



Formation of phenolic oligomers during fast pyrolysis of lignin



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HIGHLIGHTS

- The formation of phenolic oligomers during fast pyrolysis of lignin is investigated.
- A total of 569 phenolic compounds with molecular weight less than 504 Da were found.
- Phenolic monomers are most abundant products followed by dimer, trimer and tetramer.
- Reactive phenolic monomers reoligomerize during fast pyrolysis.
- A significant fraction of phenolic oligomers arise from reoligomerization.

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ABSTRACT

Bio-oil obtained from fast pyrolysis of lignocellulosic biomass usually contains up to 30% of pyrolytic lignin that mainly consists of phenolic oligomers. Phenolic oligomers are difficult to upgrade into useful products since they are non-volatile and viscous, and highly reactive. The present study investigates the origin of phenolic oligomers during fast pyrolysis. Lignin was pyrolyzed in a micro-pyrolyzer and the vapor was directly analyzed using online GC/MS, or recovered in a cold solvent then analyzed using GPC and high-resolution mass spectrometry. A total of 569 phenolic compounds with molecular weight less than 504 Da were found, which are significantly smaller than phenolic oligomers recovered from condensed bio-oil. The most abundant phenolic compounds among these smaller molecules are monomers followed by dimers, trimers and tetramers. Pyrolysis of model compounds at identical experimental conditions showed that primary phenolic monomers with high reactivity, for example, 2-methoxy-4-vinylphenol, syringol and guaiacol, could reoligomerize during fast pyrolysis via secondary reactions. It was also found that phenylcoumaran, stilbene and biphenol structures are relatively stable during fast pyrolysis. Therefore the dimers containing these structures could also be primary products of lignin during fast pyrolysis. The study suggests that a significant fraction of phenolic oligomers present in bio-oil arise from reoligomerization of small phenolic molecules formed during the pyrolytic depolymerization of lignin.

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1. Introduction

Lignocellulosic biomass is a promising alternative to petroleum for production of fuels and chemicals. Fast pyrolysis of biomass, a process that rapidly heats biomass to moderate temperatures (~500 °C) in the absence of oxygen followed by rapid quenching of pyrolysis vapor (vapor residence time <2 s), can convert up to

75 wt% of feedstock into bio-oil [1]. Bio-oil is a complex mixture of organic compounds and can be further upgraded to hydrocarbon fuels and valuable chemicals. Bio-oil is only partially water-soluble. The water-insoluble fraction of bio-oil is sometimes called pyrolytic lignin [2]. It mainly consists of lignin-derived phenolic oligomers with molecular weight (MW) up to 2500 Da as well as some phenolic monomers [3]. Phenolic monomers are valued chemicals for commodity products and are precursors for biofuels, thus higher yields are preferred. In contrast, phenolic oligomers found in bio-oil are non-volatile, viscous, and highly reactive, making them more difficult to process into useful products [4,5]. They

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have been reported to deactivate catalysts during upgrading [6]. For these reasons, conversion of lignin to monomers instead of oligomers is highly desirable. However, the yield of phenolic monomers in bio-oil is usually very low (<10 wt%) whereas phenolic oligomers are the majority of lignin-derivatives, accounting for 25–30 wt% of bio-oil [7].

The mechanisms of phenolic oligomer formation and the mode of transport of these non-volatile compounds are still debated. One model commonly cited is thermal-mechanical ejection [8]. According to this theory, phenolic oligomers arise from partially cracked lignin fragments. These fragments then become entrained as aerosols in the gas flow through the reactor as a result of gas shear forces on melted lignin fragments [9,10]. This mechanism does not require formation of phenolic compounds small enough to vaporize in the gas stream. Fratini et al. [11] found that phenolic oligomers in bio-oil consist mainly of tetramers with spread out microstructures resembling those of the original lignin. They argue that complete depolymerization to monomers followed by reoligomerization must not have occurred otherwise the phenolic products would have tangled and aggregated structures.

On the other hand, it is well known that MW of bio-oil usually increases as bio-oil ages [12]. Several studies of pyrolytic lignin [3,4,7,9,13,14] show that pyrolytic lignin contains linkages not found in lignin. Thus, random condensation of primary pyrolysis-products to phenolic oligomers during storage has also been proposed.

It should be noted that most previous studies collected bio-oil using condensers or quench vessels some distance downstream from the pyrolysis reactor, providing an opportunity for secondary reactions of phenolic monomers to occur. Moreover, these bio-oils were obtained from pyrolysis of lignocellulosic biomass; thus, carbohydrate-derived compounds were co-evolved with phenolic compounds. It is highly probable that secondary reactions occurred between phenolic compounds and carbohydrate derivatives in either the vapor phase or during the storage stage [5,15,16]. In addition, precipitating pyrolytic lignin from bio-oil by the addition of water could leave a significant amount of polar phenolic oligomers behind in the aqueous phase [9]. Therefore, analyzing pyrolytic lignin obtained from bio-oil is of limited value in understanding the chemistry of lignin and lignin-derived compounds during pyrolysis.

To exclude interactions with carbohydrates, some researchers have separately pyrolyzed lignin. Ben and Ragauskas [17] pyrolyzed lignin in a quartz tube reactor at moderately low heating rates and analyzed the resulting bio-oil using GPC and NMR to characterize overall distributions of the functional groups as a function of pyrolysis temperature. They noticed that MW and polydispersity of the heavy-oil fraction increased with pyrolysis temperature, and suggested that both condensation products and secondary-cracking products increased with temperature. More recently, Zhou et al. [10] pyrolyzed lignin in a wire-mesh reactor and analyzed the composition of the condensed products. Since the bio-oil was almost completely phenolic oligomers with only a trace amount of phenolic monomers (eugenol and vanillin), the authors concluded that the primary products of lignin pyrolysis are phenolic oligomers while phenolic monomers evolve from secondary reactions of the oligomers in the vapor phase.

Several researchers have directly analyzed the vapor stream from the pyrolysis of lignin in an effort to minimize secondary reactions [18–23]. The most commonly used method was micropyrolysis with a close-coupled gas chromatograph and mass spectrometer (Py-GC/MS). As a result, 20–30 different types of phenolic monomers were detected and identified as primary products. The major disadvantage of this approach is the difficulty of detecting phenolic oligomers and other heavy compounds of limited volatility.

To overcome this problem, some researchers replaced the GC-MS with a molecular beam MS. This allowed detection of high MW compounds that are not detectable by GC/MS. However, high MW compounds were still underrepresented in their studies due to limitations of the analytical technique at the time [14,19,20]. Later, Hempfling and Schulten [21], Hage et al. [22] and Seiro et al. [23] investigated lignin pyrolysis using low electron ionization Py-MS and field ionization Py-MS. Using these methods they obtained mass spectra with improved mass detection at a higher MW range. Numerous peaks were observed in the mass spectra, indicating the complex nature of pyrolysis products. In most of the studies, however, only a few peaks with relatively high intensity were selected for further investigation, and the majority of GC/MS non-detectable compounds were uncharacterized. It should also be noted that lignin samples were pyrolyzed relatively slowly in the studies. Considering that slow pyrolysis is prone to produce large amounts of char, water and non-condensable gases from lignin [2,20], it is unclear if the information obtained from such studies can correctly reflect depolymerization of lignin during fast pyrolysis.

Nevertheless, it is interesting to note that several phenolic oligomers with identical MW were frequently reported in these studies, for example 272, 298, and 328 Daltons. Since the exact molecular structures of the compounds could not be determined due to the absence of fragment ions, the structures of the compounds were often proposed based on characteristic features of original lignin structures [14,19,21,22,24]. For example, Evans et al. [20] proposed three possible structures for a compound with MW of 272 Daltons using three different bond linkages. In most of the cases, the tentative structures of the oligomers were assigned using backbones of phenylcoumaran, resinol, stilbene and biphenol because these structures are considered to be thermally stable [21]. Bayerbach and Meier [4] later proposed the structures of phenolic oligomers up to octamers using the combination of at least two of these linkages, stating that these structures are thermally ejected [4,13]. On the other hand, Mullen and Boateng [7] reported that neither phenylcoumaran nor resinol were found from NMR analysis of pyrolytic lignin. Instead they found that pyrolytic lignin is largely made of highly substituted aromatic rings connected by various aliphatic linkages. It should be noted that the actual molecular structures of phenolic oligomers were never confirmed using authentic compounds in previous studies.

Recently, Patwardhan et al. [18] pyrolyzed lignin in a Py-GC/MS achieving mass balances near 92%, which includes GC/MS identifiable phenolic monomers and other light condensates, char and non-condensable gases. They found that pyrolysis liquids collected after longer vapor-transport distances from the pyrolyzer had higher MWs. This finding does not support the hypothesis suggested by Zhou et al. [10], who claimed that phenolic monomers are a result of secondary reactions of phenolic oligomers in the vapor phase. Based on these findings, the authors speculated that the primary products of lignin pyrolysis are phenolic monomers, which is followed by their vapor-phase reoligomerization to the phenolic oligomers observed in bio-oils. However, GC/MS non-detectable compounds accounted for 8 wt% of the products of lignin pyrolysis, which requires additional research to identify them.

In recent years, high resolution mass spectrometry used in petroleum analysis was adopted to analyze bio-oil in the combination of GC/MS analysis [25–27]. Such studies have been providing valuable insights about non-volatile products in bio-oil. However, primary reaction products could not be distinguished from secondary reaction products since the bio-oil analyzed in these studies was recovered from conventional reactors.

In order to overcome these limitations, the present study pyrolyzed lignin in a micropyrolyzer. The pyrolysis products were investigated using gas chromatography/mass spectrometry (GC/MS), Gel permeation chromatogram (GPC) and atmospheric

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