Supriyanto; Usino, David O.; Ylitervo, Päivi; Dou, Jinze; Sipponen, Mika Henrikki; Richards, Tobias

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Identifying the primary reactions and products of fast pyrolysis of alkali lignin

Supriyanto a,b,*, David O. Usino a, Päivi Ylitervo a, Jinze Dou c, Mika Henrikki Sipponen c,d, Tobias Richards a

a Swedish Centre for Resource Recovery, University of Borås, 501 90, Borås, Sweden
b Department of Environmental Engineering, Universitas Islam Indonesia, 55584, Yogyakarta, Indonesia
c Department of Bioproducts and Biosystems, Aalto University, School of Chemical Engineering, Vuorimiehentie 1, 02150, Espoo, Finland
d Department of Materials and Environmental Chemistry, Stockholm University, Svante Arrhenius vag 16 C, SE-106 91, Stockholm, Sweden

Abstract

This study focused on the effect of temperature and residence time on the primary thermal decomposition reactions during a fast pyrolysis of softwood alkali lignin. The use of Py-GC/MS/FID (Micropyrolyser-Gas Chromatography/Mass Spectrometry/Flame Ionization Detector) allowed for rapid heating of the sample and detailed identification and quantification of the pyrolysis products at a temperature range of 400–600 °C, with residence times from 0.5–5 s. The identified primary pyrolysis products were mainly volatile guaiacyl-type compounds. There was a general increase in yield for the majority of the volatile compounds with increased temperature and time. The cleavage of the lignin polymer to linear carbonyl (acetaldehyde) and guaiacyl-type aromatic compounds increased with temperature, while that of catechol and cresol type was mainly favoured at 500 and 600 °C. Based on these results, a mechanistic pathway for the pyrolytic process was proposed, drawing a linkage from structural units of lignin to the formed primary products. In summary, our findings suggest that the primary decomposition reactions that occur under the fast pyrolysis conditions can be controlled by varying the process temperature and residence time, and deliver mechanistic insight into the product distribution from structurally complex lignin material.

Keywords:
Fast pyrolysis
Lignin
Primary reactions
Py-GC/MS/FID

1. Introduction

Pyrolytic decomposition of lignin is an attractive approach to produce aromatic chemicals from a renewable carbon source. One of the critical issues of the fast pyrolysis process is control over the yield and composition of gaseous, liquid and solid product fractions. Fast pyrolysis is a promising technology for thermal conversion of biomass into renewable fuels and chemicals. It requires a high heating rate, low mass transfer resistance, short vapour residence times (less than 2 s) and transfer resistance, short vapour residence times (less than 2 s) and temperature around 500 °C (or in the range of 400–600 °C) to maximise the yield of the pyrolysis oil product [1–3]. Fast pyrolysis of biomass produces hundreds of chemical compounds due to the complex decomposition reactions of the biomass. These reactions can mainly be categorised as primary and secondary reactions. Primary reactions are defined by products obtained directly after the fast pyrolysis [4]. Secondary reactions are reactions that proceed from the primary products in the gas phase. Among the three biomass components (cellulose, hemicellulose and lignin), lignin is the most abundant renewable aromatic compound and can be utilised as a feedstock for the production of high value chemical compounds [5]. Additionally, phenolic compounds produced by lignin pyrolysis are useful chemicals for the pharmaceutical, chemical synthesis and food industry [6].

Lignin is a complex compound that is synthesised by plants from three monophenolic precursors: p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol [5,7,8]. The resulting structural units in the lignin polymer are known as p-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) units and are mainly joined together by ether (C–O–C) and carbon–carbon (C–C) bonds [8–10]. Lignin is amorphous material and its chemical structure and composition depend on the biomass type [4,5]. Lignin exists in three main forms in biomass, and these forms can be found in softwood, hardwood and grass [5]. Softwood lignin contains more G units, hardwood contains a mixture of G and S, while grass wood contains a mixture of all three units H, G and S.

The pyrolysis of lignin results in the production of numerous diverse...
chemical compounds. However, the depolymerisation of lignin to aromatic compounds is very challenging due to its structural diversity and heterogeneity [7]. Additionally, the type of the reactor used for pyrolysis studies can also result in significant variation in the product yield [11]. The primary reactions have been the focus of researchers in order to engineer reactors with rapid heating and removal of the initial products. These reactors are effective in maximising the yield of volatile compounds [11].

A micropyrolyser used together with a gas chromatography (GC) and coupled to a mass spectrometry (MS) or a flame ionisation detector (FID) is becoming an increasingly important tool for fast pyrolysis studies [12], especially for investigating primary reactions and its product [13, 14]. The benefit of performing experiments with a micropyrolyser is that it gives a high heating rate and enables a rapid cooling of the released volatiles and at the same time uses small enough sample size that minimises limitations in internal heat and mass transfer. In the last decade, several investigations have been conducted to understand the influence of operating condition on the product yield and mechanistic pathways from the lignin primary pyrolysis. Jiang et al. [15] and Klemetsrud et al. [16] observed an increase in the yield of the total phenolic compounds with an increase in the temperature from 400 to 600 °C for pyrolysis of different lignin samples with Py-GC/MS. However, while Lazaridis et al. [17] observed an increase in yield from 400 to 500 °C for the pyrolysis of kraft lignin, the yield decreased from 500 to 600 °C to yield alkyl-phenols. Similarly, Patwardhan et al. [14] investigated the pyrolysis of lignin isolated from corn stover, with the use of Py-GC/MS/FID technique in the temperature range of 300–700 °C. They also observed an increase in the yield of the primary products obtained with higher temperatures and a maximum yield at 600 °C. The increased yield with temperature was suggested to be enhanced by demethoxylation at higher temperatures [14]. Lignin pyrolysis has been reported to undergo three main reactions: demethoxylation, demethylation and alklylation reactions [15,18]. In contrast to findings by Patwardhan et al., Jiang et al. and Klemetsrud et al. [14–16], other studies [19–21] observed a decreased yield of guaiacyl hydroxyl compounds from 400 to 700 °C and methoxylated phenols (above 480 °C) for the pyrolysis of kraft lignin and organosolv lignin, respectively. However, these studies showed an increased yield of alkylated phenols [20,21], catechol and m-hydroxy-phenyl hydroxyl compounds at higher temperature [19]. Guaiacyl was suggested to be converted into catechol and phenol at high temperatures [19].

Most of the above studies investigated the effect of temperature on the pyrolysis of lignin. However, considering the effect of residence time on the pyrolysis of pine wood, a decrease in the yield of the phenolic compounds with an increase in the residence time at temperatures of 500 and 550 °C has been reported [22]. The decrease in yield of the methoxylated phenols and phenolic compounds was attributed to secondary reactions in the vapour phase. Additionally, Lin et al. [23] investigated the effect of temperature and time on the pyrolysis of corn stover within a temperature range of 350–650 °C and residence times of 15, 30 and 60 s with Py-GC/MS. While there was an increase in the yield of phenols up to 450 °C, at a pyrolysis time of 30 s the amount decreased slightly at 550 °C. However, at a temperature of 450 °C and residence times of 15, 30 and 60 s, the yield of phenols was observed to reach a maximum at 30 s. Longer pyrolysis time could give rise to secondary reactions [4,24]. In order to understand the primary reactions, the product distribution and pathways derived from lignin have been investigated in the absence of cellulose and hemi-cellulosic components. Recently, Usino et al. [25] investigated primary reactions and products of fast pyrolysis of cellulose and xylan at various temperatures and residence times. However, detailed studies are lacking concerning the influence of temperature and residence time on the initial pyrolysis of lignin.

The aim of this study is to investigate residence time and temperature, the two central parameters of the fast pyrolysis of softwood alkali lignin. Additionally, the main chemical reaction pathways are assessed to gain insight into possible decomposition mechanisms. This information obtained from these systematic studies will be beneficial for the optimisation of the lignin thermochemical conversion processes, in terms of the yield and spectrum of aromatic products derived from the fast pyrolysis of alkali lignin.

2. Material and methods

2.1. Materials and characterisation

Alkali lignin (CAS number 8068-05-1) in powder form was purchased from Sigma-Aldrich, Sweden for this study. It was selected as a model lignin because it is one of the most frequently used commercially available lignins. It was characterised by three techniques, including heteronuclear single quantum coherence (HSQC) NMR spectroscopy, quantitative 31P NMR spectroscopy and high-performance size-exclusion chromatography (HPSEC). The first characterisation was made to correlate aromatic and side chain regions as well as anemic regions of glycosides due to the presence of carbohydrates. The second method was used to quantify the aliphatic and phenolic hydroxyl functional groups as well as carboxylic acid groups of the alkali lignin. HPSEC was used to determine the molecular weight distribution, weight average molecular weight, number average molecular weight and polydispersity index. Detailed characterisation results of lignin are provided in the supplemental material.

2.1.1. HSQC NMR spectroscopy

The solution-state HSQC nuclear magnetic resonance (NMR) experiments were performed in DMSO-d6-pyridine-d5 solvent [26] at 27 °C on a Bruker Avance III spectrometer operating at 400.13 and 100.61 MHz for 1H and 13C, respectively. Chemical shifts (δ) are denoted in ppm, and coupling constants (J values) are given in Hz. The central DMSO solvent peak was used as internal reference (δ 13C 39.5, δ 1H 2.49 ppm). Phase-sensitive 2D 1H–13C HSQC spectra were acquired (spectral widths of 13 ppm for 1H and 165 ppm for 13C) using a relaxation delay of 2 s, 1 K data points, 256 t1 increments and 64 transients. An adiabatic version of the HSQC experiment was used (hsqcetgpsip.2 pulse sequence from the Bruker Library) in order to improve the peak sensitivity.

2.1.2. Quantitative 31P NMR spectroscopy

Alkali lignin was analysed by quantitative 31P NMR spectroscopy [27]. The sample preparation and analysis have been described in detail in the literature [28]. Two replicated experiments were conducted, and the mean values with one standard deviation are reported.

2.1.3. Size-exclusion chromatography

The molecular weight distribution, weight average molecular weight (Mw), number average molecular weight (Mn) and dispersity (Mw/Mn) of alkali lignin were analysed by aqueous size-exclusion chromatography (SEC) using 0.1 M sodium hydroxide as eluent. The SEC columns were PSS MCX 8 × 300 mm, particle diameter 5 μm of pore size 100, 500 and 1000 Å connected in series. An injection volume of 50 μL was used for standards and alkali lignin solution. The column effluent was monitored at 30 °C using a UV detector operated at 280 nm. This gave a Mw of 5832 g/mol, a Mn of 1394 g/mol and dispersity of 4.18.

2.2. Py-GC/MS/FID

Prior to the pyrolysis studies, the lignin sample was pressed into small pellets and weighed on an analytical balance (KERN ABT 320-4M). Close to 500 μg of sample was pyrolysed at temperatures of 400, 500, and 600 °C and residence times of 0.5, 1, 2 and 5 s using a micro-pyrolyser, Pyrolab2000 (Pyrolab, Sweden). The micropyrolyser unit is comprised of a platinum filament, which was calibrated to the desired temperature range before conducting the experiment. A small cavity was
made at the centre of the platinum filament to ensure that the sample remains in the same position during heating of the filament. The temperature of the micropyrolyser chamber and transfer tube to GC was 150 °C. Further description of this set up is found elsewhere [25].

The helium gas flow rate in the column was 1.5 mL min⁻¹ with a split ratio of 1:7 to the GC, and the temperature was 200 °C in the injector. The gas released during the thermal decomposition of the lignin sample was directly transferred to the GC (Trace GC Ultra) for separation. The GC uses a capillary column (Zebron™ ZB-5MS, 30 m x 0.25 mm x 0.25 μm) with column phase of 5% phenyl-arylene and 95% dimethylpolysiloxane. The GC oven temperature programme was set at 60 °C for 1 min and then heated at 8 °C/min to 265 °C by a hold of 20 min. Identification and quantification of volatile compounds were made by a ISQ™ Series Single Quadrupole MS (mass spectrometry) and a FID (flame ionisation detector), respectively. The MS transfer line and the FID base temperature were set at 250 °C, while the ion source temperature was 200 °C. The MS was in electron ionisation mode (EI), and the scan was between 16–650 m/z. The NIST Library (NIST MS Search 2.0) was used to identify the major peaks. Each condition was repeated at least three times to assess reproducibility. The volatile compounds identified were based on the consistent peaks shown in the GC-FID chromatograms, while the inconsistent peaks have not been accounted for because they were very small. The difference in the temperature profile between the initial filament calibration (with no sample) and final filament temperature (with sample) accounts for less than 5%, on average, of the final pyrolysis temperature.

In order to compare the amount of volatile compounds, both within the same experiment and between different experiments, the response of each volatile compound was determined. It was calculated by multiplying the relative response factor (RRF) with the FID area of the identified volatile compound and then dividing by the mass of the sample (Eq. 1). The RRF was derived by dividing the response factor (RF) of each individual volatile compound by the total response factor of all identified volatile compounds (Eq. 2). In addition, the RF (Eq. 3) was calculated based on the Effective Carbon Number (ECN) and a mixture of standard solution, i.e. acetic acid (CAS number 64-19-7, Sigma-Aldrich), phenol (CAS number 108-95-2, Sigma-Aldrich) and vanillin (CAS number 121-33-5, Sigma-Aldrich) with acetone (CAS number 67-64-1, Sigma-Aldrich) as solvent. ECN is described as the number of effective carbons in a molecule [29]. It gives the same FID response, relative to its aliphatic equivalent.

\[
\text{Response, counts/μg} = \frac{\text{RRF} \times \text{Area}_{\text{comp}}}{\text{sample weight}}
\]  

\[
\text{RRF} = \frac{\text{RF}_{\text{comp}}}{\text{RF}_{\text{total}}}
\]  

\[
\text{RF} = \left(\frac{\text{MW}_{\text{ref}}}{\text{MW}_{\text{comp}}} \times \frac{\text{ECN}_{\text{comp}}}{\text{ECN}_{\text{ref}}}\right)\times (\text{ECN}_{\text{ref}})
\]

Where RRF = Relative Response Factor, RF = Response Factor, ECN = Effective Carbon Number, MW = Molecular Weight, ref = reference, comp = compound

3. Results and discussion

3.1. Lignin characterisation

The HSQC NMR spectroscopy provides important structural understanding of the chemical structure of the complex starting material alkali lignin. The HSQC ¹H-¹³C correlations depicted in Fig. 1 shows that the alkali lignin consists of aromatic/unsaturated (δC/δH, 96-146/6.0-8.2 ppm) and side chain (δC/δH, 48-92/2.0-6.0 ppm) regions based on the reference literature [26,30–32]. The methoxyl group and the β-aryl

Fig. 1. Aromatic/unsaturated (δC/δH 96-146/6.0-8.2 ppm) (left) and side chain (δC/δH 48-92/2.0-6.0 ppm) (right) regions in the 2D HSQC NMR spectra of alkali lignin. See Table A1 in Appendix for signal assignments.
ether were observed to be the dominant side chains. The correlation peaks of the methoxyl groups were at $\delta_C/\delta_H$ of 55.3/3.76 ppm, while that of $\beta$-aryl ether in the C$_7$-H$_8$ and C$_8$-H$_9$ were at $\delta_C/\delta_H$ of 84.2/4.41 and 59.7-60.1/3.49-3.73 ppm, respectively. In addition, C$_{\text{ar}}$-H$_{\text{ar}}$, C$_{\text{ar}}$-H$_{\text{ir}}$, and C$_{\text{ir}}$-H$_{\text{ir}}$ correlations in the phenylcoumaran were observed at $\delta_C/\delta_H$ of 86.6/5.58, 53.3/3.50, and 62.4/3.80 ppm, respectively. The correlations of the resinol ($\beta$-$\beta$) was at $\delta_C/\delta_H$ of 84.9/4.66, 53.6/3.06, and 70.4-70.8/3.76-4.15 ppm for C$_{\text{ar}}$-H$_{\text{ar}}$, C$_{\text{ar}}$-H$_{\text{ir}}$, and C$_{\text{ir}}$-H$_{\text{ir}}$, respectively. The unsaturated C$_{\text{ar}}$-H$_{\text{ir}}$ correlation of cinnamyl alcohol end-groups at 61.5-64.1 ppm was also observed.

The main signals in the aromatic region of the 2D HSQC spectra of alkali lignin originated from G units of lignin. The G units exhibited C$_2$-H$_2$ correlation at $\delta_C/\delta_H$ of 109.9/110.6/6.97-7.19 ppm and C$_2$-H$_3$ and C$_2$-H$_4$ correlations at $\delta_C/\delta_H$ of 115.1-119.4 and 6.79-7.01 ppm.

The anemic region of the HSQC spectra depicted in Fig. 2 showed that the glycoside centres of the initial alkali lignin exhibited the presence of carbohydrate compounds. This was observed at the correlations peak in the $\delta_C/\delta_H$ 101.7/4.39 ppm regions for cellulose ($\beta$-D-glucopyranoside), while that of hemicellulose was observed at 105.6/4.41 ($\beta$-D-galactopyranoside), 106.1/4.93 and 109.2/5.58 ppm ($\alpha$-L-arabinofuranoside), respectively.

Quantitative $^3$P NMR spectroscopy delivers information about the hydroxyl group functionalities present in the alkali lignin. Fig. 3 shows that the main functional groups of the alkali lignin are aliphatic hydroxyl, carboxylic acid and phenolic hydroxyl, while the main phenolic units are of G-type (guaiacyl unit) with a minor amount of H-units (p-hydroxyphenyl unit). In addition, the H/G ratio was 0.088 (H, 0.27 mmol/g lignin and G, 3.08 mmol/g lignin). All of these results are typical features of softwood alkali lignin.

### 3.2. Influence of temperature and time on the pyrolysis of lignin

Fast pyrolysis of softwood alkali lignin was carried out to identify primary decomposition reactions and types of volatile products. Temperature and time had a significant influence on the yield and distribution of product from pyrolysis of lignin. The main class of products was phenolic compounds with guaiacyl type compounds, as seen in the overall product distribution in Table S5 (supplementary material). The guaiacyl unit has been shown to be the dominant unit in softwood alkali lignin [33–36]. The mass spectrum of identified volatile compounds, Table S4 and the GC-FID chromatograms for the different operating conditions investigated, Figure S3-S13, are provided in the supplementary material. Fig. 4 shows the GC-FID chromatogram for the product distribution from the fast pyrolysis of lignin at 600 °C and 5 s. Over 20 peaks were shown in the GC-FID chromatogram, of which nineteen different compounds were identified and numbered as primary products from the fast pyrolysis of lignin. As seen in Fig. 4, 2-methoxy-4-methylphenol (7), Acetaldehyde (1), 2-methoxy-4-vinylphenol (11), 2-methoxyphenol (5) were the major products formed at 600 °C and 5 s.

Fig. 5 gives an overview of the main decomposition products released during the pyrolysis of lignin at temperatures of 400–600 °C and residence time of 0.5–5 s. As observed, there was a general increase in the yield for majority of the volatile compounds with increased temperature and time. This is similar to the result presented in the literature [1,14–16,37–40]. However, these studies did not include the influence of residence time on the yield of the primary products. In contrast, other studies [11,19–22] observed a drop in yield with temperature, for the majority of the phenolic compounds (especially the methoxylated phenol compounds). The decrease in yield with temperature was attributed to longer residence time [11] and secondary reactions in the vapour phase [20]. The consistent increase in yield with temperature and time observed in the current study suggests that mainly primary reactions took place in the reactor zone.

At 400 °C, the amount of transferred energy to the lignin sample was low; hence, the resultant low yield of the volatile compounds. In addition to the volatile products, some of the less volatile compounds condensed on the glass cell possibly due to the low temperature of the gas phase when in contact with the glass cell, but this was only a minor amount. The substrate left on the filament has not been accounted for in this study since the primary focus was on the produced volatile compounds. As confirmed by the $^3$P NMR analysis alkali lignin contained carboxylic acid groups and other hydroxyl functionalities that need to be eliminated to render the resulting phenolic fragments volatile. When the temperature was increased to a range between 500 °C–600 °C, there was a significant increase in the yield of volatile products. This indicates that there was sufficient energy to cleave oxygen rich functional groups and lignin inter-unit linkages. Our observation is in line with earlier works on pyrolysis of Kraft lignin [41], where a similar increase in yield was reported at a temperature range of 500–650 °C. The main volatile compounds produced in all operating conditions investigated in the current study were 4-ethyl-2-methoxyphenol, vanillin, 2-methoxyphe- nol, 2-methoxy-4-vinylphenol, acetaldehyde, and 2-methoxy-4-methylphenol, in order of increasing yield. From Fig. 5, it is evident that at a pyrolysis time of 0.5 s, the yield of the main volatile compounds was very small. At this short pyrolysis time, it is probably difficult to have complete conversion of the biomass due to the low energy input to the biomass surface [24]. At the lowest temperature (400 °C) and the longest residence time (5 s), 2-methoxy-4-vinylphenol was the main

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**Fig. 2.** Anomeric region of glycosides ($\delta_C/\delta_H$ of 96-112/4.0-5.9 ppm) in HSQC spectra of alkali lignin in DMSO-d$_6$/pyridine-d$_5$ (4:1). With colour codes of (blue) cellulose and (red) hemicellulose. $\beta$-D-Glcp, $\beta$-D-glucopyranoside; $\beta$-D-Galp, $\beta$-D-galactopyranoside; $\alpha$-L-Araph, $\alpha$-L-arabinofuranoside.

**Fig. 3.** Distribution of aliphatic hydroxyl, carboxylic acid and phenolic hydroxyl groups in alkali lignin. Error bars represent one standard deviation from the mean values of two replicate quantitative $^3$P NMR experiments.
chemical compound formed. However, increasing the temperature from 500 to 600 °C and the residence time from 1 to 5 s resulted mainly in the formation of 2-methoxy-4-methylphenol. This shows that the production of 2-methoxy-4-vinylphenol is favoured at lower temperatures, while 2-methoxy-4-methylphenol is favoured at higher temperature region of 500–600 °C.

In addition to the effect of temperature, there was a clear effect of residence time on the pyrolytic products. Fig. 6 shows a significant increase in the yield from 0.5 to 1 s both at 500 °C and 600 °C for the main chemical compounds. While there was a noticeable increase in the yield from 1 to 5 s at 500 °C, there was, however, a stable yield at 600 °C from 1 s to 5 s, indicating that the conversion of the lignin had reached equilibrium. This implies that mainly primary products from thermal decomposition of lignin were formed under these condition. This is in agreement with the literature [14,15,42], where a maximum yield was achieved at 600 °C for the formed phenolic compounds (mainly the methoxylated phenols). This temperature optimum also gives a reasonable choice of temperature to investigate the primary reactions.

Temperatures of 400–600 °C have been noted to give a maximum bio-oil yield, depending on the biomass type [21,24]. Comparing the yield at 5 s, going from 500 and 600 °C, a slight decrease is observed for 4-ethyl-2-methoxyphenol, 2-methoxyphenol, 2-methoxy-4-vinylphenol and 2-methoxy-4-methylphenol. These differences suggest a competitive reaction pathway for these compounds, with a higher yield at 500 °C than at 600 °C. However, the yield was stable for vanillin, while acetaldehyde showed a significant increase in the product yield with increasing temperature at 5 s. This, together with the result of stable production at residence times longer than 1 s at 600 °C, implies that there were minimal secondary reactions and that negligible conversion of the solid material to this type of six main products occurred any longer. Therefore, the results presented here show that by controlling the temperature and residence time of pyrolysis there is a good possibility at minimising secondary reactions. Longer residence time and very high temperature have been shown to give secondary reactions, resulting in the reduction of phenolic products from pyrolysis of kraft lignin [4]. It is worth noting that the current work was an increase in the number of volatile compounds released, with an increase in time and temperature as seen in Table S5 (supplementary material).

In addition, by adding all the different volatile chemical compounds together, as shown in Fig. 7, it can be observed that the yields of the

Fig. 4. Chromatogram (GC-FID) of lignin pyrolysis at 600 °C, 5 s. The six main components are: (1) Acetaldehyde; (5) 2-methoxyphenol; (7) 2-methoxy-4-methylphenol; (9) 4-ethyl-2-methoxyphenol; (11) 2-methoxy-4-vinylphenol; (14) vanillin.

Fig. 5. The effect of pyrolysis temperature and time on the product distribution of lignin. The response (i.e. FID count/μg sample) has been calculated based on the response factor. The error bars show one standard deviation from the mean values.
different groups increased with temperature and residence time from 400 to 500 °C and 0.5–5 s and remained stable at 600 °C and 1–5 s.

3.3. Mechanism of lignin pyrolysis

The yield and distribution of products obtained from the pyrolysis of lignin are influenced by a number of factors: the origin of lignin, the pyrolysis conditions, and the presence of impurities and carbohydrates [43]. Thus, the product distribution might vary from one type of lignin material to another even if its structure is composed of the same main building blocks. The structural units of lignin are phenyl propane units that are bonded by C–O and C–C bonds [44]. β-aryl ether (β-O-4) is the most common linkage in native lignin, but the thermochemical pulping process cleaves the majority of these linkages and creates more stable ones, including C–C bonds [45]. However, only approximately half of all the available linkages have been identified, for instance, in kraft lignin [45]. Furthermore, the alkali lignin used in this study has been shown to contain about 3% of inorganic impurities. Although quite low in concentration, these impurities could give rise to reactive species as the initial pyrolysis products that undergo further reactions among themselves, resulting in the formation of linkages that are not present in the original sample [46]. Also, the presence of inorganic impurities could act as a catalyst that promotes the rate of degradation (cleavage) or pyrolysis [47].

The cleavage of the bond structure with increasing temperature (400–600 °C) indicates that the primary decomposition reactions were influenced by the bond strength (bond dissociation energy (BDE)). Hence, at a low pyrolysis temperature (400 °C), the scission of the β-O-4 linkages was initiated by the cleavage of ether (C–O) bond (BDE 291 kJ/mol) because of its low BDE, which was followed by the cleavage of the C–C bond (BDE 323 kJ/mol) at high temperature (600 °C) to form condensable volatile compounds [48–50]. Although the BDEs have

![Fig. 6. The effect of pyrolysis temperature and time on the total response of 4-ethyl-2-methoxyphenol; vanillin; 2-methoxyphenol; 2-methoxy-4-vinylphenol; acetaldehyde; 2-methoxy-4-methyl-phenol.](image-url)
C radicals were generated from reactions of aliphatic side chain [9]. Additionally, the characterisation of the aliphatic side chain demethylation for both catechol and cresol type compounds, resulting from the depolymerisation reaction [18]. Alternatively, cresol type phenolic compounds are suggested to be formed by depolymerisation and dehydration reactions (P3) from the p-hydroxyphenyl unit [55]. However, acetaldehyde is suggested to be formed mainly by dehydration and fragmentation from the carbohydrates present in lignin (P8), with a small fraction from the fragmentation of the lignin side chain (P7). Formation of acetaldehyde has been observed in a previous study on the pyrolysis of alkali lignin from 400 to 700 °C but only in a minor amount compared to that of the aromatic compounds [33]. Other studies have also reported evidence of acetaldehyde from cellulose and hemicellulose pyrolysis with a similar experimental set-up [25,56,57]. Likewise, measurements made (NREL protocol) on the alkali lignin used for this investigation gave acid-insoluble Klason lignin of 80 % and content of hemicellulose sugars of about 3.6 %, which supports the evidence of polysaccharides a source of acetaldehyde. In addition, dehydration (P1 and P8) produced water, which originated from the hydroxyl groups present in the aliphatic side chains of lignin when hydrogen radicals reacted with hydroxyl radicals. Subsequently, methyl radicals originated from demethylation of guaiacyl units (P2), which reacted with either hydrogen or hydroxyls radicals in order to produce methane or methanol, respectively [9].

Table S5 (supplementary material) shows that there were compositional changes in the volatile compounds formed, depending on the residence time in the reactor. Some chemical compounds, such as the guaiacyl and cresol (4-methylphenol), were initially formed in the solid material, while others, such as the catechol, phenol and cresol compounds (phenol, 2-methylphenol and 2, 5-dimethylphenol), were formed at longer residence times, suggesting the occurrence of secondary reactions that were, however, out of the scope of the present study.

### 4. Conclusion

The effect of temperature and residence time on the pyrolysis of alkali lignin was conducted with Py-GC–MS/FID in order to gain understanding on the primary reactions. The main volatile compounds formed were 2-methoxy-4-methyl-phenol, acetaldehyde, 2-methoxy-4-vinylphenol, 2-methoxyphenol, vanillin and 4-ethyl-2-methoxyphenol, and these were observed to increase with time and temperature. These volatile compounds were the products of primary decomposition of alkali lignin, and secondary reactions were minimised in the experimental set-up. The proposed decomposition pathways for alkali lignin are depolymerisation and dehydration reactions (guaiacyl type compounds), demethylation reactions (catechol type compounds) and demethoxylation reaction (cresol and phenol type compounds) from guaiacyl units. An alternative route to cresol and phenol type compounds was by depolymerisation reaction and side-chain fragmentation of the p-hydroxyphenyl units. Acetaldehyde was shown to be formed by fragmentation of lignin side-chains and the carbohydrate impurities in the alkali lignin. The results presented in this study give insight into possible decomposition mechanisms of alkali lignin for the production of specific aromatic compounds by fast pyrolysis and show that this technique is reliable for investigating the primary reactions.
Fig. 8. Suggested primary reactions of softwood alkali lignin pyrolysis consisted of depolymerisation and dehydration (P1), side chain scission and demethylation (P2), depolymerisation (P3 and P4), demethoxylation (P5), side chain scission and demethoxylation (P6), fragmentation of lignin side chains (P7), dehydration and fragmentation of carbohydrate (P8). Dash line (green) indicates the site of cleavage of demethylation and demethoxylation. Structure of the initial alkali lignin has been modified from Karunarathna et al. [48].

Author statement

1 Conceived the original idea: Tobias Richards
2 Idea was developed: Tobias Richards, Supriyanto and David O. Usino
3 Experiment was carried out: Supriyanto and David O. Usino (Py-GC/MS/FID), Jinze Dou (2D HSQC NMR spectroscopy), Mika Henrikki Sipponen (quantitative 31P NMR spectroscopy and SEC)
4 Acquisition of data and drafting of manuscript: Supriyanto and David O. Usino
5 Revising and editing of manuscript: Supriyanto, David O. Usino, Päivi Ylitervo, Jinze Dou, Mika Henrikki Sipponen and Tobias Richards
6 Critical feedback, shaping of the research, analysis and manuscript: Päivi Ylitervo, Jinze Dou, Mika Henrikki Sipponen and Tobias Richards
7 Project supervision: Päivi Ylitervo, Mika Henrikki Sipponen and Tobias Richards

Declaration of Competing Interest

The authors report no declarations of interest.

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Supplementary data

Supplementary material related to this article can be found, in the online version, at:https://doi.org/10.1016/j.jaap.2020.104917.

References


