Full Length Article

Characterization of pyrolytic lignin and insight into its formation mechanisms using novel techniques and DFT method

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ABSTRACT

Real pyrolytic lignin (R-PLs) and pyrolytic products from model compounds (M-PL) were characterized by HPLC/Qtof-MS, GPC and 2D HSQC NMR to acquire molecular information. A huge amount of molecules were detected, analyzed and sorted into several categories according to their properties. Most compounds in R-PLs have complicated sidechains, with high molecular weight (MW) but moderate ring double bond equivalent (RDB), which might be derivatives of lignin fragments. The low MW fractions of R-PLs are considered as lignin simple monomers (LSM) and their derivatives, because the peaks of R-PLs and M-PL within low MW range of GPC are proximal. Molecules with medium MW but pretty high RDB, supposed to be coke/PAHs, were found more in M-PL than R-PLs, indicating that coke/PAHs primarily derive from LSM. Formation mechanisms of PL were proposed based on the differences between R-PLs and M-PL, which were supported by density functional theory (DFT) calculation. The results provide an in-depth understanding of pyrolytic lignin and inspire studies on high-value utilization of pyrolytic lignin.

1. Introduction

Among all kinds of renewable resources, biomass is the exclusive renewable resource which can be further converted into liquid vehicle fuels [1,2]. Bio-oil can be obtained through fast pyrolysis of biomass, which is known as crude bio-oil [3–5]. Through cold water extraction, bio-oil will be divided into two parts, water-soluble fraction and water-insoluble fraction. Generally speaking, water-soluble part mainly includes acids, ketones, aldehydes, alcohols etc., which can be easily converted [6]. As for the water-insoluble fraction, they are primarily
lignin-derived compounds with relatively higher molecular weight, and take up about 25–30 wt% in bio-oil [7], which are known as phenolic oligomers or pyrolytic lignin (PL) [8–10]. On one hand, pyrolytic lignin is an important component of bio-oil, and has significant influence on properties of bio-oil, such as increasing the instability of crude bio-oil.

To make better use of bio-oil, separating pyrolytic lignin from the liquid bio-oil becomes increasingly important. On the other hand, pyrolytic lignin has high carbon content and natural aromatic structures, so it is a renewable resource of significant potential for producing high-quality liquid fuels or high-valued platform chemicals, such as BTEX [11,12].
However, lignin is normally treated as waste or burnt for energy recovery [12], especially for pyrolytic lignin, which may lower the carbon efficiency and increase the cost of biomass utilization. To maximize the value of biomass conversion, it is crucial to characterize pyrolytic lignin and figure out its formation mechanisms. With this knowledge, more proper techniques will be developed to avoid original formation of PL or further convert it into value-added alternatives.

There is a continuous debate on the mechanism of formation of pyrolytic lignin. Some scholars support for Thermal-mechanical Ejection theory [13] that phenolic oligomers are lignin fractions formed from partially breaks of lignin and then carried by the gas flow. However, it is also proposed that pyrolytic lignin is the result of random recombination and condensation of phenolic monomers that generated during primary pyrolysis of biomass, because some linkages found in

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**Fig. 2.** Van Krevelen Diagrams of RS-PL & M-PL. Since molecules in PL primarily consist of C, H and O elements, here $A. I. = \frac{1.5 C - 0.5O - 0.3H}{C - O}$ [24].
pyrolytic lignin do not exist in lignin [14]. Although some researches [14–18] have been carried out to study the pyrolytic process of lignin, including analyzing its final products or pyrolytic vapor, the exact structures of pyrolytic lignin and the formation mechanisms during pyrolysis still remain unclear, most conclusions are primarily based on prediction. In addition, GC/MS test is the predominant method for pyrolytic lignin analysis, but this method has some limitations in detection of larger molecules that are difficult to volatilize, so that some vital information may be missed in this way.

To obtain an in-depth knowledge on compositions and structures of pyrolytic lignin, three analytical methods HPLC/Qtof-MS, GPC and $^1$H-$^1$C HSQC NMR were applied in this paper for characterization of three kinds of real pyrolytic lignin (R-PLs). Meanwhile, three simple phenolic monomers (guaiacol, eugenol, and vanillin) were used to simulate pyrolytic vapors to obtain model pyrolytic lignin product (M-PL). Through comparison of data of R-PLs and M-PL, mechanisms of formation of phenolic oligomers could be explained. Furthermore, DFT calculation was performed as well to give a theoretical explanation of formation of pyrolytic lignin. As the experimental methods are not sufficient for explaining the detailed reaction process, DFT method will be a great tool to deduce formation routes of typical pyrolytic lignin, and is of significant help for understanding reaction mechanisms. In this work, the structures of pyrolytic lignin are confirmed and formation mechanisms of them are proposed according to the results of all the analysis and theoretic calculation mentioned above, which provide a new sight of pyrolytic lignin. The conclusion that relatively low coke/PAHs are contained in pyrolytic lignin gives confidence to those researchers who have devoted to make high-value utilization of pyrolytic lignin.

### 2. Material and methods

#### 2.1. Materials

Bio-oils of the following feedstock: rice straw, cotton stem, and walnut shell, were produced on the CFB facility of University of Science and Technology of China, China. The model compounds guaiacol, eugenol, vanillin and acetic acid used in this work were purchased from Sigma Aldrich Company. The solvents methanol (MeOH), dichloromethane (DCM) and tetrahydrofuran (THF) were produced by Sinopharm Chemical Reagent Co., Ltd.

#### 2.2. Real pyrolytic lignin (R-PLs)

Three kinds of pyrolytic lignin were obtained from the bio-oils using the precipitation method which was similar to the method of Scholze and Meier [19]. The heaviest part of bio-oil was collected from the bottom of container, and then was added into deionized water dropwise with continuous stirring using a homogenizer in cold water. After that, the mixture was filtered and the precipitate was dried under room temperature. Finally, three kinds of pyrolytic lignin from rice straw (RS-PL), cotton stem (CS-PL), and walnut shells (WS-PL) were obtained as black fine powder.
2.3. Pyrolytic products from model compounds (M-PL)

The equipment for pyrolysis of model compounds was illustrated in Fig. S1. Guaiacol, eugenol and vanillin (molar ratio 1:1:1) were mixed together as model compounds of lignin simple monomers (LSM), and acetic acid was also added with molar ratio 10:1 to each model compounds to simulate an acidic environment. The mixture (0.1 mL) was added into a test tube connected to a bend tube with a rubber hose. An airbag was put at the end of the rubber hose. The whole system was sealed and vaccumized. The test tube with model compounds was put into a vertical tube furnace for pyrolysis at 550°C for 2 min with intermediate heating rate of ~10 K/min. After that, it was cooled down under room temperature and the products were washed using MeOH and DCM. The solvent was then evaporated with rotary evaporator under room temperature. Finally, model pyrolytic lignin product (M-PL) was obtained as solids.

2.4. HPLC/Qtof-MS, GPC and 2D HSQC NMR test

Waters UPLC (Waters Corp., Milford, MA, USA) equipped with Agilent SB-C18 column (3.5 μm, 2.1 × 100 mm; Agilent Corp.) and UV detector (254 nm) was used in all the HPLC/Qtof-MS tests. The distribution of molecular weight of R-PLs and M-PL was determined by GPC (Waters 1525/2414). The linkages of R-PLs and M-PL were characterized by 2D 1H–13C HSQC NMR, which was carried out on an Agilent 600 MHz DD2 (DirectDrive2) spectrometer. The detailed methods were shown in Supplementary Materials.

2.5. DFT calculation

All calculations were carried out using the Gaussian 03 suite of program (Gaussian Inc., USA). The equilibrium geometries of reactants, intermediates, transition states, and products were optimized using density functional theory (DFT) methods employing B3LYP/6-31G(d) [20]. Single point energies were calculated with a larger 6-311+G(d,p) basis set at the same level of theory. The transition states were located by the TS method and were determined by the presence of merely one imaginary frequency and by performing intrinsic reaction coordinate (IRC) calculations to ensure that the established transition states connect the right reactants and products. Meanwhile, the reactants, intermediates, and products were confirmed by all real vibration frequencies. Activation energies (the reaction energy barriers) of reaction were estimated based on the energy difference, including the zero-point energy correction (ZPE) [21], between the transition state and the reactant. For free-radical reactions, the bond dissociation energies (BDE) were employed as approximations of the activation
energies.

3. Results and discussion

3.1. Compounds analysis via HPLC/Qtof-MS

All samples were dissolved in methanol for the test. In this experiment, only the compounds with molecular weight higher than 100 Da would be detected. The Total Ion Chromatogram (TIC) of RS-PL, CS-PL, WS-PL, and M-PL were displayed in Supplementary Materials, see Fig. S2.

Since the three R-PLs samples were substantially the same, RS-PL was selected as representative for R-PLs to compare with M-PL in detail. The in-depth analyses and comparisons mainly included molecular formula, molecular weight (MW) distribution, ring double bond equivalent (RDB). All molecules with peak intensity > 100 were extracted from RS-PL and M-PL by XIC Manager. Among all the detected molecules, the authentic ones were filtered by limiting the Retain Time Error within 5% and the Mass Error within 5 ppm. Furthermore, the Molecular formulas of the two samples were determined applying the Kendrick Mass Defect analysis [22,23]. The mass ratio of C, H, and O of each molecule could be calculated by molecular formula. It was found that the ratio of C was about 70 wt% maximally and the ratio of O was about 25 wt% for most molecules in RS-PL, which was consistent with the content of C and H in phenolic oligomers reported in the previous literatures [19]. RDB of the compounds would be calculated by the identified molecular formulas either. RDB embodies the unsaturation of organic molecules. Referring to previous literature [14], molecules with RDB < 8 were generally considered to be monomers, with 8 ≤ RDB < 12 to be dimers, and with RDB ≥ 12 to be trimers, polymers or PAHs/coke.

As shown in the Fig. 1, the plots are general view of distribution of molecules in RS-PL and M-PL samples. RS-PL plot could be divided into several regions. RT = 7.5 min and RT = 12.5 min were the times when dimers began to appear apparently and monomers began to disappear obviously. Similarly, MW = 165 Da, MW = 275 Da and MW = 450 Da were the molecular weights at which dimers began to appear visibly, monomers began to largely disappear, and all molecules started to vanish significantly, respectively. The plot of M-PL was separated in the same way as the RS-PL, and then the molecular properties of each region would be summarized and compared.

It can be seen from the figure that a large number of molecules exist in the RS-PL (1). Since the MW of the molecules in this region is relatively large and RDB is < 8, they should be mainly phenolic monomers with complicated sidechains, here named as lignin complex monomers (simply as LCM). They are supposed to originate from lignin monomeric fragments (LF-M). However, the same region in the plot of M-PL sample, M-PL (1), has few molecules, which means lignin simple monomers (denoted as LSM), such as the model compounds we used, will not be able to convert into LCM or original lignin structures easily.

Fig. 5. Possible formation mechanisms of pyrolytic lignin. The structure of Lignin/Phenolics-Carbohydrate Complex comes from the previous paper [43].
once they are formed through sidechains elimination of LCM. However, molecules in Region (2) of both samples have relatively low MW and RDB, so they are supposed to be LSM primarily. As for the Region (3), the two samples are very similar, they include a large amount of molecules with moderate MW (165–275 Da) and medium RDB value (mostly ≥ 8). Since M-PL is produced only from three LSM, it is speculated that molecules in Region (3) should be some phenolic dimers with simple structures, named lignin simple dimers (LSD), and they should come from recombination-condensation of LSM. This speculation will be further proved via subsequent tests. When coming to Region (4)/(5)/(6), molecules have much higher RDB (much darker red color), indicating higher degree of condensation. Although molecules in Region (4)/(5) have bigger RDB, their MW are higher accordingly, so they should be phenolic dimers/polymers with complex structures, named lignin complex dimers/polymers (LCD/P). They probably result from recombination-condensation of LCM or derive from dehydrogenation, decarbonylation or dehydration of lignin dimeric/polymeric fragments (LF-D/P). While molecules in Region (6) have a
As shown in Table 1, the area ratios P1/P2 of R-PLs are different kinds of compounds can be obtained semi-quantitatively. As shown in Table 1, the area ratios P1/P2 of R-PLs are about 4, with the minimum is 2.94 and the maximum is 4.72, which manifests that majority of compounds in pyrolytic lignin have higher molecular weight. Meanwhile, because of the very different Peak1 characteristics of R-PLs and M-PL, including Mw, Mn and d of Peak2 in all samples are really close, while significantly differences are observed regarding Peak1. It is speculated that the formation mechanisms of the compounds in Peak1 and Peak2 of R-PLs are different. Combined with the results of HPLC/Qtof-MS test, for R-PLs, Peak2 should be LSM, LCM and LSD, and Peak1 is considered mainly composed of LCD/P; when coming to M-PL, Peak2 should be LSM and LSD, and Peak1 is considered primarily coke/PAHs. At the same time, by comparing area ratio of Peak1 to Peak2, the relative content of different kinds of compounds in pyrolytic lignin may have chance to remain structures of individual aromatic ring, and have potential for further utilization, such as converting into high-grade liquid fuel or high value-added platform chemicals.
3.3. Structure identification through HSQC NMR

Since the two-dimensional HSQC spectra can separate the overlapping peaks acquired from the single-dimensional carbon spectrum or the hydrogen spectrum and has been used for analyzing complex compounds of pyrolysis oils in detail [26,27], it is of great help for better understanding of the structure of the pyrolytic lignin as well. The full spectra of the four samples were displayed in Fig. S5.

According to chemical shift \( \delta^H/\delta^C \), the HSQC spectrum can be divided into aromatic region (\( \delta^H/\delta^C 90-160/5.5-9.0 \)) and aliphatic sidechain region (\( \delta^H/\delta^C 0–70/0–5 \)) including C-O region and C-C region, see Fig. 4. Benzaldehyde was added into all the samples as an internal standard, and the signal peak in pink (\( \delta^H/\delta^C 128.0-136.0/7.4-8.0 \)) are from its aromatic carbons. According to the information of various literatures and databases published [26–33], the belonging of each resonance peak can be determined.

For the three R-PLs, their aromatic and aliphatic sidechain region are very similar, all of them contain resonance signals of p-hydroxyphenyl units (H-type), guaiacyl units (G-type), and syringyl units (S-type), among which G-type units are dominated, while the content of S-type units is the lowest. Since the model compounds adopted here for simulation of practical fast pyrolysis are G-type units including guaiacol, vanillin and eugenol, there’s no doubt that no signals belong to S-type units in M-PL. Meanwhile, since vanillin contains a carbonyl group, M-PL has a distinct resonance peak of G2 in aromatic region, while that is not found in R-PLs. The structure that aromatic rings directly connecting to the carbonyl group should be in low content in real pyrolytic lignin.

In the aliphatic sidechain region, the resonance peaks in red are attributed to \(-\text{CH}_2\) or \(-\text{CH}\) groups, and that in blue are from \(-\text{CH}_2\) groups [34]. For R-PLs, only signals derived from methoxyl and ethanol residue was included in the C-O sidechain region, and no typical lignin structures containing C-O-C linkages were observed, such as \(\beta\)-O-4, \(\alpha\)-O-4, etc. This result is consistent with the work of Wen Chen [35] who did similar HSQC analysis. It also indicates that the typical C-O-C linkages are easy to be destroyed and then transform into more stable linkages like C-C linkages under pyrolytic condition. Moreover, the resonance signals in C-O region of R-PLs are more various when comparing with that of M-PL. There are signals corresponding to methoxyl linked with aromatic rings, methoxyl linked with carbonyl and ethanol residues in R-PLs. The various signals in C-O region are due to the complex structures in raw lignin. For example, it has been reported in the literature [36,37] that herbaceous plants contain a huge amount of \(\beta\)-O-4 ferulic acid structure, which is present as the cross-linked part of lignin and cellulose or hemicellulose in cells. The compounds in pyrolytic lignin that related to the resonance signal from methoxyl linked with carbonyl are more possibly derived from ferulic acid structure that formed via cross-couple reaction between ferulate radicals and \(-\text{OCH}_3\). The product, methyl ferulate (\(\text{C}_{11}\text{H}_{14}\text{O}_{4}\), \(m/z\) 209.0819, RDB 5), was also detected through HPLC/Qtof-MS, whereas only signals from

![Fig. 8. Reaction pathways and potential energy profiles along formation of o-quinonemethide from Guaiacol.](image)
methoxyl linked with aromatic rings are found in C-O sidechain region in M-PL.

This characteristic is more apparent in C-C sidechain region. More signals with higher intensity are observed concerning R-PLs, especially for the signals derived from –CH2 and –CH3 or –CH not linked with aromatic ring directly, see Fig. 4. Due to more such signals in R-PLs than in M-PL, it is suggested that sidechains of real pyrolytic lignin should be longer and more complicated, however, pyrolysis of LSM can only form short and simple sidechains, like –CH3 linked with aromatic rings directly. This also indicates that pyrolytic lignin is mainly LCD/P including lignin fragment derivatives and LCM’s rearranged and condensed products.

3.4. Formation mechanisms of pyrolytic lignin

Based on HPLC/Qtof-MS, GPC and 2D HSQC analysis above, the possible reaction pathways of formation of pyrolytic lignin in bio-oil were proposed, as shown in Fig. 5. All molecules displayed as examples in the figure can be found in HPLC/Qtof-MS test result, and the structural formulas were presumed according to various tests herein and related literature reports [7,10,38,39].

It has been demonstrated that the bond dissociation energy (BDE) of ether bonds in lignin such as -O-4, -α-O-4 bond is relatively low, and the content of such chemical bonds is very high [40]. For instance, -β-O-4 linkage accounts for more than half of the linkage structures of lignin [41]. Therefore, they will be preferentially cleaved during pyrolysis and initially form dimeric or polymeric lignin fragments (LF-D/P) with typical lignin linkages or monomeric lignin fragments (LF-M) with complex sidechains such as coniferyl alcohol and sinapyl alcohol (Process 1), as shown in Fig. 5. LF-D/P and LF-M will further transform into relatively stable phenolic fragments, namely LCD/P and LCM, via dehydration, dehydrogenation, demethoxylation, demethylation or condensation processes (Process 4 and Process 5). LCD/P usually have larger molecular weight (MW > 275 Da) and higher degree of unsaturation (RDB > 8), corresponding to molecules in Region (4) (Fig. 1). Meanwhile, LCD/P have moderate molecular weight (275 Da > MW > 165 Da) and relatively higher degree of unsaturation (8 > RDB > 4), consistent with molecules in Region (1) of Fig. 1. It is speculated that LF-M may further undergo C-C bond cleavage, dehydration or dehydrogenation reaction and convert into Lignin Simple Monomers (LSM) (Process 2). LSM have simple sidechains, and either molecular weight (MW < 165) or degree of unsaturation (4 < RDB < 8) of them is relatively low, which is similar to the properties of molecules in Region (2) of Fig. 1. Furthermore, LSM may react with each other or with other small free radicals, like -H and -CH3, and easily condense into simple phenolic dimers or stable phenolic monomers (Process 6). However, LSM tend to form coke/PAHs with lower H/C ratio (Process 7) either. Since coke/PAHs usually have a medium molecular weight but a much larger RDB, they are corresponding to the molecules in Region (6) of Fig. 1.

According to molecular properties acquired through various analyses and the possible formation mechanisms of pyrolytic lignin, we propose that compounds with larger molecular weight in real pyrolytic lignin are primarily LCD/P and LCM, and both of them only present in R-PLs, marked as “Compounds Only Existing in R-PLs” in Fig. 5. In addition, it is suspected that due to short resident time, generation of water and multi-step reactions towards coking production during practical fast pyrolysis of biomass, further reactions of lignin derivatives and secondary reactions of LSM might be suppressed, so less coke/PAHs would be produced. Nevertheless, as for generation of M-PL, model compounds used to simulate pyrolytic vapor are LSM, so the reactions actually begin with Process 3, and then LSD or new LSM and coke/PAHs will be easily formed via Process 6 and Process 7, respectively. This proportion of compounds can be found both in R-PLs and M-PL, and is marked as “Compounds Only Existing in R-PLs” in Fig. 5. “Compounds Only Existing in R-PLs” are mostly molecules with large MW, relatively less condensed and more complicated structures; whereas “Compounds in Common” are predominately molecules with low MW and simple structures. These two kinds of compounds are consistent with the molecules included in the two peaks of GPC chromatogram (Fig. 3) very well. Therefore, the proposed formation mechanisms of pyrolytic lignin should be creditable.

3.5. DFT calculation results

DFT calculation was performed as well to support the proposed reaction pathways during fast pyrolysis by comparing potential energy of some selected intermediates and products determined in the previous tests. Fig. 6 shows the C-O cleavage, dehydrogenation, dehydration, and decarbonylation reaction possibly taking place in Process 4 of Fig. 5. As for LF-D/P with β-5 and β-β linkages, after C-O cleavage, they will condense into more stable molecules with C-C linkages between two aromatic rings through dehydrogenation, decarbonylation and methyl transfer reaction. Potential energy of product molecules is much lower than that of initial ones, as shown in Fig. 6(a) and Fig. 6(b). When coming to molecules with β-O-4 linkage, they could undergo the similar dehydrogenation, decarbonylation and methyl transfer reaction as molecules with β-5 and β-β linkages, but potential energy of product molecules is little higher than that of original structure, see black lines of Fig. 6(c). Therefore, this kind of phenolic dimers may further cleave into more stable products with relatively low energy barrier (249.75 kJ/mol), see blue lines of Fig. 6(c). However, the energy barrier of cleavage of β-O-4 linkages initially is only 194.46 kJ/mol, see red lines in Fig. 6(c), so β-O-4 linkages are more likely to cleave at first time due to the much lower energy barrier and potential energy of its products.

Process 5 is similar to Process 6. Phenolic monomers, including LF-M and LSM, will generate phenolic dimers through recombination-condensation of free radicals. For this research, Process 6 was chosen as the representative for free-radical reactions of phenolic monomers. As show in Fig. 7, three model compounds, guaiacol, vanillin and eugenol were selected for calculation, and all possible free radicals produced through bond cleavage were displayed with bond dissociation energy (BDE) marked aside. A large amount of CH3 and H, which were generated from small molecules or cleavage of O-CH3 and O-H because of their low BDE, may exist in the reaction system and contribute to transformation and dehydration reactions. Although BDE of some chemical bonds is relatively high, the corresponding free radicals may still generate because of high pyrolytic temperature. These radicals may randomly collide with other radicals and quencher into stable compounds, such as the formation process of C12H10O2 and C14H14O4, shown in the bottom of Fig. 7. C3H2O2 (m/z 185.0608, RDB 8) and C8H8O4 (m/z 245.0819, RDB 8) were common molecules detected in R-PLs and M-PL via HPLC/Qtof-MS, because they have similar RT and the same MS2 spectra (see Fig. 56).

At the same time, LF-M may also eliminate sidechains to produce LSM through dehydrogenation, dehydration, decarbonylation reactions and so on (Process 2); and for LSM, deeper condensation probably takes place to form coke/PAHs (Process 7). Some scholars [42] clarified that o-quinonemethide was a key coking intermediate during pyrolysis, and detected a coking product (C13H10O) originated from o-quinone-methide with MW = 182 by TG-MS and determined its structure. This compound (C13H10O, m/z 181.0659, RDB 9) was found in our HPLC/Qtof-MS test and considered to be a kind of coking processor as well, demonstrated in Fig. 5. Therefore, we take the formation pathways of the important coking intermediate, o-quinonemethide, as example to perform DFT calculation. Besides the pathway reported in this literature [42] that o-quinonemethide is formed through cleavage of O-H bond, hydrogen transfer, radical rearrangement and dehydration reaction (marked in blue in Fig. 8), it could be generated through two simple steps: first, intermediate IM1 is formed via a transition state TS2;
second, the intermediate IM1 go through another transition state TS3 and convert into o-quinonemethide straightly (marked in red in Fig. 8). The energy barriers of both steps are relatively low, comparing with the pathways reported before. The calculation result suggests that LSM have a strong tendency to coke under pyrolysis conditions regardless of reaction pathways. Therefore, although M-PL embraces compounds with larger molecular weight, the RDB of them is much higher, thus most of them are believed to be coke/PAHs.

4. Conclusion

High MW molecules in R-PLs are mainly phenolic dimers or polymers with complex sidechains and C-C linkages, which should be originated from lignin fragments that generated at initial stage of pyrolysis. Low MW molecules in R-PLs are similar with the compounds in M-PL but poor in content, which indicates that recombination-condensation of LSM is difficult to take place during fast pyrolysis probably because of short resident time and multi-steps towards LSM. Numerous molecules in M-PL with medium MW but high RDB should be coke/PAHs, suggesting that LSM have strong tendency to coke. The proposed formation mechanisms of PL are well supported by DFT calculation. The results provide a new knowledge of pyrolytic lignin, which may help facilitate high-value utilization techniques of PL in the future.

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Appendix A. Supplementary data

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