FAST PYROLYSIS OF SULFUR-FREE LIGNIN FROM ALKALINE PULPING WITH A HOT-WATER PRETREATMENT STAGE

JONI LEHTO,[*] MARKO HUTTUNEN,[**] MARYAM GHALIBAF[***] and RAIMO ALÉN[**]

[*]*VTT Technical Research Centre of Finland, Ltd., P.O. Box 1000, 02044 VTT, Finland*
[**]*Laboratory of Applied Chemistry, Department of Chemistry, University of Jyväskylä, P.O. Box 35, 40014 University of Jyväskylä, Finland*
[***]*Natural Resources Institute Finland (Luke), Tietotie 4, 31600 Jokioinen, Finland*
✉ *Corresponding author: Joni Lehto, joni.lehto@vtt.fi*

Received May 4, 2022

The pyrolytical conversion of birch (*Betula pendula/pubescens*) lignin fractions separated from hot-water pretreatment/sulfur-free delignification black liquors was investigated by pyrolysis-gas chromatography-mass spectrometry (Py-GC/MS). Based on pyrolytical data, the main condensable compounds were organized into respective component groups, and the relative mass portions of the pyrolysis products (mainly monomer-related fragmented products) formed during pyrolysis of various feedstocks were determined. It could be concluded that relatively pure aromatic fractions, mainly of guaiacol and syringol origin, without carbohydrate impurities, could be produced by this integrated biorefinery approach, in which all biomass fractions can be utilized for manufacturing biobased chemicals and chemical precursors. It could be determined that the formation of the individual pyrolytical components was characteristically dependent on the utilized production conditions (*i.e.*, alkali charge, temperature, pretreatment), creating the possibility for adjustment of the process parameters for pronounced production of desired product fractions. Hence, it could be concluded that this sulfur-free concept facilitated the environmentally friendly production of aromatics, without the need for removing sulfur or carbohydrates-derived impurities from the liquid feedstocks. The practical importance of the approach presented in this manuscript lies in the development of rapid and reliable characterization tools for various lignocellulosics-originated feedstocks possessing potential for thermochemical conversion and for creating novel biorefinery concept alternatives for producing aromatics and chemical precursors from currently underutilized feedstock, lignin.

Keywords: fast pyrolysis, hot-water extraction, lignin, lignocellulosic biorefineries, pretreatment, soda-anthraquinone cooking

INTRODUCTION

The utilization of lignocellulosic biomass in the manufacture of energy, chemicals and biomaterials has been in the spotlight during the past few decades.[1-3] Analogous to oil-based petroleum refineries exploiting non-renewable fossil resources, lignocellulosic biorefineries utilize biomass-derived feedstocks in their manufacturing processes. Modern biorefineries are designed for fractionating and converting CO_2-neutral raw materials in an environmentally friendly way into useful products, simultaneously maximizing the value of biomass, and minimizing the formation of waste.[4-6] Within this approach, modification of conventional pulp mills into integrated multi-product biorefineries utilizing a variety of lignocellulosic feedstocks has been considered as one of the most promising alternatives for producing new biomass-derived chemicals and biofuels, besides the main products, pulp, board and paper.

All lignocellulosic feedstocks are mainly composed of the so-called structural substances, which are cellulose, lignin and hemicelluloses.[7-9] During the conventional kraft-pulping process (*i.e.*, sulfate cooking performed with aqueous solution of NaOH and Na_2S), the major part of hemicelluloses and lignin are solubilized by using an alkaline cooking solution (*i.e.*, white liquor). For producing energy for the pulping process and for recycling the used cooking chemicals, these dissolved wood components and their degradation products are eventually combusted in a recovery

boiler.[10,11] However, especially the recovery and conversion of hemicelluloses (instead of utilizing them as a low-value fuel in a recovery boiler) into useful bioproducts has gained special interest when developing modern IFBRs.[12,13] The recovery of hemicelluloses can be performed by several methods (*i.e.*, chemical, enzymatical, thermochemical, or physical), but one of the most promising alternatives has been considered to be a pretreatment (acidic or alkaline) stage integrated to chemical pulping.[14-17] By pretreatment, hemicelluloses-derived carbohydrates and their degradation products can be recovered from wood into aqueous hydrolysates, which can then be further refined into purified product fractions.

Besides the effects on the chemical and physical characteristics of the pretreated raw materials, previous studies[18-20] have shown that pretreatments also have an effect on the subsequent pulping outcomes (*i.e.*, pulp quality and chemical composition of the black liquors) of the overall process. Pretreatments can facilitate the subsequent pulping stage by enhancing the delignification *via* alterations in physical wood structure (*e.g.*, increased porosity, leading into improved impregnation of cooking liquors) and chemical composition (*e.g.* by removing acetyl groups prior to pulping and by affecting the composition of lignin). After cellulose, lignin is the second most abundant structural component of lignocellulosics and the most abundant aromatic polymer substance in the world. Hence, it also plays an extremely important role in modern biorefineries aiming at full utilization of all biomass constituents.[21,22] As lignin is the major organic by-product formed not only in pulping, but also in growing second-generation biofuel industries, it creates a huge potential raw material source for the chemical industry.[23-25] For these reasons, lignin has a high potential for replacing fossil non-renewable petrochemical resources in the manufacture of fuels, polymers, and low-molar-mass (low-MM) phenolic applications.

After sulfate cooking, conventional kraft lignin contains approximately 2-3% sulfur,[26] making its utilization in the manufacture of useful bioproducts (*e.g.* low-MM phenolic compounds) a challenging task. Sulfur is generally considered undesirable in liquid feedstocks aimed for pyrolytical manufacture of chemicals and fuels, because it can increase the acidity of the manufacturing process and it is a notorious catalyst poison during catalytical upgrading of lignocellulosic feedstocks. From an environmental point of view, sulfur causes air pollution problems and hinders cleaning of the exhaust gases during various combustion processes. For these reasons, and depending on the amount and chemical form of sulfur in the manufacturing process, various removal methods are needed to minimize the detrimental effects of sulfur. As inorganic gas (*e.g.* H_2S and SO_2), sulfur can be removed through already commercialized absorption methods (either chemical or physical absorption). If sulfur is present in the solid char fraction, special measures and instrumentation for handling exhaust gas emissions are needed after combustion of sulfur-containing char. If pyrolytic liquid contains organic sulfur compounds (*e.g.*, thioether or thiophene), their removal processes may require high investments in equipment for processing this kind of challenging fractions. For the above-mentioned reasons, it can be concluded that sulfur is generally an undesirable component in various biorefinery processes, mainly from environmental (*i.e.*, air pollution problems during combustion) and process design (*i.e.*, adverse effects on the catalysts used during catalytic upgrading and during the cleaning of exhaust gases) points of view. Hence, especially considering the further refining of lignin-containing liquid feedstocks, such as pulping effluents and black liquors, and their utilization for the manufacture of valorized biochemicals and fuels, integrated process schemes combining pretreatment processes with sulfur-free pulping operations enabling the production of sulfur-free lignin fractions not needing capital-intensive sulfur-removal operations would be highly desirable.

Thermochemical conversion of different biomass fractions (including lignin) have been shown to be promising process alternatives for production of novel biochemicals and fuels. Within this approach, analytical fast pyrolysis has traditionally been utilized for evaluating the possibilities for production of liquid biofuels, biochemicals, and biopolymer precursors from different lignocellulosic materials.[27-34] In this study, sulfur-free lignin fractions separated from alkaline NaOH-anthraquinone (*i.e.*, soda-AQ) pulping liquors of untreated reference (Ref) and hot-water-extracted (HWE) silver/white birch (*Betula pendula/pubescens*) sawdust were characterized by analytical pyrolysis (pyrolysis-gas chromatography equipped with mass-selective detector, Py-GC/MSD). The main scientific purpose was to detect differences in the

thermochemical behavior of these lignin fractions having varying chemical composition and origin for evaluating their suitability for pyrolysis and production of various (mainly low-MM) novel sulfur-free pyrolysis degradation products.

EXPERIMENTAL

Chemical analysis of the feedstock materials

A Retsch SM 100 cutting laboratory mill (Retsch GmbH, Haan, Germany), equipped with a bottom sieve with trapezoidal holes (perforation size < 1.0 mm), was used for grinding the untreated (*i.e.*, no pretreatment) air-dried and pretreated sawdust samples prior to chemical analyses. TAPPI T264 cm-97 standard was used to determine the moisture content of the ground samples. TAPPI T280 pm-99 standard was utilized for analyzing the total content of extractives. This method included a 4-h Soxhlet extraction conducted with acetone with 6–10 percolations per h. The obtained acetone-extract was concentrated almost to dryness with a rotary evaporator (Heidolph VV2000, Gemini BV Laboratory, Apeldoorn, Netherlands), and drying of the extracts was finalized by a gentle nitrogen stream, by which the extracts were dried to complete dryness. The amount of the extractives were determined gravimetrically after the drying process.

Extractives-free wood samples were hydrolysed by using two-stage sulfuric acid hydrolysis conducted according to TAPPI T249 cm-00 standard. After sulfuric acid hydrolysis, an HP 5890 Series II Plus gas chromatography (GC) apparatus (Hewlett Packard Company, Wilmington, NC, USA), equipped with a flame-ionization detector (FID) and an analytical DP-1701 capillary column (60 m × 0.32 mm with a film thickness of 0.25 μm; Agilent Technologies, Palo Alto, CA, USA), was used for the analysis of the resulting monosaccharides. Prior to the GC analyses, hydrolysed monosaccharides were derivatized (*i.e.*, per(trimethylsilyl)ated) by silylating them with a mixture containing 99% *N*,*O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA, Regis Technologies, Morton Grove, IL, USA) and 1% trimethylchlorosilane (TMCS, Regis Technologies) in pyridine. The mixture was shaken for 60 min and filtered prior to the analysis. Xylitol (Fluka Chemical Corporation, Seeltze, Germany) was used as an internal standard (IS) in GC analysis. Additionally, for each individual monosaccharide, IS was calibrated (*i.e.*, mass-based response factors were determined) based on separate standard runs with the corresponding model monosaccharides: arabinose, xylose, galactose, glucose and mannose (from Fluka Chemicals, Seeltze, Germany).

The lignin content of the extractives-free samples was calculated as the sum of the Klason lignin (insoluble lignin fraction) and the acid-soluble lignin, according to TAPPI T222 om-98, T249 cm-00, and T250 UM standards. The content of acid-soluble lignin in Klason hydrolysates was determined spectrophotometrically by using a Beckman DU 640 UV/Vis device (Beckman Instruments Inc., Fullerton, CA, USA) at 205 nm after 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 follows:

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

where a is the absorptivity (110 L/(gcm))[35] and b is the length of the light path (cm).

Pretreatments

Hot-water extraction of silver/white birch (*Betula pendula/pubescens*) wood meal was conducted by using a pilot-scale pressurized hot-water flow-through extraction reactor (from Viitos-Metalli Ltd., Heinola, Finland) at Finnish Forest Research Institute (Metla). The extraction system included a pump (KSB, 18.5 kW), water heating (by Loval Oy), and heat exchange systems (by Alfa-Laval, 150 kW), a reservoir for hot water, an extraction vessel, and tanks for the hot-water extract. The applied extraction time was ~38 min, temperature 170 °C, and pressure 2 MPa, corresponding to a P-factor of ~380. After the pretreatment, the extracted sawdust was air-dried and stored for subsequent experiments. The gravimetric yield after the extraction was 71.9% of the oven-dry (od) raw material.

Soda-AQ cooking

The soda-AQ cooking experiments were performed in an oil-heated laboratory-scale batch digester (CRS CAS 420), equipped with 1.25-liter rotating stainless steel autoclaves. The soda-AQ pulping conditions for all materials are presented in Table 1.

After sufficient cooking time, the autoclaves were first rapidly cooled down with cold tap water and then placed in a cold-water bath. Black liquors (BLs) were recovered by using filtration bags (280 × 300-mm, from L.K. Suodatin, Siivikkala, Finland) manufactured from monofilament nylon. Separation of BLs was finalized by pressing and recovered BLs were stored in a refrigerator for further analyses. The detailed chemical compositions of the produced BLs have been previously described elsewhere.[6,19]

Separation of lignin

Lignin in the BLs was precipitated by carbonation. About 100 mL of BL was carbonated in an open beaker equipped with continuous stirring, by using CO_2 for lowering the pH of the liquor below a value of 9. The carbonated lignin slurry was centrifuged for 30 min at 3,500 rpm (with a Megafuge 1.0 from Heraeus Instruments GmbH, Hanau, Germany) for separating the precipitated lignin from the liquid phase. Precipitated lignin was washed twice with ultra-high quality (UHQ) water (internal resistance ≥18.2 MΩcm at 25 °C, Millipore, Bedford, USA) and centrifuged in

order to remove impurities (*e.g.*, aliphatic acids and extractives). Precipitated and washed lignin samples were air-dried at room temperature in a fume hood, ground manually into homogeneous powder, and stored in brown glass jars.

Analytical pyrolysis

Lignin pyrolysis products were analyzed by using a Py-GC/MSD system, consisting of a CDS Pyroprobe 1000 resistively heated platinum induction coil filament (T_{max} 1,400 °C) pyrolyzer, an HP 5890 II gas chromatograph (from Hewlett Packard Company, Wilmington, NC, USA), equipped with a Zebron ZB-35HT inferno column (30 m x 0.25 mm inner diameter (i.d.), film thickness 0.25 µm), and an HP 5972 Series mass selective detector (MSD). The lignin sample was placed in a quartz tube (3.0 cm × 1.0 mm i.d.) between two pieces of quartz wool and pyrolyzed under an inert atmosphere in the heated interface. Pyrolysis temperature was set to 700 °C and the heating-up time of 20 °C/ms, with 20 seconds residence time, was used during the pyrolysis experiments. The applied GC column temperature program was: 2 min at 60 °C, 3 °C/min to 150 °C, 8 °C/min to 320 °C, and 15 min at 320 °C. A constant helium flow of 1 mL/min was used as a carrier gas. The temperature of the GC inlet and MSD was adjusted to 280 °C and splitless injection ratio was used. The MS equipment was operated with electron ionization (EI) technique at 70 eV. All the mass spectra were analyzed with an Agilent MSD5973 data analysis software and for the identification of chromatogram peaks, the mass spectral library databases from Wiley and National Institute of Standards and Technology (NIST) were used.

The process used for lignin separation and pyrolysis is presented in Figure 1.

Table 1
Soda-AQ cooking conditions

Parameter	Birch (Ref. and HWE)
Effective alkali charge (% odw*)	18, 20, 22
AQ charge (% odw)	0.1
Liquor-to-feedstock ratio (L/kg)	5
Maximum cooking temperature (°C)	170
Cooking time (min)	90, 120, 150

*oven-dried wood

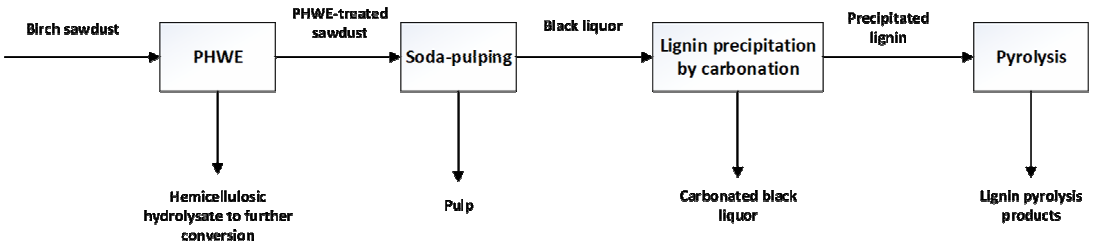

Figure 1: Process for production of sulfur-free lignin products (PHWE refers to pressurized hot-water extraction)

RESULTS AND DISCUSSION

Feedstocks

The chemical composition of the untreated (*i.e.*, no hot-water extraction) birch feedstock was as follows: carbohydrates 67.5% (arabinose 0.4%, galactose 1.0%, glucose 43.4%, mannose 1.4%, and xylose 21.3%), lignin 22.1% (acid-soluble 4.5% and Klason 17.6%), extractives 2.9%, and others 7.5%. After the hot-water extraction, the corresponding feedstock composition was: carbohydrates 72.7% (arabinose 0.1%, galactose 0.6%, glucose 60.8%, mannose 1.0%, and xylose 10.2%), lignin 20.7% (acid-soluble 2.5% and Klason 18.2%), extractives 2.8%, and others 3.8%.

Pretreatments

The yield (calculated as % of dry wood) of the extracted wood meal after hot-water pretreatment was 71.9%. The main effect of the hot-water extraction on the treated wood was the dissolution of mainly hemicelluloses-derived carbohydrates (*i.e.*, xylan) and minor degradation of lignin, cellulose, and extractives. In a previous study,[19] it could be concluded that roughly 23% of total wood carbohydrates and 33% of the initial wood lignin were dissolved during hot-water extraction. Corresponding losses of acid-insoluble and acid-soluble lignins were roughly 26% and 60%, respectively. Due to the pretreatments, the

carbohydrates-to-lignin mass ratio of the extracted wood increased from 3.1 to 3.5.

Pyrolysis experiments

The pyrolysis behavior of lignin is greatly influenced by variations in different pyrolysis variables, such as variations in temperature and residence time, feedstock composition, extraction processes, and the type of the pulping process.[36-38] If the pyrolysis residence time is too short, random breakage of chemical bonds and insufficient depolymerization can take place and lead to decreased formation of pyrolysis gas, and heterogeneous liquid products. On the other hand, secondary decomposition of the pyrolysis products formed in the early stages of the pyrolysis, leading to the decrease in the yield of pyrolysis oil and to the increase in the yield of gaseous products can result from too long residence times. Hence, choosing a sufficient pyrolysis residence time, efficient devolatilization and increasing yields of pyrolysis oil and gas can be ensured. Increasing the rate of heating can lower the needed residence time at low temperatures, result in the higher pyrolytic conversion of lignin, and lead to decreased formation of char. Additionally, the pyrolysis atmosphere and heating rate have an effect on lignin pyrolysis, as *e.g.*, oxidation reactions are generally favored under air atmosphere, whereas under inert gas atmosphere the release of volatiles is pronounced.

One important factor affecting the pyrolysis of lignocellulosics is the content of alkali metals. It has been shown that high hydrogen-to-carbon ratio and the high concentration of alkali metals in pyrolysis feedstocks can catalytically affect the pyrolysis process, generally by enhancing pyrolysis efficiency and improving tar quality.[39] The effect of especially volatile alkali metals has also been reported,[40] suggesting that their interaction with the formed char surface can have a catalytic effect on the pyrolysis process, and that alkali metals incorporated in the char can hinder the graphitization process during pyrolysis.[41] Additionally, migration of alkali metals in the pyrolysis process has been proposed, but the actual mechanism of the migration on the characteristics of biomass pyrolysis and its impact on formation of individual pyrolysis products at varying temperatures are still largely unclear.

Lignin pyrolysate fractions are generally classified into three main product groups (*i.e.*, large-molar oligomers/pyrolytic lignins, the monomeric phenolic compounds, such as phenols, hydroxylphenols, guaiacols, and syringols, and light compounds such as methanol and acetic acid).[42] During the lignin pyrolysis, devolatilization and formation of char are two main competing reactions, accompanied with a variety of secondary reactions. The formation of char takes place mainly *via* crosslinking reactions and is generally favored at low temperatures (*i.e.*, below 300 °C). With the increasing temperature, the devolatilization reactions increase the formation of pyrolysis oil and gaseous products *via* side chain cracking, and by cleaving the C–C and C–O bonds between phenylpropane units.[43] The breakage of ether C-O and C–C bonds between lignin's structural units first leads to increased guaiacol and syringol yields, but as the demethoxylation and demethylation reactions start to take over, the yields decrease with rising reaction temperatures, and eventually the formation of mainly phenols and catechols starts to take place.[44] At low reaction temperatures, a variety of other degradation products (*e.g.*, aldehydes and ketones) can be formed due to the breakage of glucosidic bonds linked to lignin.

The main products formed in the pyrolysis experiments (presented as yield percentages based on pyrogram peak area ratios) of alkaline reference (R) and pretreated (P) birch lignins separated from different BLs (*i.e.*, cooked with 18%, 20%, and 22% alkali charges) are presented in Tables 2, 3 and 4, respectively. The pyrograms of the lignin samples separated from the mildest (*i.e.*, 18% alkali charge and 90 min cooking) and harshest (*i.e.*, 22% alkali charge and 150 min cooking) cooks are presented in Figure 2. The total yield % and relative portions of each main compound group prepared under different conditions are presented in Figure 3.

The main identified monomer-related pyrolysis products were arranged into respective component groups (Tables 2-4), and their formation under varying conditions were determined. The dominating product class was composed of syringyl-type (S-type) compounds. However, the total content of S-type compounds in the separated lignin samples originating from the HWE feedstock was clearly lower, when compared to the samples prepared without pretreatment.

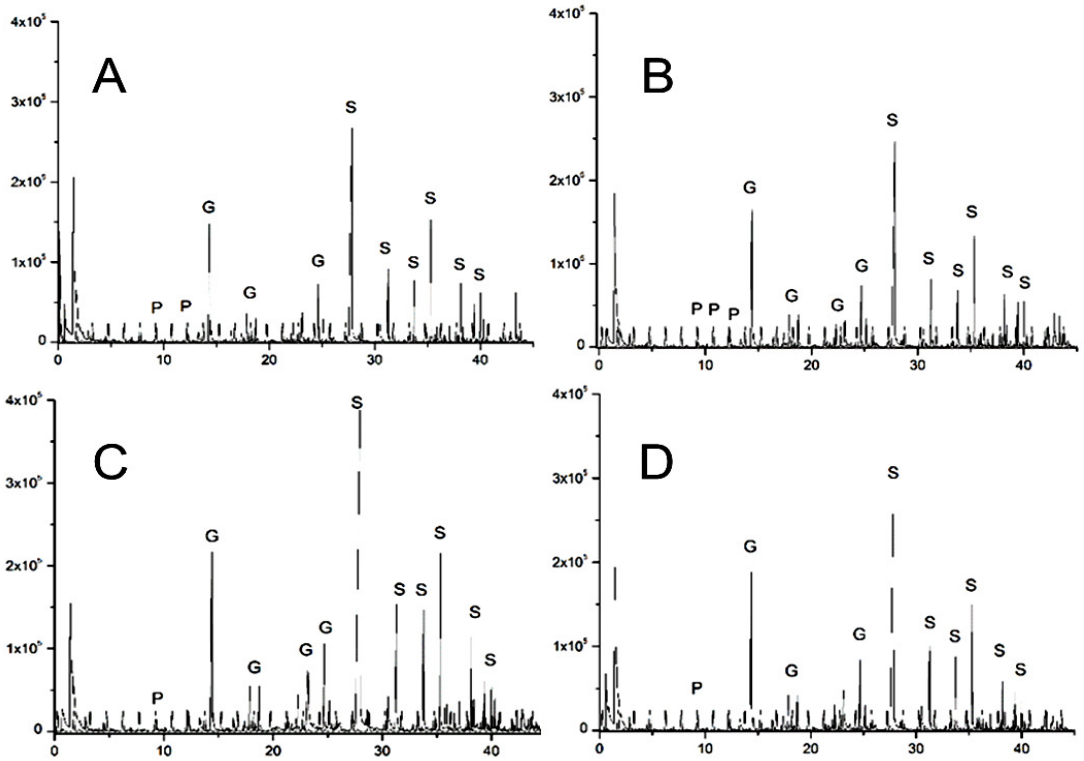

Figure 2: Pyrograms of lignin samples separated from 18/90/R (A), 18/90/P (B), 22/150/R (C), and 22/150/P (D) black liquors (P = phenols, G = guaiacols, S = syringols)

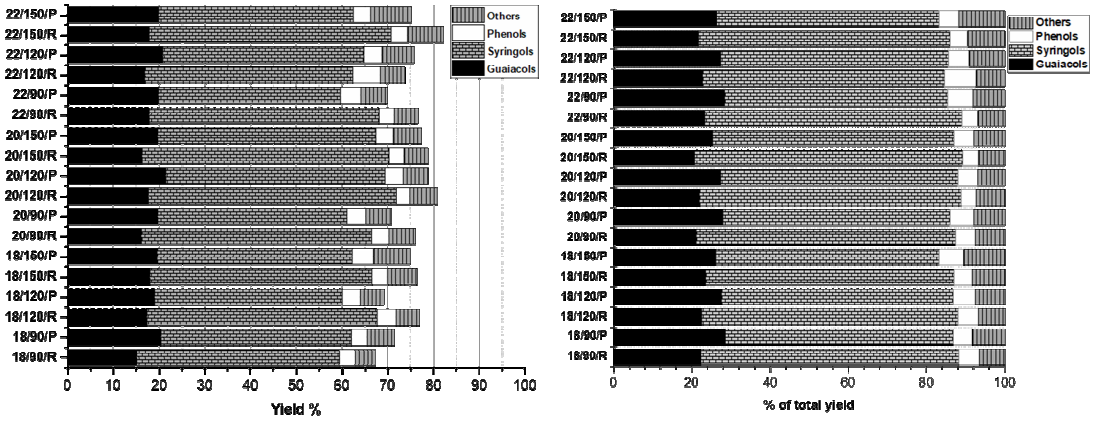

Figure 3: Total yield % of identified component groups (left) and relative portions (as % of total yield, right) of each main component group

This suggested the partial removal of S-type lignin already at hot-water extraction stage. On the contrary, the total content of guaiacyl-type (G-type) components was higher in the lignin samples separated from the BLs recovered from the pulping of the pretreated samples when compared to the untreated samples. This indicated the enrichment and increased relative concentration of the G-type lignin in the pretreated feedstocks. From these data, it could be concluded that the main part of the lignin dissolved during the pretreatment stage is composed of the S-type lignin subunits and that the G-type lignin is clearly more resilient against these kinds of pretreatments.

Table 2
Total yield percentages (based on pyrogram peak area ratios) of the main products formed in the pyrolysis experiments of alkaline reference (R) and pretreated (P) birch lignins (alkali charge 18%)

RT*	Compound	IUPAC name	m/z	90/R	90/P	120/R	120/P	150/R	150/P
	Guaiacol-type (total)			15.01	20.46	17.35	19.06	18.07	19.63
14.8	guaiacol	2-methoxyphenol	124/109/81	7.15	9.72	8.49	9.26	9.26	10.14
17.9	3-methylguaiacol	2-methoxy-3-methylphenol	138/123	1.74	2.10	2.05	1.78	1.88	2.35
18.8	4-methylguaiacol	2-methoxy-4-methylphenol	138/123	1.13	1.60	1.30	1.48	1.17	1.46
22.3	4-ethylguaiacol	2-methoxy-ethylphenol	152/137	1.04	1.37	1.18	1.25	1.08	1.39
24.7	4-vinylguaiacol	4-ethenyl-2-methoxyphenol	150/135/107	2.82	3.41	3.40	3.35	3.05	3.19
26.0	4-propylguaiacol	2-methoxy-4-propylphenol	180/137	-	0.34	-	-	-	-
30.5	*trans*-isoeugenol	2-methoxy-4-[(1*E*)-1-propen-1-yl]phenol	164/149/131	1.13	1.23	0.92	1.42	1.18	1.09
34.9	guaiacylacetone	1-(4-hydroxy-3-methoxyphenyl)propan-2-one	180/137	-	0.70	-	0.52	0.46	-
	Syringol-type (total)			44.27	41.55	50.23	40.92	48.35	42.59
28.0	syringol	1,3-dimethoxy-2-hydroxybenzene	154/139/96	26.16	22.6	29.50	22.88	29.20	24.73
31.3	4-methylsyringol	2,6-dimethoxy-4-methylphenol	168/153/125	3.99	4.09	4.71	3.89	4.12	3.83
33.8	4-ethylsyringol	4-ethyl-2,6-dimethoxyphenol	182/167	2.64	3.02	3.20	3.13	2.86	3.29
35.4	4-vinylsyringol	4-ethenyl-2,6-dimethoxyphenol	180/165/137	4.61	4.29	5.82	4.28	5.37	4.20
35.8	homosyringaldehyde	1-(4-hydroxy-3,5-dimethoxyphenyl)-ethanal	196/167	-	0.42	-	0.34	0.30	0.45
35.9	4-allylsyringol	4-allyl-2,6-dimethoxyphenol	194/179/150	0.53	0.57	0.62	0.41	0.46	0.41
37.1	*cis*-4-propenylsyringol	4-(1-propenyl)-2,6-dimethoxyphenol	194/179/150	0.54	0.62	0.49	0.58	0.59	0.65
38.2	*trans*-4-propenylsyringol	4-propenyl-2,6-dimethoxyphenol	194/179/150	1.76	1.82	2.12	1.70	1.88	1.70
38.4	syringaldehyde	4-hydroxy-3,5-dimethoxybenzaldehyde	182/181/167	1.08	0.61	0.64	0.43	0.62	0.39
39.4	propylsyringone	2,6-dimethoxy-4-propylphenol	210/181	0.53	0.50	0.59	0.48	0.60	0.41
39.5	acetosyringone	4'-hydroxy-3',5'-dimethoxyacetophenone	196/181	1.04	1.44	1.15	1.70	1.09	1.32
40.0	syringylacetone	4-(4-hydroxy-3,5-dimethoxyphenyl)-2-butanone	210/167	1.38	1.54	1.39	1.10	1.25	1.21
	Phenol-type (total)			3.44	3.43	4.00	3.86	3.51	4.70
9.3	phenol	phenol	94/66	-	0.53	-	-	-	-
12.2	*o*-cresol	2-methylphenol	108/107/67	0.64	0.71	0.84	1.04	0.89	1.22
13.4	*p*-cresol	4-methylphenol	108/107	1.05	1.07	1.15	1.21	0.90	1.25
14.6	2,6-xylenol	2,6-dimethylphenol	122/121/107	0.92	0.91	1.05	0.72	0.88	1.09
16.5	2,4-xylenol	2,4-dimethylphenol	122/121/107	0.83	0.74	0.95	0.89	0.83	1.13
	Others (total)			4.49	5.98	5.26	5.34	6.48	7.9
2.9	toluene	methylbenzene	92/91	0.60	0.65	0.79	0.84	0.71	1.03
17.4	*o*-dimethoxybenzene	1,2-dimethoxybenzene	138/123	-	0.94	-	0.72	0.69	1.24
23.2	3-methoxycatechol	1,2-dihydroxy-3-methoxybenzene	124/123/78	2.27	2.41	3.21	2.26	3.53	3.71
25.2	methylsyringol	1,2,3-trimethoxybenzene	168/153	1.13	1.51	1.16	1.14	1.13	1.41
28.7	3,4,5-trimethoxytoluene	1,2,3-trimethoxy-5-methylbenzene	182/167	0.49	0.48	-	0.38	0.42	0.52

*Retention time (min)

Table 3
Total yield percentages (based on pyrogram peak area ratios) of the of the main products formed in the pyrolysis experiments of alkaline reference (R) and pretreated (P) birch lignins (alkali charge 20%)

RT*	Compound	IUPAC name	m/z	90/R	90/P	120/R	120/P	150/R	150/P
	Guaiacol-type (total)			16.04	19.78	17.69	21.48	16.33	19.70
14.4	guaiacol	2-methoxyphenol	124/109/81	7.64	9.57	7.96	10.91	8.50	10.11
17.9	3-methylguaiacol	2-methoxy-3-methylphenol	138/123	1.91	2.15	1.84	1.98	1.34	2.13
18.8	4-methylguaiacol	2-methoxy-4-methylphenol	138/123	1.20	1.57	1.33	1.74	-	1.60
22.3	4-ethylguaiacol	2-methoxy-ethylphenol	152/137	1.18	1.54	1.15	1.66	4.39	1.47
24.7	4-vinylguaiacol	4-ethenyl-2-methoxyphenol	150/135/107	3.39	3.60	3.63	3.70	1.05	3.41
30.5	*cis*-isoeugenol	2-methoxy-4-[(1*E*)-1-propen-1-yl]phenol	164/149/131	0.71	1.35	1.27	1.49	0.60	0.98
35.0	guaiacylacetone	1-(4-hydroxy-3-methoxyphenyl)propan-2-one	180/137	-	-	0.50	-	0.45	-
	Syringol-type (total)			50.25	41.16	54.07	47.70	53.82	47.57
27.9	syringol	1,3-dimethoxy-2-hydroxybenzene	154/139/96	29.53	23.37	31.87	28.10	32.59	27.53
31.3	4-methylsyringol	2,6-dimethoxy-4-methylphenol	168/153/125	4.56	4.26	4.73	4.79	4.72	4.64
33.8	4-ethylsyringol	4-ethyl-2,6-dimethoxyphenol	182/167	3.09	3.29	3.44	3.74	3.32	3.62
35.4	4-vinylsyringol	4-ethenyl-2,6-dimethoxyphenol	180/165/137	5.69	4.33	6.73	4.77	5.75	4.74
35.8	homosyringaldehyde	1-(4-hydroxy-3,5-dimethoxyphenyl)-ethanal	196/167	0.39	0.38	0.39	0.48	0.43	0.49
35.9	4-allylsyringol	4-allyl-2,6-dimethoxyphenol	194/179/150	0.65	0.58	0.69	0.44	0.51	0.53
37.1	*cis*-4-propenylsyringol	4-(1-propenyl)-2,6-dimethoxyphenol	194/179/150	0.72	0.54	0.53	0.62	0.73	0.67
38.2	*trans*-4-propenylsyringol	4-propenyl-2,6-dimethoxyphenol	194/179/150	2.05	1.79	2.31	2.08	2.05	1.93
38.4	syringaldehyde	4-hydroxy-3,5-dimethoxybenzaldehyde	182/181/167	0.59	-	0.52	-	0.76	0.38
39.3	propylsyringone	2,6-dimethoxy-4-propylphenol	210/181	0.60	0.46	0.69	0.40	0.63	0.49
39.4	acetosyringone	4'-hydroxy-3',5'-dimethoxyacetophenone	196/181	0.98	1.00	0.95	1.11	1.09	1.28
40.0	syringylacetone	4-(4-hydroxy-3,5-dimethoxyphenyl)-2-butanone	210/167	1.39	1.16	1.22	1.18	1.23	1.26
	Phenol-type (total)			3.80	4.17	2.94	3.95	3.29	3.91
12.2	*o*-cresol	2-methylphenol	108/107/67	0.96	0.72	0.58	0.95	0.71	0.86
13.3	*p*-cresol	4-methylphenol	108/107	0.98	1.37	0.96	1.17	1.08	1.14
14.6	2,6-xylenol	2,6-dimethylphenol	122/121/107	0.96	1.00	0.75	0.90	0.78	1.01
16.4	2,4-xylenol	2,4-dimethylphenol	122/121/107	0.91	1.09	0.64	0.93	0.73	0.89
	Others (total)			5.86	5.73	6.09	5.53	5.3	6.19
2.9	toluene	methylbenzene	92/91	0.80	0.70	0.58	-	0.62	0.64
17.4	*o*-dimethoxybenzene	1,2-dimethoxybenzene	138/123	-	0.93	-	0.73	-	1.00
23.2	3-methoxycatechol	1,2-dihydroxy-3-methoxybenzene	124/123/78	3.50	2.20	4.07	2.74	3.09	3.14
25.2	methylsyringol	1,2,3-trimethoxybenzene	168/153	1.11	1.43	0.95	1.48	1.05	1.42
28.7	3,4,5-trimethoxytoluene	1,2,3-trimethoxy-5-methylbenzene	182/167	0.45	0.47	0.49	0.58	0.54	-

*Retention time (min)

Table 4
Total yield percentages (based on pyrogram peak area ratios) of the main products formed in the pyrolysis experiments of alkaline reference (R) and pretreated (P) birch lignins (alkali charge 22%)

RT*	Compound	IUPAC name	m/z	90/R	90/P	120/R	120/P	150/R	150/P
	Guaiacol-type (total)			17.85	19.87	16.85	20.73	17.82	19.88
14.4	guaiacol	2-methoxyphenol	124/109/81	7.99	9.70	8.09	10.37	8.23	10.14
17.9	3-methylguaiacol	2-methoxy-3-methylphenol	138/123	1.75	2.23	1.93	2.08	1.75	2.33
18.7	4-methylguaiacol	2-methoxy-4-methylphenol	138/123	1.63	1.63	1.28	1.69	1.59	1.57
22.3	4-ethylguaiacol	2-methoxy-ethylphenol	152/137	1.12	1.36	1.17	1.44	1.23	1.44
24.7	4-vinylguaiacol	4-ethenyl-2-methoxyphenol	150/135/107	3.62	3.62	3.34	3.87	3.33	3.31
30.5	*trans*-isoeugenol	2-methoxy-4-[(1*E*)-1-propen-1-yl]phenol	164/149/131	1.18	1.34	1.05	1.28	1.23	1.08
34.9	guaiacylacetone	1-(4-hydroxy-3-methoxyphenyl)propan-2-one	180/137	0.56	-	-	-	0.45	-
	Syringol-type (total)			50.22	39.81	45.36	43.89	52.75	42.49
27.9	syringol	1,3-dimethoxy-2-hydroxybenzene	154/139/96	28.43	24.17	26.54	25.04	31.85	25.42
31.3	4-methylsyringol	2,6-dimethoxy-4-methylphenol	168/153/125	4.88	4.18	4.48	4.37	5.13	4.09
33.8	4-ethylsyringol	4-ethyl-2,6-dimethoxyphenol	182/167	2.93	2.87	2.63	3.17	3.31	3.32
35.4	4-vinylsyringol	4-ethenyl-2,6-dimethoxyphenol	180/165/137	6.28	4.30	5.47	4.71	5.76	4.28
35.8	homosyringaldehyde	1-(4-hydroxy-3,5-dimethoxyphenyl)-ethanal	196/167	0.35	-	0.35	0.45	0.47	0.40
35.9	4-allylsyringol	4-allyl-2,6-dimethoxyphenol	194/179/150	0.54	-	0.47	0.50	0.50	0.39
37.1	*cis*-4-propenylsyringol	4-(1-propenyl)-2,6-dimethoxyphenol	194/179/150	0.49	0.41	0.43	0.60	0.69	0.49
38.2	*trans*-4-propenylsyringol	4-propenyl-2,6-dimethoxyphenol	194/179/150	2.13	1.62	1.88	1.89	1.90	1.66
38.4	syringaldehyde	4-hydroxy-3,5-dimethoxybenzaldehyde	182/181/167	1.07	-	0.78	0.76	0.75	0.62
39.3	propylsyringone	2,6-dimethoxy-4-propylphenol	210/181	0.61	-	0.52	0.36	0.57	-
39.4	acetosyringone	4'-hydroxy-3',5'-dimethoxyacetophenone	196/181	1.21	1.13	0.82	1.12	0.89	1.02
40.0	syringylacetone	4-(4-hydroxy-3,5-dimethoxyphenyl)-2-butanone	210/167	1.31	1.10	0.98	0.93	0.94	0.81
	Phenol-type (total)			3.21	4.44	6.05	4.00	3.73	3.80
9.3	phenol	phenol	94/66	-	-	0.8	-	0.60	-
12.2	*o*-cresol	2-methylphenol	108/107/67	0.80	1.04	1.36	1.08	0.74	1.06
13.3	*p*-cresol	4-methylphenol	108/107	1.01	1.18	1.24	1.01	1.03	1.38
14.6	2,6-xylenol	2,6-dimethylphenol	122/121/107	0.73	1.15	1.04	0.99	0.71	0.71
15.7		2-ethylphenol	122/107	-	-	0.64	-	-	-
16.4	2,4-xylenol	2,4-dimethylphenol	122/121/107	0.67	1.06	0.97	0.92	0.66	0.66
	Others (total)			5.31	5.81	5.41	6.93	7.84	8.92
2.9	toluene	methylbenzene	92/91	0.60	0.75	1.01	0.68	0.58	0.74
17.4	*o*-dimethoxybenzene	1,2-dimethoxybenzene	138/123	-	1.06	-	0.89	0.49	1.14
22.7	3-methylcatechol	3-methylbenzene-1,2-diol	124/123/78	-	-	-	-	0.78	0.78
23.2	3-methoxycatechol	1,2-dihydroxy-3-methoxybenzene	124/123/78	3.28	2.60	2.97	3.77	4.41	4.41
25.2	methylsyringol	1,2,3-trimethoxybenzene	168/153	0.94	1.40	0.96	1.17	0.95	1.32
28.7	3,4,5-trimethoxytoluene	1,2,3-trimethoxy-5-methylbenzene	182/167	0.49	-	0.48	0.42	0.62	0.52

*Retention time (min)

In deciduous woods, such as birch, lignin is mainly syringyl (S)/guaiacyl (G)-type, originating from *trans*-coniferyl and *trans*-sinapyl alcohols (in a rough ratio of 50:50). S and/or G units are linked together by C-O-C and C-C bonds. The ether linkages, such as β-*O*-4 bonds, are both abundant and labile to various treatments, making them the main targets for the pretreatment and pulping processes, whereas the carbon-carbon linkages like biphenyl 5-5 links involving aromatic C-5 positions are resistant and abundant especially in G units. Due to their abundancy and significance in pulping, the mechanism of the lignin β-*O*-4 bond cleavage has been studied widely and the general mechanism for its dissociation during alkaline pulping is relatively well known (Vuori and Bredenberg, 1987).[44] The cleavage of the β-*O*-4 bond includes an intramolecular S_N2-type neighbouring group participation reaction, where the dissociation of α-alkoxide effects the neighbouring β-carbon, resulting in the cleavage of ether linkage and the simultaneous formation of a new phenolic subunit. In addition, as an intermediate product, a subunit with an epoxide side-chain is formed. However, this epoxide intermediate is rapidly transformed to a side chain comprising glycerine structure by the action of the hydroxide anions present in alkaline cooking solution. S/G ratios for each pyrolyzed alkaline birch lignin samples were calculated (Table 5).

Table 5
Syringyl/guaiacyl-ratios of the pyrolyzed reference (R) and pretreated (P) lignins

Alkali charge (%)	90/R	90/P	120/R	120/P	150/R	150/P
18	2.95	2.03	2.90	2.75	2.68	2.17
20	3.13	2.08	3.06	2.22	3.30	2.42
22	2.81	2.00	2.69	2.12	2.96	2.14

The highest ratio 3.3 was calculated for sample 20/150/R and the lowest 2.0 for sample 22/90/P. For the S/G ration calculations, all identified S- and G-type products were taken into account. For an alkali charge of 18%, a prolonged cooking time lowered the S/G-ratio, but for alkali charges of 20% and 22%, such a clear tendency was not observed. However, hot-water-extracted samples had clearly lower S/G ratios when compared to the reference samples and the ratio increased roughly to the same extent for every alkali charge. This phenomenon can be explained by the different vulnerabilities of S and G units, and especially by differences in the breaking of β-*O*-4 linkages present in the S and G units.[45,46] In previous studies,[47] it has been proven that especially α-hydroxy groups present in S-type lignins are relatively more acidic than to those present in G-type lignin. Hence, during the β-*O*-4 bond cleavage, the nuclei present in S-type lignin are generally considered to be better leaving groups than the corresponding nuclei in G-type lignin, resulting in the increased vulnerability and easier cleavage of β-*O*-4 bonds of S-type lignin, when compared to their counterparts in G-type lignin. It is probable that the structure of especially S-type lignin has been altered already during the hot-water pretreatment stage, leading to at least partial solubilization of the S-groups during the pretreatment stage. In our previous study[48] conducted with FTIR-ATR analysis of the pretreated wood, it could be concluded that increasing the pretreatment severity (*i.e.*, increasing the treatment temperature and time) led to a clear decrease in the relative intensities in ester structures and conjugated carbonyl groups, indicating the destruction of β-*O*-4 structures of lignin.

Of the individual pyrolysis compounds, syringol, guaiacol, 4-methylsyringol and 4-vinylsyringol were the main pyrolysis products of alkaline birch lignins from all cooking trials. Again, the resilient nature of the G-type compounds against the hot-water pretreatment was evident. The content of guaiacol was clearly higher in the pretreated samples when compared to the reference samples, and the same general trend could be observed in the case of other minor G-type compounds. Based on the Py-GC/MSD data, it could be determined that compounds conventionally originating from pyrolysis of carbohydrates (*i.e.*, anhydrosugars, cyclopentenones, furanoic compounds, lactones, and pyrone derivatives) could not be determined from the chromatograms, suggesting their extensive removal and transformation already during the combined pretreatment-cooking-lignin separation process. For this reason, this concept

can be considered promising for the production of relatively pure sulfur-free lignin fractions, which can be converted further to useful products, such as aromatics, polymer precursors and bio-oils, without the need of additional heavy sulfur-removal processes.

Only one pyrolysis product of aromatic hydrocarbons (methylbenzene) was identified. In most samples, 3-methoxycatechol was identified as the only catechol-type product, but 3-methylcatechol was also identified for the samples 22/150/R and 22/150/P. Some compounds, such as 1,2-dimethoxybenzene, 1,2,3-trimethoxybenzene and 1,2,3-trimethoxy-5-methylbenzene, were included in the group "others", as their clear classification into guaiacols, syringols, phenols, catechols, or aromatic hydrocarbons was not straightforwardly possible according to their structure.

CONCLUSION

The chemical characteristics of lignin fractions separated from hot-water pretreatment/soda-AQ delignification process BLs were determined by Py-GC/MSD. By applying a hot-water pretreatment prior to delignification, the hemicellulose fraction could be partially recovered from the feedstocks and simultaneously, the subsequent environmentally friendly sulfur-free delignification process could be facilitated. This concept enabled the efficient utilization of the whole biomass, helped to minimize the amount of formed wastes, and created the possibility for manufacturing sulfur-free lignin fractions (*i.e.*, mainly various aromatic compounds), which could be utilized in the manufacture of novel biochemicals and polymers. It could be concluded that relatively pure (*i.e.*, no carbohydrates-derived impurities) lignin fractions could be separated from the process effluents, thus minimizing the need for further purification. In addition, it could be concluded that applying a hot-water extraction stage prior to pulping affected significantly the composition of the aromatic lignin-derived fraction. Especially syringyl-derived lignin was found to decompose partly during the hot-water extraction, indicating pronounced vulnerability of this fraction to pretreatments when compared to the guaiacyl fraction. Hence, the formation of individual lignin-originated pyrolysis products was shown to be characteristically dependent on the chemical composition of the pyrolyzed feedstock and hence, also on the used pretreatment and delignification conditions. The main scientific outcomes of the research approach presented in this manuscript comprises the development of rapid and reliable analytical characterization tools for various differently treated lignocellulosic feedstocks possessing potential for thermochemical conversion. This also enables the development of novel biorefinery concept alternatives for producing different pure and sulfur-free aromatics and chemical precursors from currently underutilized feedstock, lignin.

REFERENCES

[1] M. FitzPatrick, P. Champagne, M. F. Cunningham and R. A. Whitney, *Bioresour. Technol.*, **101**, 8915 (2010), https://doi.org/10.1016/j.biortech.2010.06.125

[2] M. Moshkelani, M. Marinova, M. Perrier and J. Paris, *Appl. Therm. Eng.*, **50**, 1427 (2013), https://doi.org/10.1016/j.applthermaleng.2011.12.038

[3] M. Machani, M. Nourelfath and S. D'Amours, *Biomass Bioenerg.*, **63**, 126 (2014), https://doi.org/10.1016/j.biombioe.2014.02.024

[4] R. Alén, in "Biorefining of Forest Resources", edited by R. Alén, Paperi ja Puu Oy, 2011, pp. 18-114

[5] B. Kamm, M. Kamm, P. R. Gruber and S. Kromus, in "Biorefineries – Industrial Processes and Products, Status Quo and Future Directions", edited by B. Kamm, P. R. Gruber and M. Kamm, Wiley-VCH Verlag GmbH & Co. KGaA, 2006, pp. 3-40

[6] J. Lehto, PhD Thesis, University of Jyväskylä, Jyväskylä, Finland, 2015, 173 p.

[7] R. Alén, in "Forest Products Chemistry", edited by P. Stenius, Fapet Oy, 2000, pp. 11-57

[8] E. Sjöström, "Wood Chemistry – Fundamentals and Applications Academic Press, 1993, 239 p

[9] E. Sjöström and U. Westermark, in "Analytical Methods in Wood Chemistry, Pulping and Papermaking", edited by E. Sjöström and R. Alén, Springer, 1999, pp. 1-15

[10] R. Alén, in "Forest Products Chemistry", edited by P. Stenius, Fapet Oy, 2000, pp. 58-104

[11] T. N. Adams, in "Kraft Recovery Boilers", edited by T. N. Adams, TAPPI Press, 1997, pp. 3-38

[12] F. Carvalheiro, L. C. Duarte and F. M. Gírio, *J. Sci. Ind. Res.*, **67**, 849 (2008)

[13] A. van Heiningen, *Pulp Pap.-Can.*, **107**, 38 (2006)

[14] H. Rabemanolontsoa and S. Saka, *Bioresour. Technol.*, **199**, 83 (2016), https://doi.org/10.1016/j.biortech.2015.08.029

[15] J. Lehto and R. Alén, *J. Wood Chem. Technol.*, **33**, 77 (2013), https://doi.org/10.1080/02773813.2012.748077

[16] H. Chen, Y. Fu, Z. Wang and M. Qin, *BioResources*, **10**, 3005 (2015), https://doi.org/10.15376/biores.10.2.3005-3016

[17] A. Pranovich, B. Holmbom and S. Willför, *J. Wood Chem. Technol.*, **36**, 140 (2016), https://doi.org/10.1080/02773813.2015.1104543

[18] J. Lehto, H. Pakkanen and R. Alén, *Appita J*., **68**, 149 (2015)
[19] J. Lehto and R. Alén, *Holzforschung*, **69**, 257 (2015), https://doi.org/10.1515/hf-2014-0094
[20] J. Lehto and R. Alén, *Tappi J*., **14**, 237 (2015), https://doi.org/10.32964/TJ14.4.237
[21] I. Sumerskiy, A. Pranovich, B. Holmbom and S. Willför, *J. Wood Chem. Technol*., **35**, 387 (2015), https://doi.org/10.1080/02773813.2014.965331
[22] I. Sumerskiy, A. Pranovich, B. Holmbom and S. Willför, *J. Wood Chem. Technol*., **35**, 398 (2015), https://doi.org/10.1080/02773813.2014.990637
[23] P. Schulze, A. Seidel-Morgenstern, H. Lorenz, M. Leschinsky and G. Unkelbach, *Bioresour. Technol*., **199**, 128 (2016), https://doi.org/10.1016/j.biortech.2015.09.040
[24] W. Zhu, G. Westman and H. Theliander, *Holzforschung*, **69**, 143 (2015), https://doi.org/10.1515/hf-2014-0062
[25] W. Fang, M. Alekhina, O. Ershova, S. Heikkinen and H. Sixta, *Holzforschung*, **69**, 943 (2015), https://doi.org/10.1515/hf-2014-0200
[26] T. Han, N. Sophonrat, P. Evangelopoulos, H. Persson, W. Yang *et al*., *J. Anal. Appl. Pyrol*., **133**, 162 (2018), https://doi.org/10.1016/j.jaap.2018.04.006
[27] É. Le Roux, P. N. Diouf and T. Stevanovic, *J. Anal. Appl. Pyrol*., **111**, 121 (2015), https://doi.org/10.1016/j.jaap.2014.11.023
[28] H. Lappi and R. Alén, *J. Anal. Appl. Pyrol*., **86**, 274 (2009), https://doi.org/10.1016/j.jaap.2009.07.005
[29] H. Lappi and R. Alén, *J. Anal. Appl. Pyrol*., **91**, 154 (2011), https://doi.org/10.1016/j.jaap.2011.02.003
[30] B. Zhang, Z. Zhong, M. Min, K. Ding, Q. Xie *et al*., *Bioresour. Technol*., **189**, 30 (2015), https://doi.org/10.1016/j.biortech.2015.03.092
[31] M Brebu, T. Tamminen and I. Spiridon, *J. Anal. Appl. Pyrol*., **104**, 531 (2013), https://doi.org/10.1016/j.jaap.2013.05.016
[32] M. Zhang, F. L. P. Resende, A. Moutsoglou and D. E. Raynie, *J. Anal. Appl. Pyrol*., **98**, 65 (2012), https://doi.org/10.1016/j.jaap.2012.05.009
[33] D. J. Nowakowski, A. V. Bridgwater, D. C. Elliot, D. Meier and P. de Wild, *J. Anal. Appl. Pyrol*., **88**, 53 (2010), https://doi.org/10.1016/j.jaap.2010.02.009
[34] W. Mu, H. Ben, A. Ragauskas and Y. Deng, *BioEnerg. Res*., **6**, 1183 (2013), https://doi.org/10.1007/s12155-013-9314-7
[35] B. Swan, *Svensk Papperstidn*., **68**, 791 (1965)
[36] X. Zhao and D. Liu, *Ind. Crop. Prod*., **32**, 284 (2010), https://doi.org/10.1016/j.indcrop.2010.05.003
[37] Z. Luo, S. Wang and X. Guo, *J. Anal. Appl. Pyrol*., **95**, 112 (2012), https://doi.org/10.1016/j.jaap.2012.01.014
[38] P. J. de Wild, W. J. J. Huijgen and H. J. Heeres, *J. Anal. Appl. Pyrol*., **93**, 95 (2012), https://doi.org/10.1016/j.jaap.2011.10.002
[39] Y. Zhang, J. Wang, J. Wei, Y. Bai, X. Song *et al*., *J. Fuel. Chem. Technol*., **49**, 752 (2021), https://doi.org/10.1016/S1872-5813(21)60025-7
[40] T. Okuno, N. Sonoyama, J. I. Hayashi, C. Z. Li, C. Sathe *et al*., *Energ. Fuels*, **19**, 2164 (2005), https://doi.org/10.1021/ef050002a
[41] X. M. Li, H. Zhang, M. J. Liu, L. F. Zhi, J. Bai *et al*., *J. Fuel. Chem. Technol*., **48**, 897 (2020), https://doi.org/10.1016/S1872-5813(20)30062-1
[42] X. Zhu and Q. Lu, in "Biomass", edited by M. N. B. Momba and F. Bux, Sciyo, 2010, pp. 147-164, https://doi.org/10.5772/9773
[43] T. Hosoya, H. Kawamoto and S. Saka, *J. Anal. Appl. Pyrol*., **83**, 78 (2008), https://doi.org/10.1016/j.jaap.2008.06.003
[44] A. I. Vuori and J. B. Bredenberg, *Ind. Eng. Chem. Res*., **26**, 359 (1987)
[45] S. Shimizu, P. Posoknistakul, T. Akiyama, T. Yokoyama and Y. Matsumoto, *J. Wood Sci*., **64**, 664 (2018), https://doi.org/10.1007/s10086-018-1739-3
[46] E. I. Evstigneyev and S. M. Shevchenko, *Wood Sci. Technol*., **53**, 7 (2019), https://doi.org/10.1007/s00226-018-1059-1
[47] S. Shimizu, T. Akiyama, T. Yokoyama and Y. Matsumoto, *J. Wood Chem. Technol*., **37**, 451 (2017), https://doi.org/10.1007/s10086-018-1739-3
[48] J. Lehto, J. Louhelainen, T. Kłosińska, M. Drożdżek and R. Alén, *Biomass Convers. Bioref*., **8**, 847 (2018), https://doi.org/10.1007/s13399-018-0327-5