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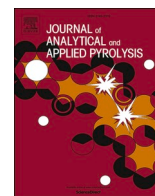
Valorization potential of technical lignins from Norway spruce (*Picea abies*) via pyrolysis

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ABSTRACT

Analytical pyrolysis (Py-GC/MS) on mg-scale of Norway spruce (*Picea abies*)-derived kraft lignin, ethanosolv lignin, and dried lignin-rich soda-anthraquinone (AQ) black liquors was studied at 500 °C to compare the valorization potential of these materials, focusing on the type and yield of condensable pyrolysis products. Of particular interest was the relatively selective formation of guaiacol (2-methoxyphenol) from the dried soda-AQ black liquors in contrast to the formation of complex phenolic product mixtures from the pyrolysis of the kraft and ethanosolv lignins. It was shown that this finding could be attributed to differences in composition and structure as was assessed by various NMR and 2D-GC/FID analyses. From a comparison between the analytical pyrolysis results and the results of Norway spruce-derived pyrolysis oils that were produced in earlier research with a state-of-the-art kg-scale bubbling fluidized bed pyrolysis reactor, it was concluded that analytical pyrolysis is suitable to predict the pyrolysis behavior of lignin also on a larger scale. However, it was found that the prediction of reliable product yields for larger-scale pyrolysis from the semi-quantitative analytical pyrolysis yield results was less accurate, mainly due to differences in process conditions, such as heating rate and hot-vapor-residence times leading to secondary degradation reaction of the individual monomers.

1. Introduction

Biorefining involves the conversion of biomass to value-added compounds, such as energy carriers, transportation fuels, and biobased chemicals and materials with a minimum amount of waste and energy [1,2]. A modern pulp mill can be regarded as an integrated biorefinery that produces several end products, like cellulosic fiber (pulp) and extractives, soluble lignin fractions, and various hemicelluloses-derived materials [2,3]. However, to date, the lignin fraction is typically used as a relatively cheap solid fuel for generating process heat.

Biorefinery economics could benefit from recovery and higher value applications for the lignin fraction, i.e., by lowering the manufacturing costs for their main products [4–8]. For instance, the lignin fraction is a renewable source for replacing aromatic petrochemical compounds in various high-tech-performance materials (e.g., phenol-formaldehyde resins and carbon fibers). Lignin can also be deployed as feedstock for production the of low-molar-mass phenolics and advanced fuel additives

with substantial energy densities [9–14] via thermochemical conversions, such as pyrolysis [10–13,15–18]. Currently, there is much interest in lignin valorization for aromatic chemicals [19,20]. To date, most lignin is incinerated for the generation of process heat and the thermochemical production of higher-value biobased aromatics from lignin is still in its infancy and forms a major research challenge [20–22]. Hence, for example, the heterogeneity of technical lignins from different sources as well as complex product mixtures obtained by current conversion technologies pose significant hurdles for successful utilization. However, thermochemical approaches, such as pyrolysis seem especially suited for degrading lignins toward value-added aromatics [23, 24].

Currently, about 90% of the chemical pulps are produced via the kraft process, mainly from woody types of biomass [2,25]. In this aqueous alkaline process, sodium hydroxide and sodium sulfide are the active cooking chemicals. The resulting process liquid (kraft black liquor) contains a great variety of inorganic and organic compounds;

while the inorganic species mainly constitute the residual cooking chemicals, the organic fraction is a highly complex mixture of various degraded biomass components. Evaporated kraft black liquors are incinerated in a recovery boiler for recycling of cooking chemicals and generation of process heat [26–28].

Although the cost-efficient recovery of individual components from kraft black liquor is challenging, it was earlier shown that with a relatively simple pyrolysis process, high-value components, such as guaiacol and syringol are obtainable from kraft black liquors [18]. However, low product yields and difficulties in handling the black liquor feedstock precluded commercialization.

Besides kraft lignins, other technical lignins with potential for valorization, such as organosolv and soda lignins are available at various production scales. In general, organosolv lignins are sulfur-free and very pure (ash-free and low in residual carbohydrates). Their chemical composition depends on the used feedstock and process conditions. Organosolv lignins are typically obtained from the delignification of lignocellulosics by the aid of organic solvents, an emerging biomass fractionation technology, which so far has primarily been realized on a laboratory and pilot scale [2].

More traditional pulping methods for non-wood feedstocks are soda and soda-anthraquinone (AQ) processes [2,29–32]. In these methods, the active cooking chemical is sodium hydroxide with or without the addition of AQ as a catalyst. In general, soda lignins from non-wood biomass, like wheat straw and reed canary grass, contain higher amounts of minerals, nitrogen, and extractives than wood lignins, due to the biochemical composition of the parent biomass material [33–35]. In contrast to kraft pulping, the soda-AQ process (i.e., the active sulfur-free cooking chemical is sodium hydroxide and AQ is a catalyst for delignification) enables the production of sulfur-free lignins and lignin-derived products [36].

Black liquors from alkaline delignification (kraft and soda-AQ pulping) contain significant amounts of carbohydrates-derived aliphatic carboxylic acids (i.e., formic, acetic, and a great variety of hydroxy acids) together with highly degraded alkali lignin [1]. In contrast, ethanol organosolv (ethanosolv) methods mainly remove lignin by dissolution and partial hydrolysis. The delignification method has a clear effect on the structure of the dissolved lignin which is important regarding the pyrolytic depolymerization. To our best knowledge, so far the pyrolysis of black liquors based on soda-AQ cooking has not been investigated.

For this research, spruce-derived kraft lignin, ethanosolv lignin, and dried soda-AQ black liquors from untreated (BL_ref) and hot-water-extracted (BL_HWE) sawdust were investigated. The work described in this paper is schematically depicted in Fig. 1; it shows the interconnections between the used feedstocks, the applied characterization and pyrolysis techniques, and the obtained products and their mutual comparison.

Analytical pyrolysis is conducted with small samples (mg-size) under well-controlled conditions such as heating rate, temperature, and solid and gaseous residence times. Consequently, the type and yield of the pyrolysis products can be attributed to a well-defined set of conditions. This is valuable for a detailed understanding of the pyrolysis behavior of the specific feedstock. In larger-scale pyrolysis experiments, process conditions are often more varied, for instance by the occurrence of temperature gradients, different heating rates, and residence times that depend on factors such as sample size, sample shape, reactor type, etc.

Despite the differences between large-scale pyrolysis and analytical pyrolysis, the latter is widely recognized in the field as a versatile and efficient method to characterize various types of biomass and to gain insight into their large-scale pyrolysis behavior. This is illustrated by various excellent articles. For instance, Azeez et al. [38] presented a thorough comparison of results from Py-GC/MS with results from bench-scale fluidized bed pyrolysis at 470 °C for five biomass types (spruce, beech, iroko, albizia and corncob). It was concluded that the close agreement, observed in the composition of the volatile pyrolysis products from Py-GC/MS and bench-scale pyrolysis, implies that the former constitutes a reliable on-line technique for qualifying pyrolysis products and offers potential for the study of their mechanisms of formation. Butler et al. [39] compared fluidized bed pyrolysis and analytical pyrolysis of lignocellulosic biomasses. They concluded that differences between absolute masses of compounds determined by GC/MS-FID of the bio-oils compared with Py-GC/MS-FID suggest a greater role of secondary reactions at the fluidized bed scale, with reduced concentrations of certain lignin-derived, furan, and pyran compounds. Another example of the versatility of analytical pyrolysis as a method to rapidly indicate pyrolysis behavior in larger-scale reactors is provided by Gamliel et al. [40]. They studied in-situ and ex-situ catalytic pyrolysis of miscanthus in a bench-scale spouted-bed reactor and compared product yield and selectivity results with results from in-situ and ex-situ Py-GC/MS configurations. One of the primary goals of their study was to understand if Py-GC/MS can accurately predict the effects of operating conditions and determine the pyrolysis product distribution obtained from a more realistic bench-scale reactor system. It was concluded that ex-situ catalytic pyrolysis in the Py-GC/MS set-up more accurately predicts the molecular composition of bio-oil produced by catalytic pyrolysis in a bench-scale spouted-bed reactor. However, it was also seen that the char-/-coke formed by in-situ catalytic pyrolysis in the Py-GC/MS had a nearly identical structure to that formed in the bench-scale spouted-bed.

The main goal of this research was to establish the valorization potential of Norway spruce–derived technical lignins towards value-added phenols via (analytical) pyrolysis (Py-GC/MS). In addition, the analytical results were briefly compared with those from larger-scale pyrolysis experiments (a bubbling fluidized bed (BFB) pyrolysis reactor) to get some insight into the predictive value of the analytical pyrolysis method
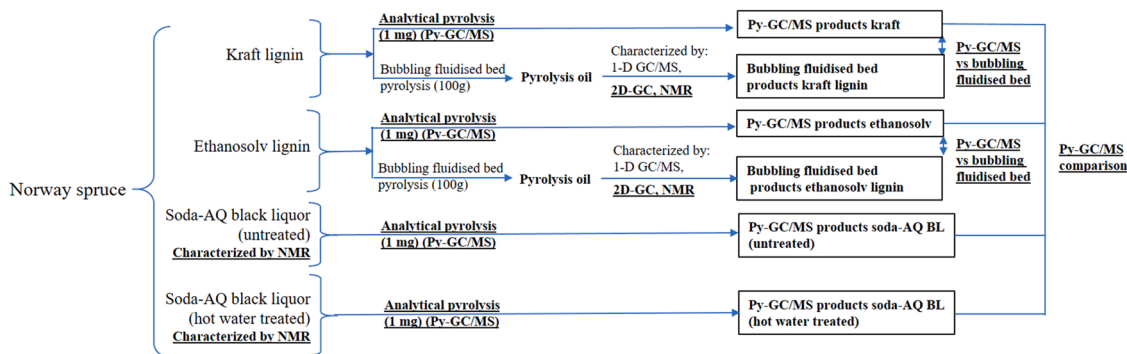
Fig. 1. Roadmap of spruce-derived lignin and black liquor pyrolysis activities. The bold and underlined activities are conducted in the framework of this research. In earlier work, pyrolysis oil production by a bubbling fluidized bed (BFB) reactor has been conducted [37]. AQ refers to anthraquinone, NMR to nuclear magnetic resonance, Py to pyrolysis, GC/MS to gas chromatography with mass spectrometric detection, BL to black liquor, and 2D-GC to 2-dimensional gas chromatography.

that was applied. Hence, for the Norway spruce–derived lignin feedstocks, the comparison will support the potential use of analytical pyrolysis as a fast characterization or fingerprinting tool, enabling the examination of the feasibility of forthcoming up-scaling research on dried soda-AQ black liquors for producing guaiacol-type chemicals.

2. Experimental

2.1. Materials

2.1.1. Kraft lignin, ethanosolv lignin and lignin-rich soda-AQ black liquors

To compare their analytical (Py-GC/MS) pyrolysis behavior, Norway spruce (*Picea abies*) kraft lignin ("Lignoboost™ lignin" [41]), ethanosolv lignin [42] and BL_{ref} and BL_{HWE} from soda-AQ cooking [43] were investigated. The Lignoboost™ lignin was provided by Innventia, Sweden, as a free test sample. The ethanosolv lignin was provided by ECN (now TNO-ET), also as a free test sample. Both lignins contain > 95 wt% of pure lignin with only minor amounts of residual carbohydrates and ash. Details on their preparation and chemical composition can be found in Refs. [41,42]. The chemical compositions of BL_{ref} and BL_{HWE} are shown in Table 1.

2.1.2. Pyrolysis oils from kraft and ethanosolv lignins

Lignin pyrolysis oils were produced at 550 °C, using a 1 kg/h feedstock intake, state-of-the-art, BFB reactor [37]. 2D-GC/FID was applied to characterize the pyrolysis oil regarding the type and yield of products. The aim was to compare the results of this larger-scale pyrolysis experiment with those of the analytical pyrolysis, to assess the predictive value of analytical pyrolysis when scaling up to larger-scale experiments.

2.2. Py-GC/MS experiments of kraft lignin, ethanosolv lignin and black liquors

The lignin and black liquor samples were pyrolysed using a Gerstel Pyro automated pyrolyser. The experimental conditions for the analytical pyrolysis experiments (such as temperature, heating rate, and residence times) were chosen based on the literature information and our earlier work [37] to mimic the experimental conditions in the larger-scale BFB reactor as good as possible (but not to replicate). For each experiment, 1 mg of sample was weighed with an accuracy of 0.01 mg in a quartz sample holder (of an open tube type) and covered with quartz wool.

The sample tube was attached to a sample holder, which was introduced into the pyrolysis unit by an autosampler (Multi-Purpose Sampler, MPS). Subsequently, the pyrolysis was performed at 500 °C with a heating rate of 250 °C/s and a hold time of 1 min. Before the gas chromatography/mass spectrometry (GC/MS) analysis, the pyrolysis products were trapped on a Gerstel cooled injection system (CIS) PTV-type inlet that was used as a cryo-focussing trap for the pyrolysis products. The GC/MS analyses were conducted on an Agilent 7890 A GC equipped with an Agilent 5975 C MS detector. A full scan GC/MS

analysis was conducted, followed by an analysis with deconvolution software 'AMDIS'. After the cold-trap collection at − 150 °C, the pyrolysis products were thermally desorbed and injected on a capillary column (Zebron ZB-WAXplus, 30 m × 0.25 mm i.d. × 0.25 μm). The injection temperature was set at 250 °C and a split ratio of 1:40 was applied. Helium was used as the carrier gas at a constant flow mode of 1 mL/min.

The following GC oven program was used: 50 °C isotherms for 5 min and then heated up to 245 °C at a rate of 10 °C/min. After each experiment, the sample holder was left to cool and weighed to obtain an estimate of the residual char in the sample holder. Pyrolysis products were identified by comparison to the NIST library. The compounds found were those whose MS spectrum had the best "fit" with respective compounds in the NIST library. Only the fits with a match of ≥ 80 (similarity index) were reported and hence, all the detected peaks were not included. Additionally, it was not always possible to distinguish between some connections; for example, isomeric compounds often had the same MS. However, 2D-GC/FID was applied for more quantification analysis due to a wide range of degradation products.

2.3. NMR analyses of black liquors and pyrolysis oils

For ^{13}C and Heteronuclear – Single Quantum – Coherence (HSQC) NMR analysis up to 0.2 g of sample was dissolved in 0.8 g of dimethyl sulphoxide-d_6 (for pyrolysis oils from kraft and ethanosolv lignins) or 0.8 g of D_2O (for black liquor samples) [44]. Spectra were recorded using a Bruker 600 MHz spectrometer and the obtained data were processed using the Mestrenova software. Assignment and processing were performed according to a previously published procedure [44,45]. From the HSQC analysis, the number of linkages was determined by integration of the aromatic C-H region (divided by 3 as these concerns only guaiacyl-type (G) lignins) and the signals for the α-position of the respective linkage and expressing these as linkage amounts per 100 aromatic C-9 units [45,46]. The NMR characterization experiments aimed to elucidate the potential structure effects of the different feedstocks on the pyrolysis results.

2.4. 2D-GC/FID analyses of kraft and ethanosolv lignin pyrolysis oils

Sample preparation and quantification analyses were conducted using a procedure given in Ref. [47]. The lignin oil phase was injected after a tenfold dilution of the original oil sample with tetrahydrofuran (THF) containing 1000 ppm (mg/kg) of di-*n*-butyl ether (DBE) as an internal standard. A test mixture for quantification analyses was made consisting of group-type chemicals (present in the lignin oil), such as aromatic hydrocarbons, naphthalenes, phenolics, and guaiacols. At least three components were selected as representatives for a certain group. All chemicals were of analytical grade and obtained from Sigma Aldrich. The 2D-GC/FID analyses were performed using a Thermo Finnigan Trace GC Ultra from Interscience equipped with a dual-jet CO_2 cryogenic modulator trap system. A modulation time of 6 s was applied. A capillary RTX-1701 column (30 m × 0.25 mm i.d. and a 0.25 μm film) connected by a press fit to Rxi-5Sil MS column (120 cm × 0.10 mm i.d. and a 0.10 μm film) were used. Helium (constant flow of 0.8 mL/min) was used as the carrier gas. A split ratio of 1:50 was applied and injector and FID temperatures were set to 280 °C. The oven temperature was programmed as 40 °C for 5 min and then raised to 250 °C at a 3 °C/min rate. The aim of the 2D-GC/FID analysis was to extend the 1D-GC/MS/FID analysis results concerning the comparison with the analytical Py-GC/MS results.

3. Results and discussion

The utility of the analytical pyrolysis applied lies in its versatility to quickly screen biomass materials on micro- to mg-scale to get valuable insights on type and (relative) amounts of pyrolysis products that are

Table 1
The main organic components in soda-AQ BL_{ref} and BL_{HWE} in g/L[a].

Component	Soda-AQ BL_{ref}	Soda-AQ BL_{HWE}
Lignin	44.5	39.5
Volatile acids	9.5	7.3
Formic acid	4.4	6.0
Acetic acid	5.1	1.3
Hydroxy acids[b]	15.6	27.8
Total	69.6	74.6

[a] Data from Ref. [43], the black liquors are made from untreated (BL_{ref}) and hot-water-extracted (BL_{HWE}) sawdust.

[b] Main acids are glycolic, lactic, 2,5-dihydroxypentanoic, xyloisosaccharinic, and glucoisosaccharinic acids.

likely to be formed in larger-scale pyrolysis [38–40]. This work was mainly aimed at comparing the potential of direct pyrolytic valorization of Norway spruce-derived kraft lignin, ethanosolv lignin and lignin-containing dried black liquors towards value-added chemicals using state-of-the-art Py-GC/MS analytical pyrolysis. To assess the predictive value of analytical pyrolysis for scale-up to larger-scale experiments, the Py-GC/MS compositional results for the kraft and ethanosolv lignin samples were compared with the composition of their pyrolysis oils, produced by a larger-scale reactor (BFB) at 550 °C [37]. However, due to the limited amounts of black liquor samples available, no pyrolysis oil samples from these feedstocks could be prepared.

3.1. Analytical Py-GC/MS

Table 2 gives the residual amount of char that was weighed after each experiment with the lignin and black liquor samples. Under the conditions used, the char yields were typical for lignins and the relatively higher values for the black liquors was probably attributed to the higher content of inorganic matter when compared to the kraft and the ethanosolv lignin samples.

Fig. 2 presents representative examples of the pyrograms of the samples at the same Y-axis scale to enable a semi-quantitative comparison of the yields of different products from the four samples. Although it was ensured that the amount pyrolysed was 1 mg for each sample, the resulted yields were at best semi-quantitative because the lignin content of dried soda-AQ black liquor samples could be only roughly estimated.

The soda-AQ black liquor samples clearly produced less lignin-derived pyrolysis products when compared to the kraft and ethanosolv lignins (Fig. 2). This was attributed to the lower content of lignin, as determined by UV/Vis-spectroscopy at 280 nm [43] and the NMR study carried out in this paper.

The Py-GC/MS data were normalized on the lignin content in the feedstock materials; 95 wt% for the kraft and ethanosolv lignins, 39 wt % for the black liquor from untreated sawdust, and 33 wt% the black liquor from hot-water-extracted sawdust (Supporting Information 1 a, b)).

While the analytical pyrolysis of kraft and ethanosolv spruce lignins typically produced a complex mixture of mainly (substituted) guaiacols and catechols (often in a 4-substituted configuration that indicated the major intra-lignin β-O-4 bond), pyrolysis of soda-AQ black liquor samples yielded primarily guaiacol with only a minor amount of other aromatics. This finding was corroborated by the earlier work of Goheen et al. [18]; they discovered the same phenomenon for kraft black liquor. This general finding was also important because obtaining a particularly guaiacol-rich stream offers the possibility to easily separate and purify guaiacol, which has many potential applications, for example as a precursor for vanillin or as a high-value food and fragrance additive. The pyrolysis product patterns for both black liquor samples were comparable, indicating that a hot-water extraction of sawdust before the soda-AQ delignification does not affect the final pyrolysis products when compared to the product spectrum of the black liquor from untreated sawdust. It has been shown [45] that during the conventional soda-AQ pulping of Scots pine (*Pinus sylvestris*) (i.e., as softwood containing mainly "guaiacyl lignin") guaiacol shows up as the most abundant lignin monomer in black liquor followed by vanillin

(4-hydroxy-3-methoxybenzaldehyde), dihydroconiferyl alcohol (3-(4-hydroxy-3-methoxyphenyl)– 1-propanol) and a mixture of acetovanillone (4-hydroxy-3-methoxyacetophenone) and apocynol (1-(4-hydroxy-3-methoxyphenyl)ethanol). As was measured by the NMR measurements in Section 3.4, the black liquor samples yielded relatively strong methoxy signals but weak lignin-derived signals, such as aromatics and intra-molecular lignin bonds. This observation indicated the presence of small methoxylated species in corroboration with the study described above [45]. The dominant presence of guaiacol in the black liquor pyrograms might be due to the thermal scission of the C-4 substituents from the aromatic ring of some of the above-mentioned monomers in the (dried) soda-AQ black liquor samples.

We next turned our attention to identifying why pyrolysis of kraft and ethanosolv lignin resulted in a much more complex product slate. As shown in Fig. 2, guaiacol and some of its C-1 substituted isomers were abundant products from the pyrolysis of the kraft and the ethanosolv lignin. Kraft lignin is typically more condensed and higher-molar-mass lignin when compared to the lignin in the soda-AQ black liquor samples, because monomers and dimers are not precipitated by the Lignoboost separation method with carbon dioxide [2].

As result pyrolysis of kraft lignin will yield not only guaiacol, but also various substituted alkyl phenolics that originated from random thermal degradation of the kraft lignin structure. Regarding the pyrolysis products from the ethanosolv lignin, delignification of softwood with ethanol is difficult and gives relatively large lignin fragments that apparently show the same pyrolysis behavior as the kraft lignin [48]. For kraft and ethanosolv lignins, guaiacol, 4-methylguaiacol, 4-vinylguaiacol and catechol isomers were dominant pyrolysis products. In addition, the pyrolysis of the ethanosolv lignin yielded small amounts of typical carbohydrate pyrolysis products, such as acetic acid, furfural and levoglucosan, indicating the presence of some carbohydrate-derived impurities. In the black liquor samples, there are no significant amounts of carbohydrates. In contrast, there are a lot of carbohydrate-degradation products, low-molar-mass aliphatic carboxylic acids. These acids are readily converted to permanent gases, such as CO, CO_2, CH_4, and other light hydrocarbons, which could not be measured by the applied analytical equipment. In the black liquor samples, the progressive thermal degradations might be catalyzed by the abundant presence of inorganic material, such as Na^+ which is known to have a catalytic cracking effect. This catalytic thermal degradation effect on carbohydrate moieties was not observed for the ethanosolv and kraft lignins, probably because these lignins did either not contain significant amounts of inorganic material (ethanosolv) or were devoid of carbohydrate impurities (kraft).

3.2. Comparison mg-scale Py-GC/MS versus kg-scale BFB

To assess the predictive value of analytical pyrolysis for larger-scale pyrolysis in the framework of technology scale-up, the composition and yields of the main pyrolysis products as estimated from the Py-GC/MS results can be compared with the composition and yield results from the kg-scale BFB pyrolysis. To ensure a full conversion of the lignin samples, a relatively long hold time of 1 min was used in the presented work. After pyrolysis, residual char was determined by careful back weighing. Results were concordant with those from BFB experiments, indicating a complete conversion. The rationale for using a relatively high amount of sample (1 mg) was the possibility to produce larger amounts of pyrolysis products, thereby improving the resolution of the final pyrogram [49–51]. It was expected that matrix effects during the pyrolysis reaction were similar for both set-ups, because of similar reaction conditions (i.e., solid residence time, pyrolysis temperature, and heating rate). However, since the hot-vapor residence time in the BFB reactor is (clearly) longer than in the Py-GC/MS set-up, progressive re-polymerization reactions will take place to a larger extent when compared to the Py-GC/MS. In our approach, this was inevitable, because of differences in the way which products are collected, via
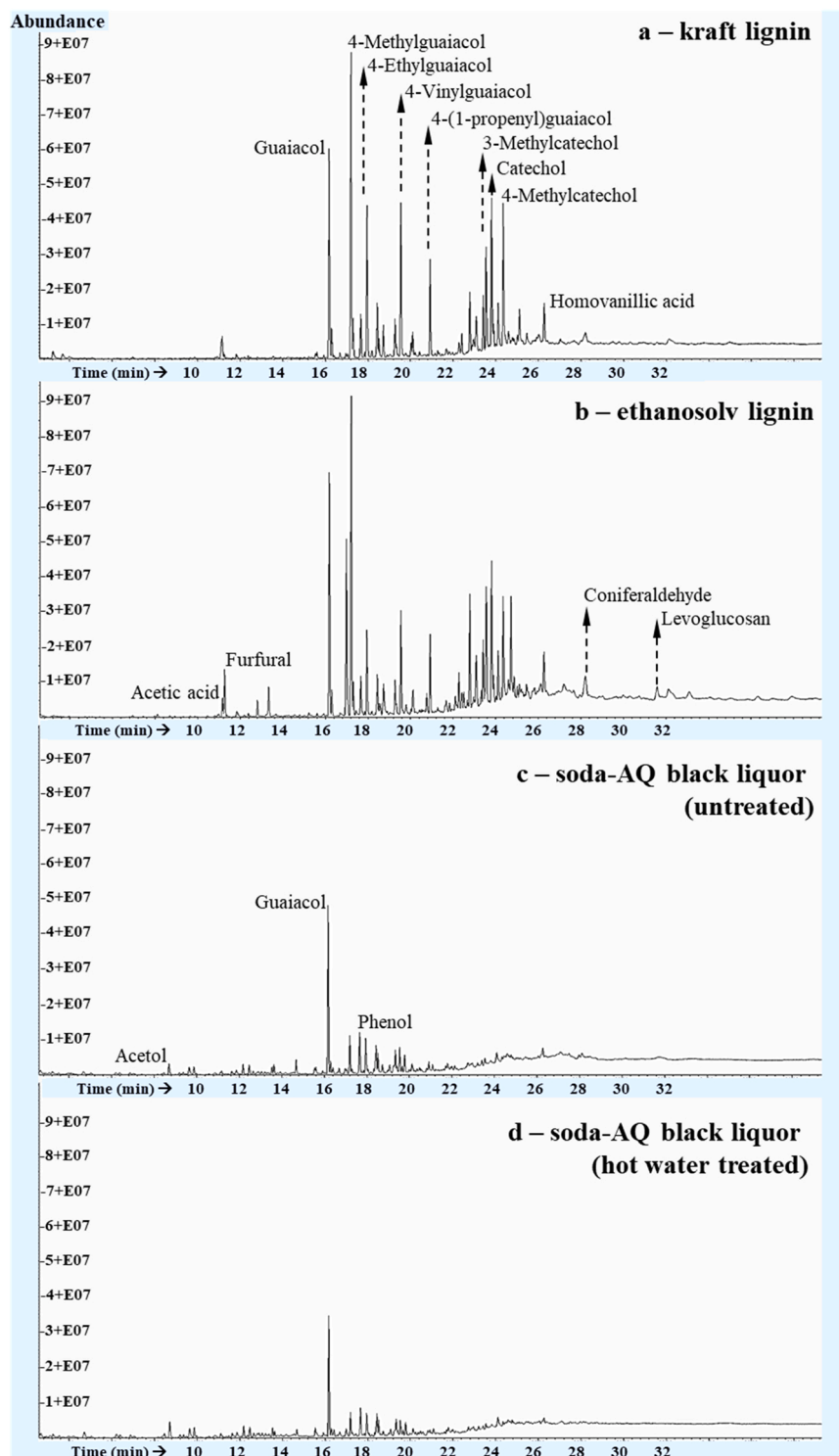
Table 2
Estimated char yields in the Py-GC/MS experiments.

Sample	Sample mass (mg)	Residue after pyrolysis (mg)	Residue (wt%)
Kraft lignin	0.95	0.34	36
Ethanosolv lignin	1.05	0.40	38
Soda-AQ black liquor from untreated sawdust	0.87	0.39	45
Soda-AQ black liquor from hot-water-extracted sawdust	1.07	0.42	39

Fig. 2. Pyrogram at 500 °C of a) kraft lignin, b) ethanosolv lignin, c) black liquor from untreated sawdust (BL_ref) and d) black liquor from hot-water-extracted sawdust (BL_HWE).

quenching using condensation and electrostatic precipitation procedures for the larger-scale BFB and via quick cold trapping for the Py-GC/MS method, whereby progressive formation of non-monomeric compounds via re-polymerization would be less.

The soda-AQ black liquor-derived pyrolysis oil samples could not be prepared by a BFB reactor due to the limited availability of the feedstock materials, the comparison between Py-GC/MS and BFB was restricted to the kraft and ethanosolv lignins.

A comparison of the relative yields of the predominant phenolic groups, guaiacols, alkylphenols, and catechols, was taken into consideration and presented in Fig. 3. For the analytical pyrolysis, the relative yield was the ratio between the cumulative peak area of a certain family of phenols (e.g., the sum of all the peak areas designated to guaiacols) and the total peak area of all the identified compounds. For the pyrolysis oils, the relative yield was the ratio between the cumulative yield of a certain family of phenols (e.g., the sum of all identified and quantified
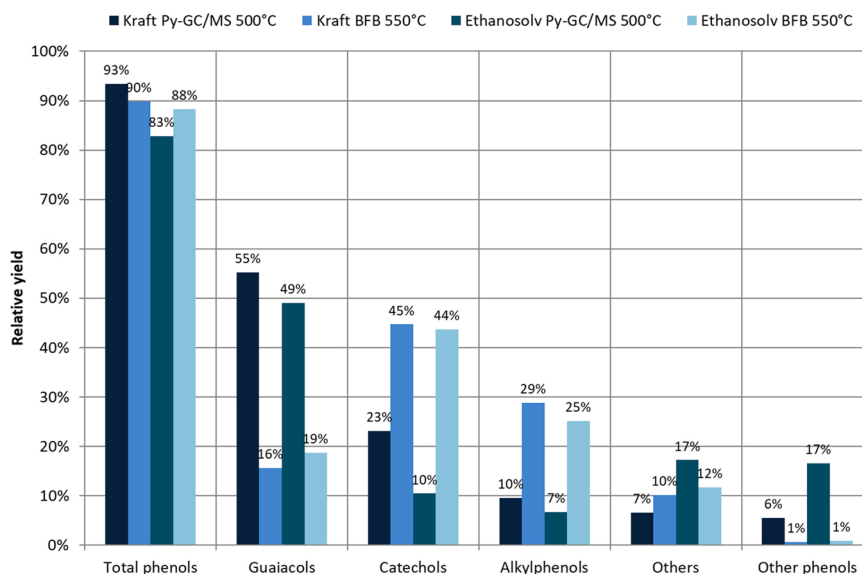
Fig. 3. Comparison of results on oils from kraft lignin (Py-GC/MS), kraft lignin (BFB), ethanosolv lignin (Py-GC/MS) and ethanosolv lignin (BFB).

guaiacols) and the total yield of all identified and quantified compounds as measured by 1D-GC/MS.

For all identified pyrolysis products, the yields from the Py-GC/MS analysis and the 1D GC/MS analysis of the pyrolysis oils are presented in the Supplementary information SI-1a,b and SI-2, respectively.

Py-GC/MS and BFB pyrolysis were only partially comparable in the sense that the same types of phenolic compounds could be detected for both pyrolysis methods. While the difference in total relative yield of phenolic monomers was small and amounted to 3% for kraft to 5% for ethanosolv, differences within the individual phenol groups were much larger. When comparing the pyrolysis results for the kraft lignin with those for ethanosolv lignin, significant differences showed up; analytical pyrolysis of < 1 mg kraft and ethanosolv lignins yielded different product spectra when compared to those of BFB pyrolysis with samples of 500 g, concordant with the work of Butler et al. [39]. Apparently, the longer hot-vapor-residence time in the BFB reactor and the 50 °C higher pyrolysis temperature caused progressive secondary reactions, resulting in the conversion of guaiacols into catechols and alkylphenols, a phenomenon that is known from literature in sequential pyrolysis [52].

In conclusion, analytical pyrolysis provided valuable information about what type of products to be expected from larger-scale experiments. However, it failed in predicting accurate information about the yields of specific products, due to inherent differences in process conditions, such as heating rate and hot-vapor-residence times leading to secondary degradation reaction of the individual monomers. Therefore, further, knowledge on the differences expected allows research to adjust expectations based on Py-GC/MS.

3.3. NMR analyses

HSQC NMR was conducted to provide insight into the structure of the lignin in black liquor samples when compared to the structure of the more extensively degraded lignin in the pyrolysis oils from the kraft and ethanosolv lignins. This was relevant because - while the materials originated from the same Norway spruce feedstock - their preparation occurred via different processes (kraft, ethanosolv and soda-AQ pulping). Structure differences might pose clues to an explanation of the underlying causes for the formation of different pyrolysis products from spruce-derived lignin.

The HSQC NMR data presented in Supplementary information SI-3 clearly revealed a major difference between the pyrolysis oils when compared to the black liquor samples. Typical HSQC NMR data of

pyrolysis oils showed significant aromatic content with aliphatic impurities and small amounts of residual lignin linkages as previously reported elsewhere [45,46]. However, the soda-AQ black liquor samples showed significantly less aromatic content with a significant increase in aliphatic and oxygenated aliphatics. This was expected as the low-molar-mass carbohydrate derived components present in the black liquor samples gave very strong signals. However, the presence of expected guaiacyl units from softwood biomass could clearly be seen in all spectra in Supplementary information SI-3 from the strong signals originating from methoxy-groups (designated by the red signals).

Results from quantitative analysis using ^{13}C NMR are presented in Fig. 4. The NMR spectra revealed the same contrast between the pyrolysis oils and the black liquor samples in terms of the content of aromatics. While the pyrolysis oils showed signals that were attributed to the presence of substantial aromatic contents, these signals were less dominant in the spectra of the black liquor samples due to the presence of sharp signals from low-molar-mass oxygenated aliphatic compounds. Upon integration, the content of oxygenated aliphatics was revealed and tabulated in Table 3. The aromatic carbon content of the black liquor samples was established to be less than half of that of the pyrolysis oils based on both the integration of the aromatic region as well as the signal corresponding to the methoxy signals of guaiacyl units. The analysis by ^{13}C NMR also revealed some differences between the BL_{ref} and BL_{HWE} samples. The BL_{HWE} sample contained slightly more aromatic units compared to that of BL_{ref}. On the other hand, the latter sample seemed to contain more sharp carbonyls signals which indicated the presence of additional carbonyl-containing small molecules.

3.4. 2D-GC/FID analyses

In general, the composition of spruce lignin-derived kraft and ethanosolv pyrolysis oil is very complex. In this study, 2D-GC/FID was conducted to get additional insight into the various GC-detectable product groups present in the lignin pyrolysis oil, especially the formation of phenolic compounds. It allowed rapid assessment of major organic compound classes derived from biomass. In typical 1D-GC/MS analysis, it is likely that several different compounds elute at the same time from the chromatographic separation column, thereby obscuring the identification and quantification of specific individual compounds [47,53]. Representative chromatograms of the products are given in Fig. 5 (including the selected product groups). Results clearly indicated that a good resolution of the main compound groups could be obtained,

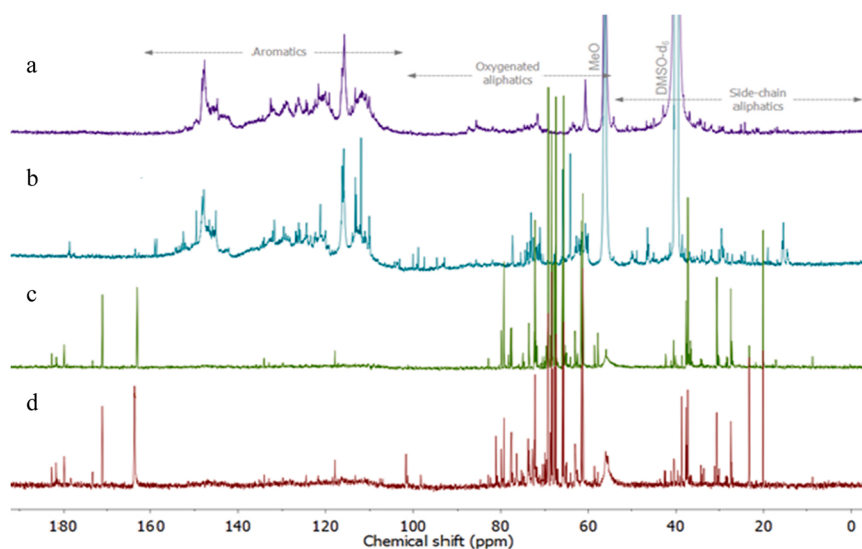**Fig. 4.** Quantitative ^{13}C NMR spectra of a) pyrolysis oil from kraft lignin (DMSO-d_6), b) pyrolysis oil from ethanosolv lignin (DMSO-d_6), c) BL$_{ref}$ (D$_2$O) and d) BL$_{HWE}$ (D$_2$O).

Table 3

Relative contents of aromatic, side-chain aliphatics and oxygenated aliphatics in pyrolysis oils and black liquor samples, together with their methoxy concentrations (% lignin) as obtained from ^{13}C NMR.

Functional group	Kraft	Ethanosolv	BL$_{ref}$	BL$_{HWE}$
Aromatic (%)	73.2	69.3	30.6	31.7
C-H[a]	51.6	43.7	59.6	61.0
C-C[a]	27.7	27.7	22.5	21.5
C-O[a]	20.7	28.6	17.9	17.5
Aliphatic-O (%)	6.0	11.1	49.6	39.4
Aliphatic (%)	1.7	3.5	10.7	10.8
Methoxy-aromatic (% lignin)	19.2	16.1	7.6	9.5
Others (carbonyls, 166–190 ppm)	0	0	1.5	8.6

[a] Relative contents referred to the total aromatic carbon.

thus enabling a distinction between separate regions.

The quantification of various product groups is presented in Table 4 suggesting that the main 2D-GC/FID detectable groups are alkylphenolics, followed by catechols (catechols), methoxy phenols, naphthalenes and acids. A somewhat higher total amount of these products was obtained for ethanosolv pyrolysis oil. However, no significant differences in the relative proportions of the main product groups in kraft and ethanosolv pyrolysis oils were found, indicating similar degradation routes for both lignins.

Table 4 shows that for both GC analysis methods, the amount of GC-detectables in pyrolysis oil (corresponds to wt% of pyrolysis oil) were in line with all quantified groups except to alkylphenolics and catechols, which were the dominant species. Differences could be explained by differences in analysis methods and corresponding calibration protocols. The higher identified and quantified of pyrolysis products from the 2D-GC analysis when compared to the 1D-GC analysis was obviously due to the detection of a larger slate of products within specific families. In Fig. 5, character **c** indicates regions that could not be quantified due to overlapping with unidentified parts and depends on the pyrolysed degree of lignin, thus resulting in a lower amount for catechols and guaiacols. In general, guaiacols were intermediate degradation products, whereas catechol and its derivatives, methyl-, dimethyl-, ethyl- and vinyl-phenols were also formed by secondary decomposition reactions of guaiacols [54].

In this study, a total higher GC-detectables was obtained from pyrolysis of kraft and ethanosolv lignins compared with that shown in the other works. For example, in work [55] only 0.5 wt% of the lignin
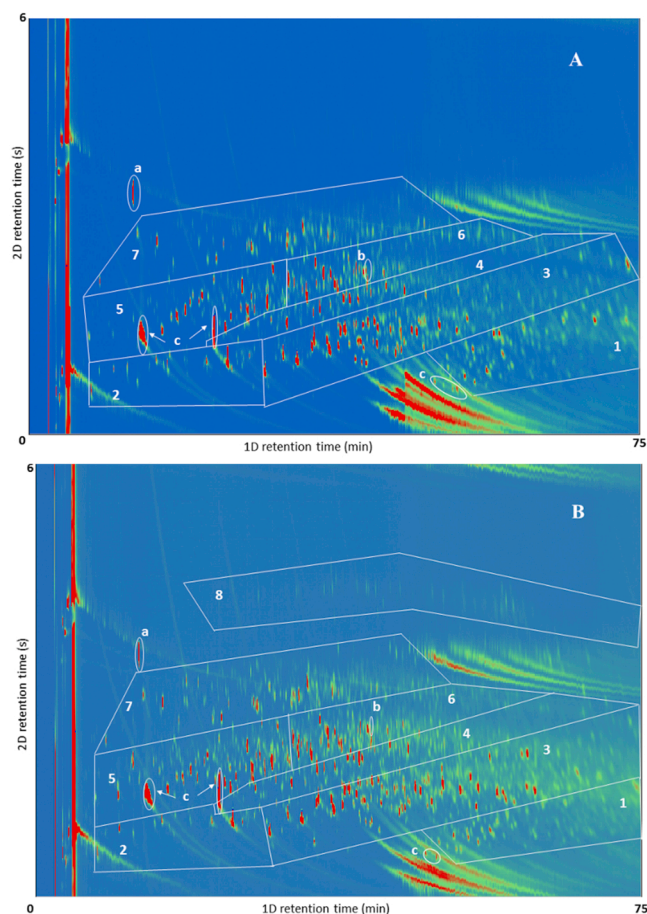

Fig. 5. 2D-GC/FID chromatograms of organic phase from A) kraft pyrolysis (BFB) oil and B) ethanosolv pyrolysis (BFB) oil. 1 Catechols, 2 acids, 3 alkylphenolics, 4 guaiacols, 5 aldehydes/ketones, 6 naphthalenes, 7 aromatics and 8 linear and branched alkanes — a = internal standard (di-n-butyl ether, DBE), b = dibutylhydroxytoluene (BHT, stabiliser in THF) and c unidentified.

fractions has been reported. Also, in the pyrolysis of kraft lignin a maximum (3.22 wt%) of phenolic compounds has been shown [56] as well as about 10% of light oil [57]. The observed results in low

Table 4
The main product groups determined by 1D-GC/MS and 2D-GC/FID from kraft and ethanosolv pyrolysis oils (wt% on pyrolysis oil).

Compound groups	Kraft lignin		Ethanosolv lignin	
	2D-GC/FID	1D-GC/MS	2D-GC/FID	1D-GC/MS
Acids	1.0	0.3	1.6	0.3
Alkanes	–	–	0.01	–
Aldehydes/ketones	0.4	0.1	0.8	0.1
Aromatics	0.6	–	0.8	–
Naphthalenes	1.2	–	1.2	–
Alkylphenolics	6.4	3.6	5.2	2.7
Catechols	2.3	5.5	3.0	4.6
Guaiacols	1.0	1.9	1.7	2.0
Total	12.9	11.4	14.3	9.7

GC-detectable pyrolysis products could be concluded so that the lack of syringyl units in softwood lignin enables more possible branching points, so the formation of a higher amount of cross-linked higher-molar-mass fragments is possible [58,59] which are not detectable by GC. Additionally, as shown in Ref. [60], the presence of condensed structures and small amounts of remaining β-*O*-4 structures prevent the thermal motion of spruce lignin, thereby resulting in low yields of GC-detectable products. Besides, softwood kraft lignin is linked to glucomannan "polymeric glucomannan-lignin complex" and they also are chemically linked to fatty acids, which results in less degradation to low-molar-mass compounds and less detectable by GC [33,61,62]. The delignification process applied in this study was based on essential degradation (kraft and soda-AQ pulping) or mainly "direct dissolution" and partly degradation (ethanosolv cooks) of lignin.

4. Conclusions

In this study, the pyrolytic behavior of different sources of spruce lignin (recovered kraft and ethanosolv lignins and unrecovered lignin in soda-AQ black liquor samples) was compared via analytical pyrolysis. Typically, the pyrolysis oils from kraft and ethanosolv spruce-lignin were complicated mixtures consisting of several (oxygenated) aromatics-containing product groups. However, when aiming at a selective conversion towards guaiacol, the dried soda-AQ black liquor samples seemed to be attractive alternatives. This was corroborated by earlier work on kraft black liquors and it would be an important factor in the purification and upgrading of lignin-derived pyrolysis oils from softwood.

The deployed analytical pyrolysis is a versatile and cheap method on mg scale to screen lignins as a potential feedstock for value-added chemicals. However, this work suggested that its predictive value for larger-scale experiments regarding the g scale-up of lignin pyrolysis is limited. While the type of lignin pyrolysis products that might be produced by larger-scale experiments is accurately predicted by analytical pyrolysis, this is not the case regarding the prediction of yields of these products, due to differences in process conditions. Analytical pyrolysis is a semi-quantitative method and does not necessarily correspond to (quantitative) results from the larger-scale preparative BFB pyrolysis. Hence, for the estimation of the actual valorization potential of lignin in the soda-AQ black liquor samples, the pyrolysis of these samples should be performed with a typical state-of-the-art fast pyrolysis reactor (e.g., a BFB reactor) in forthcoming studies.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jaap.2022.105549.

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