In the previous study [54], the E_a values for xylan were between 150 and 250 kJ mol^{-1} in the temperature range 185–215 °C.

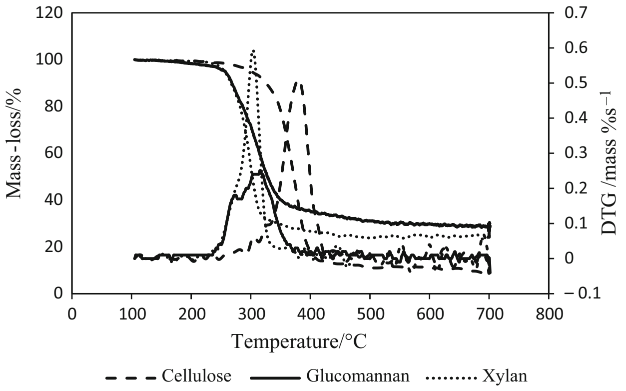

Fig. 1 TG and DTG curves of cellulose, glucomannan, and xylan at 20 °C min^{-1}

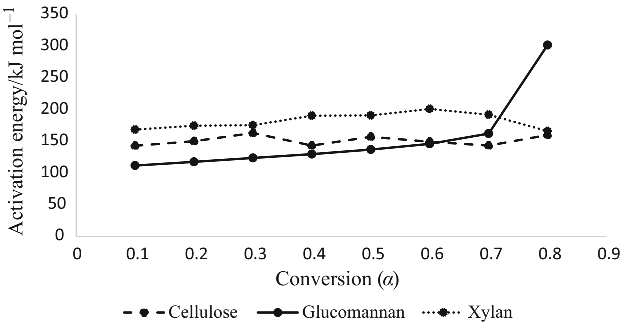

Fig. 2 Activation energy (E_a) as a function of fractional conversion (α) for cellulose, glucomannan, and xylan

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

Pyrolysis: gas chromatographic analyses

The integrated chromatographic system GC/MS applied resolved most of the low-molar-mass compounds released from the model substances during pyrolysis; altogether, 42 from cellulose, 47 from glucomannan, and 41 from xylan were identified in conformity with pure compounds and MS library. For simplicity, the dominant GC-amenable pyrolysis products were classified into illustrative compound groups by the same system as that used earlier for similar purposes [4, 5]. It could be roughly concluded that the groups of anhydrosugar (A), cyclopentenone (C), furan (F), indene (I), lactone (L), and pyrone (Y) derivatives originated from carbohydrates, and those of guaiacol (G) and phenol (P) derivatives originated from lignin. The characteristic groups of naphthalene (N) derivatives were obtained from extractives, whereas the groups of other aromatics, benzene (B) and linear ketones (LK) derivatives, were probably formed from all the model substances; examples of a typical pyrogram profile at 700 °C and 20 s, for each sample, are presented in Fig. 3, and the main compounds identified are listed in Table 2. Practically, pyrolysis experiments under the same conditions also led to reproducible results with reasonable accuracy. During the pyrolysis, a wide range of components have been detected and the mechanisms of the formation of several major products in this study are considered similar to those reported by Wang et al. [13]. It was assumed that principally, the formation of each compound group occurs via characteristic mechanisms and pathways. In the case of cellulose pyrolysis [15], ring-opening of glucopyranose units takes place to form open-chain structures, followed by dehydration and cyclization to generate 5-(hydroxymethyl)furfural (5-HMF), which further converts through the elimination of the hydroxymethyl group to produce furfural, and LG is produced by the cleavage of the β-(1→

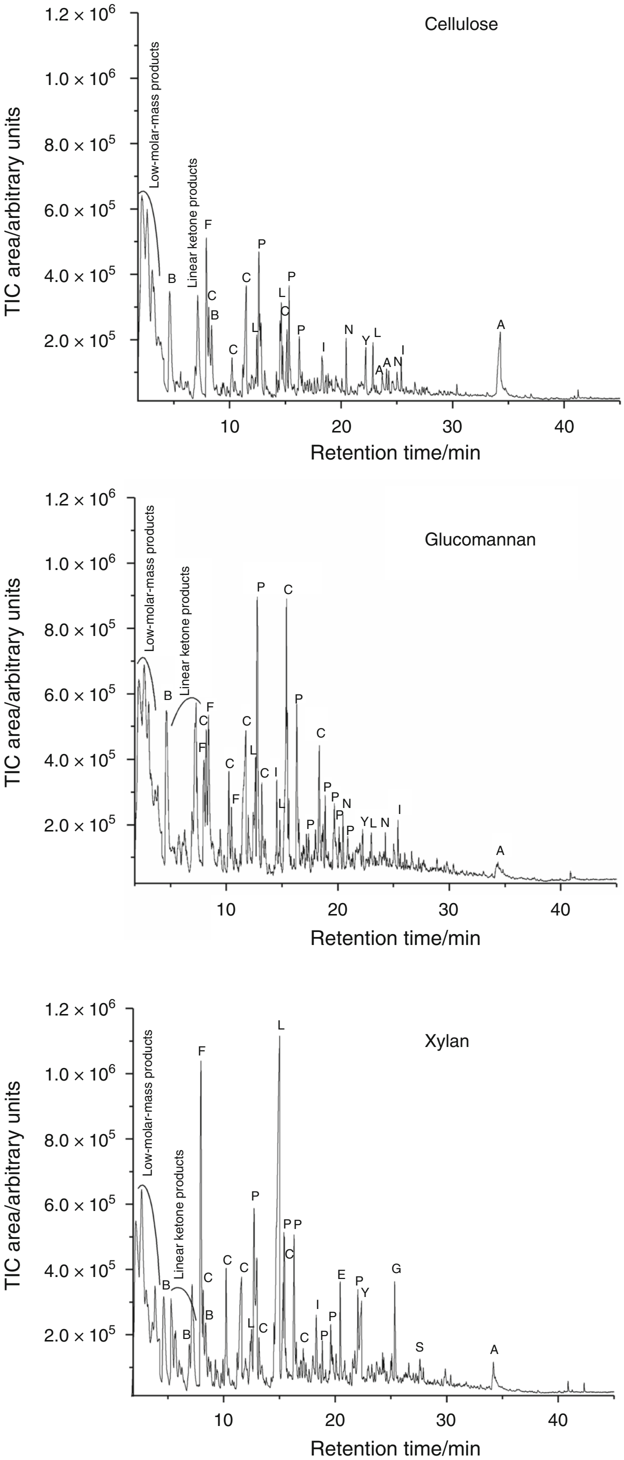

Fig. 3 The main products formed in the pyrolysis experiments (700 °C and 20 s) with cellulose, glucomannan, and xylan. Letters indicate compound groups to which identified products belong: A (anhydrosugar derivatives), B (benzene derivatives), C (cyclopentenone derivatives), E (catechol derivatives),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

Table 2 The main products formed in the pyrolysis experiments with model substances

Product	RT[a]/min	Cellulose	Glucomannan	Xylan	Group symbol
Anhydrosugars					A
1,4:3,6-Dianhydro-α-D-glucopyranose	24.0	+	−	−	
2,3-Anhydro-D-mannosae	24.2	+	−	−	
1,6-Anhydro-β-D-glucopyranose (levoglucosan)[b]	34.5	+	+	+	
Benzene derivatives					B
Toluene[b]	4.6	+	+	+	
Cyclopentenone derivatives					C
Cyclopent-2-en-1-one[b]	8.3	+	+	+	
2-Methylcyclopent-2-en-1-one[b]	10.3	−	+	+	
2-Cyclopentene-1,4-dione	11.2	+	−	+	
2-Hydroxycyclopent-2-en-1-one	11.8	+	+	+	
3-Methylcyclopentane-1,2-dione[b]	15.4	+	+	+	
Catechol derivatives					E
2,3-Dihydroxybenzaldehyde	20.5	+	+	+	
Furan derivatives					F
Furfural (furan-2-carbaldehyde)[b]	8.0	+	+	+	
5-Methylfurfural[b]	12.8	+	+	−	
2,5-Furandicarboxaldehyde[b]	19.1	+	-	-	
5-(Hydroxymethyl)furfural[b]	24.7	+	-	-	
Guaiacol derivatives					G
2-Methoxyphenol (guaiacol)[b]	17.2	−	−	+	
2-Methoxy-4-methylphenol[b]	20.7	−	−	+	
Lactone derivatives					L
5*H*-Furan-2-one	12.7	+	+	+	
3-Hydroxy-2-penteno-1,5-lactone	15.0	+	−	+	
4-Hydroxy-2,5-dimethylfuran-3-one[b]	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[b]	12.9	+	+	+	
2-Methylphenol[b]	15.5	+	+	+	
4-Methylphenol[b]	16.4	+	+	+	
2,4-Dimethylphenol	18.9	+	+	+	
4-Ethenylphenol	22.1	−	−	+	
Syringol derivatives					S
2,6-Dimethoxyphenol (syringol)[b]	27.6	−	−	+	
Pyrone derivatives					Y
Pyran-2-one	14.5	+	−	−	
3-Hydroxy-2-methylpyran-4-one[b]	19.3	+	−	−	
Dihydro-6-methyl-2*H*-pyran-3(4*H*)-one	22.4	+	+	+	

+ Indicates the presence of this compound

[a] RT refers to retention time

[b] Confirmed by pure standards

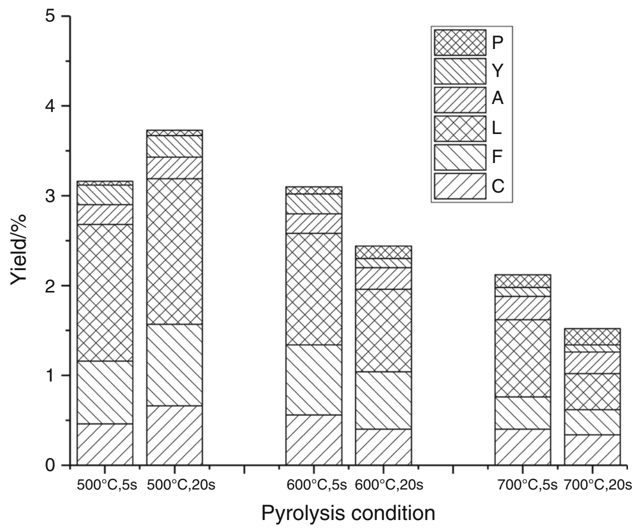

Fig. 4 Effects of pyrolysis temperature and residence time on yields of main product groups from cellulose. For the letter symbols, see Fig. 3

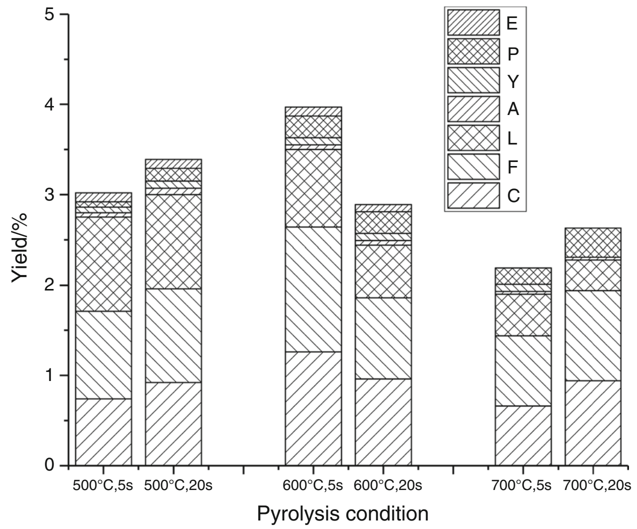

Fig. 5 Effects of pyrolysis temperature and residence time on yields of main product groups from glucomannan. For the letter symbols, see Fig. 3

4)-glycosidic linkage in the cellulose macromolecules, followed by an intramolecular rearrangement. In the case of xylan pyrolysis Shen et al. [36] and Patwardhan et al. [51] have reported that the depolymerization and ring scission of xylan form ring-opened intermediates, which further produce linear ketone products, such as hydroxyacetone (via carbon chain fracture), furfural and lactones (by cyclization), and alicyclic ketones, such as cyclopentenones through the combination of C=C bonds. The degradation of glycosidic linkages between monomer units of glucomannan results in anhydrosugars and more stable furan rings (such as 5-HMF, 5-MF, and furfural) [14, 53].

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

Figure 7 shows the formation examples of the selected main pyrolysis products from model substances and their formation decreased at the longer holding time (20 s) and the higher reaction temperature (700 °C). It could be noted that, for example, 3-hydroxy-2-penteno-1,5-lactone (lactone) was primarily formed from xylan (also partly from cellulose), 5*H*-furan-2-one (lactone) from glucomannan (also partly from cellulose), 3-methylcyclopentane-1,2-dione (cyclopentenone) from glucomannan, furfural (furan) from cellulose and xylan, and 5-HMF (furan) from cellulose. Based on the our previous studies [4–6], of these major pyrolysis products, especially 3-hydroxy-2-penteno-1,5-lactone was produced by a factor of three from hardwood [4] than from softwood [5] indicating the presence of a higher portion of xylan in hardwood. However, its yield from hardwood was still less than that from xylan, probably due to an effect of its integration with cellulose and lignin. In the case of 5*H*-furan-2-one, its formation was less in spruce than pure glucomannan due to their interaction. On the other hand, it decreased in delignified glucomannan-poor softwood samples even by a factor of six, and it could be claimed that this compound originated from glucomannan more readily than from cellulose. A decreasing trend of LG formation in untreated and treated softwood samples manifested that it was formed from both glucomannan and cellulose, but more from cellulose. Also 3-methylcyclopentane-1,2-dione and furfural, are

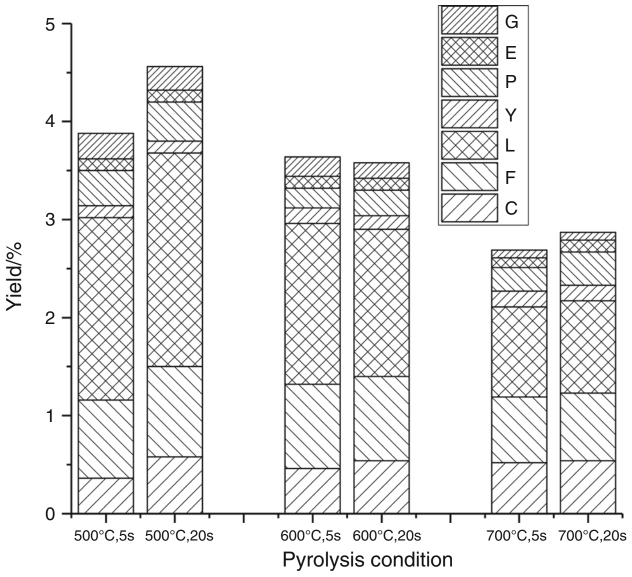

Fig. 6 Effects of pyrolysis temperature and residence time on yields of main product groups from xylan. For the letter symbols, see Fig. 3

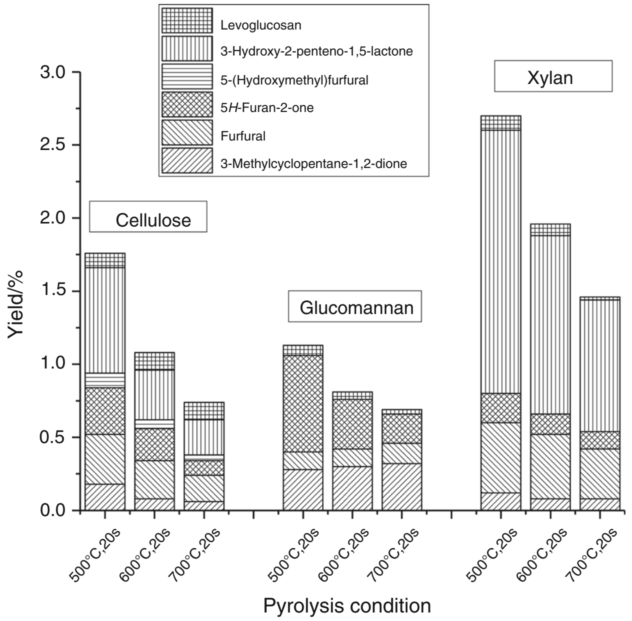

Fig. 7 Effects of temperature and time on yields of some prominent pyrolysis products

prominent products from birch wood and spruce wood as well as non-wood [6].

Formation of pyrolysis products

It was expected that the total amounts and the relative proportions of varying compounds and compound groups were characteristically dependent on pyrolysis conditions, although the total yield of pyrolysis products that are normally recovered and identified from laboratory-scale pyrolyzers is generally known to be low [61, 62]. A great number of studies have been performed to clarify the reaction networks between the basic structural unit of cellulose, D-glucose, or β-(1→4)-glycosidic bond-containing low-molar-mass model compounds (e.g., to clarify the role of the dehydration and retroaldol condensation reactions of anhydrosugars and the cleavage of glycosidic bonds) [11, 32, 46]. Typically, the products of cellulose pyrolysis in the classic lumped kinetic models are roughly divided into gases, tar, and char, rather than utilizing the detailed compound distribution. Earlier kinetic studies have been carried out under a variety of pyrolysis conditions, leading to somewhat conflicting data with a wide range of kinetic parameters [37]. Hence, it can be concluded that the kinetics and elementary-reaction chemistry of carbohydrate pyrolysis are still debated [29].

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

Tables 3 and 4 indicate that no distinct compound group was selectively formed at certain temperatures and the major product groups 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. In practice, this finding means that if a mixture of cellulose, glucomannan, and xylan with equal proportions would be pyrolyzed at 500 °C, about half of the condensable liquids will consist of lactone derivatives. In the case of cellulose, the proportion of lactone derivatives decreased, and that of anhydrosugar derivatives increased steadily as the temperature increased. For glucomannan and xylan, the proportion of lactone derivatives also decreased and the proportion of cyclopentenone derivatives was slightly depressed toward the maximum temperature. However, for all model substances, no significant changes in the proportion of furan derivatives could be detected. The corresponding major product groups were also prominent ones identified in our earlier pyrolysis experiments, especially at 500 °C, with wood and non-wood feedstocks [4–6] existing together with the lignin-derived significant product groups, guaiacol, and syringyl derivatives. Particularly in the wood

Table 3 Relative proportions (%) of major product groups obtained from cellulose, glucomannan, and xylan under varying pyrolysis conditions

Product group[a]	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)

The values given in parentheses refer to yields (% of the initial feedstock dry matter)

Data from Figs. 4–6, calculated average values for heating times of 5 and 20 s

[a] L refers to lactone derivatives, F to furan derivatives, and C to cyclopentenone derivatives

Table 4 Relative proportions (%) of minor product groups obtained from cellulose, glucomannan, and xylan under varying pyrolysis conditions

Product group[a]	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	–

Data from Figs. 4–6, calculated average values for heating times of 5 and 20 s

[a] P refers to phenolic derivatives, Y to pyrone derivatives, and A to anhydrosugar derivatives

pyrolysis cases, estimated in view of the present results, approximate calculations suggested that the proportions of these compound groups were almost equal to the expected ones.

Conclusions

Pyrolysis-based technologies can be described as direct thermochemical conversion methods of lignocellulosic 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, and char. In many biorefinery concepts, pyrolysis has been applied to prepare fuels and platform chemicals. The pyrolytic degradation of biomass is dominated by the behavior of its structural components, carbohydrates (cellulose and hemicelluloses, such as glucomannan and xylan) and lignin.

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

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

Pyrolysis products	RT[a] /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*H*-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*H*-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*H*-furan-2-one	14.4	0.06	0.1	0.1	0.1	0.22	-
1*H*-Indene	14.5	-	-	-	-	-	0.02
2*H*-Pyran-2,6(3*H*)-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*H*-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*H*-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*H*-pyran-3(4*H*)-one	22.4	0.12	0.14	0.12	0.1	0.1	0.08
(1*R*,5*S*)-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-*α*-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*H*-indene-1-one	25.4	-	-	-	0.02	-	-
Levoglucosan	34.5	0.1	0.1	0.1	0.12	0.14	0.12

[a] RT refers to retention time (min).

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

Pyrolysis products	RT[a] /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*H*-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*H*-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*H*-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*H*-furan-2-one	14.4	0.12	-	0.1	0.1	0.1	-
1*H*-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*H*-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*H*-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*H*-pyran-3(4*H*)-one	22.2	0.06	0.08	0.08	0.08	0.08	-
(1*R*,5*S*)-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	-	-	-
Levoglucosan	34.5	0.05	0.07	0.05	0.05	0.03	0.03

[a] RT refers to retention time (min).

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

Pyrolysis products	RT[a] /min	500 ^{o}C, 5 s	500 ^{o}C, 20 s	600 ^{o}C, 5 s	600 ^{o}C, 20 s	700 ^{o}C, 5 s	700 ^{o}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-3*H*-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
5*H*-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-5*H*-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-2*H*-pyran-3(4*H*)-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	-	-	-	-

[a] RT refers to retention time (min).

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

Compound	RT[a] /min	Major ion(s) (*m/z*)	Quantification[b]	r^2 Value[c]	Slope
Linear ketones, acids, esters derivatives (<C5)					
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		
Benzene derivatives					
Toluene	4.6	51, 65, 91	Standard	0.99	298.5
1,2-Dimethylbenzene	7.3	91, 106	Standard	0.99	230.0
Ethenylbenzene	8.4	78, 104	Standard	0.96	191.7
Furan derivatives					
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
Lactone derivatives					
5-Methyl-3*H*-furan-2-one	9.1	55, 70, 98	Standard	0.99	56.0
5*H*-Furan-2-one	12.7	39, 55, 84	Standard	0.99	24.8
3-Methyl-5*H*-furan-2-one	14.5	69, 98	5-Methyl-3*H*-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*H*-furan-2-one	17.9	69, 98	5-Methyl-3*H*-furan-2-one		
(1*R*,5*S*)-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		
Cyclopentenone derivatives					
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		
Phenol derivatives					
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		
Pyran derivatives					
Pyran-2-one	14.3	39, 68, 96	3-Hydroxy-2-methylpyran-4-one		
2*H*-Pyran-2,6(3*H*)-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*H*-pyran-3(4*H*)-one	22.4	56, 84, 114	3-Hydroxy-2-methylpyran-4-one		
Indene derivatives					
1*H*-Indene	14.5	63, 89, 116	Standard	0.99	211.2
1-Methyl-1*H*-indene	18.4	115, 130	1*H*-Indene		
2,3-Dihydro-1*H*-indene-1-one	25.6	78, 104, 132	1*H*-Indene		
Guaiacol derivatives					
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
Anhydrosugar derivatives					
(1*S*,5*R*)-6,8-Dioxabicyclo[3.2.1]oct-2-en-4-one (levoglucosenone)	19.8	39, 68, 98	Levoglucosan		
1,4:3,6-Dianhydro-α-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-β-D-glucopyranose (levoglucosan)	34.5	60, 73, 126, 145	Standard	0.99	67.0
Naphthalene derivatives					
Naphthalene	20.5	51, 102, 128	Standard	0.99	178.8
1-Methylnaphthalene	24.3	71, 115, 142	Naphthalene		
Catechol derivatives					
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
Syringyl derivatives					
2,6-Dimethoxyphenol (syringol)	27.6	96, 139, 154	Standard	0.99	76.3

In all cases, the intercept was 0.0.

[a] RT refers to retention time (min).

[b] Quantification is done by pure compounds.

[c] r^2 refers to coefficient values.

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