

Thermal Depolymerization of Lignin

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Abstract

Lignin can be considered as a clean source of renewable energy, which may be a substitute to fossil fuel and thus reduce some of the environmental pollution. This paper presents a review of the thermal process of depolymerization of lignin; which results in production of oil and gaseous fuels from such important renewable energy source. Also, thermal hydro-cracking of lignin enhances the liquefaction of other solid fossil fuels such as coal, by producing intermediates which then react further with coal producing lower molecular weight material, which is more desirable.

Keywords: Lignin, depolymerization, thermal hydrocracking.

1. Introduction

Lignin can be considered as a clean source of renewable energy, utilization of lignin may reduce the environmental pollutions. Lignin depolymerization has attracted much attention in recent years. It is one of the primary composition of biomass tissue in addition to cellulose and hemicellulose [1]. They are present in all biomass material with different proportions and the composition of hemicellulose and lignin vary according to tree species; they account for 95-98 % of woody tissue. In addition to these three major groups there are extractive materials and inorganic substances present that account for about 2-5 % of biomass [2]. Although they exist in very small amounts, but they highly contribute to the physical properties of biomass, such as, color, smell, and decay resistance [3]. Cellulose is the most abundant compound found in biomass. Roughly half of the total weight of woody material is comprised from cellulose. It can be characterized as a linear high molecular weight polymer made up exclusively of β -D-glucose. The structure of cellulose does not vary from one tree species to another. Due to its chemical and physical properties, as well as its super molecular structure, cellulose acts as the main structural component of the plant cell walls. Hemicellulose is considered polysaccharide compound with low molecular weights that are different from cellulose, and can possess some degree of branching. These compounds are composed of a variety of monosaccharides such as glucose, mannose, galactose, xylose, and arabinose occasionally acetylated and/or in combination with uronic acids, pectins, and starch [4]. The classification of hemicelluloses is in accordance

with sugars present in the molecule, such as, in galactoglucomannans, glucuronoxylans, arabinogalactans, etc. The composition of hemicellulose varies in tree species especially between hardwoods and softwoods [5]. Materials that can be extracted from biomass by either polar or non-polar solvents are called extractives. In most biomass, there are very small percentages of extractive material. Generally, extractives are those compounds which are soluble in organic solvents, or, in some cases, even in water. But there are also variations depending on the geographical site and season. They are concentrated in the resin canals and the ray parenchyma cells; lower amounts can be also found in the middle lamellae, intercellulars and cell walls of tracheids and libriform fibers. Some extractives are toxic or deterrent for bacteria, fungi and termites. Others give color or odor to the biomass. Extractives are identified to be aliphatic, aromatic and cyclic compounds, hydrocarbons, alcohols, ketones, and various types of acids, esters, and phenolic compounds. Furthermore, sterols, tannins, essential oils, resins, dyestuffs, lignans, proteins, waxes, and some alkaloids are found [5]. The objective of this paper is to present thermal depolymerization of lignin, which is an extension to a previously published work [6].

2. Biomass Depolymerization

In a recent study biomass depolymerization was presented [6]. It was found that the thermal stability of briquetted biofuel was higher than the wood based on the activation energy levels, particularly for hemicellulose and cellulose. The intrinsic hemicellulosic and cellulosic biopolymers contributed

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positively wards the thermal stability of the briquetted biofuel. It was concluded that during formation of briquette the intrinsic hemicellulosic and cellulosic biopolymers undergoes through changes which leads to higher thermal stability in briquette [7].

3. Lignin

Lignin, an abundant by-product of the paper and pulp industry, is a renewable raw material. It is a phenolic copolymer derived from biomass and can be viewed as an inexpensive, attractive source of aromatic compounds. The word "lignin" is derived from the Latin word "lignum" meaning wood. Lignin is the second most found substance in wood behind cellulose; roughly it is 30% by weight. Unlike cellulose, which is a linear polymer partially aggregated in crystalline configuration, lignin has a random, noncrystalline network structure.

A simplified representation of lignin's complex nature in chemical terms is given in Figure 1. The main physiological function of lignin is to provide rigidity and strength to the plant cell walls. Lignin is responsible for increasing the mechanical strength properties to such an extent that huge trees with height of even more than 100 meters can remain upright. Lignin is chemically separated from biomass by a process called delignification. It is predominantly aromatic and is almost insoluble in a variety of common organic solvents such as benzene, toluene, naphthalene, or pentane. Lignin is considered as a mono-aggregative substance, i.e., it does not dissolve in any solvent without itself being changed [8]. Lignin can be regarded as mixtures of different molecules, having similar chemical structures, but with some structural differences. Compounds that have the same molecular weight but different molecular structure are called isomeric compounds. Compounds that have different molecular weight but the same structure are called homologs. Lignin is not considered either isomeric compounds or homologs. Lignification is a transformation process that occurs in most plants by which the aromatic polymer, lignin, is eventually formed from carbon dioxide through intermediates of a carbohydrate nature.

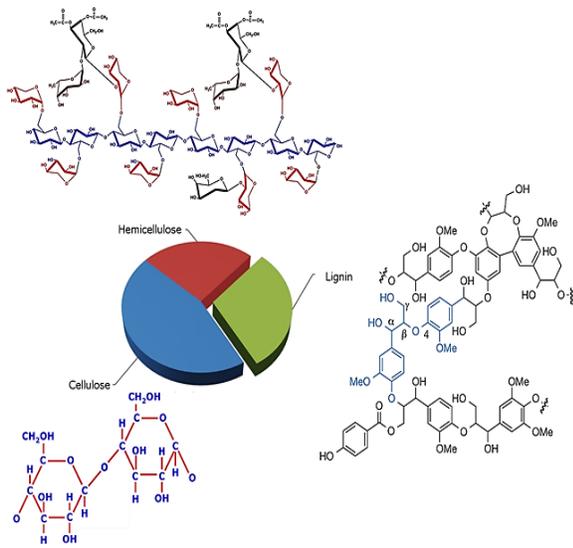


Figure 1. Simple structures of cellulose, hemicellulose, and lignin: Major components of biomass.

The biochemical pathway of the lignification process can be divided into two steps:

- the formation of lignin building compounds, such as trans-p-coumaryl alcohol, trans-p-sinapyl alcohol, and trans-p-coniferyl alcohol. Figure 2 illustrates their chemical structure;
- the conversion of these building blocks into lignin itself.

Lignin structure has been studied by a number of investigators and differs among species [9,10]. The structure proposed by Freudenberg for lignin has substantial merits in providing a reasonable picture of the molecular architecture of lignin, and in forming a basis for mapping the course of various chemical reactions [10]. Freudenberg's lignin structure is shown in Figure 3. Lignin is three-dimensional network formed from phenyl propane units. The "most common linkages between the phenyl propane units are shown in Figure 4 and their percentages are given in Table 1. It is apparent that ether linkages are very important in lignin, with β -aryl ethers (Figure 4 A) most abundant and benzyl (a)-aryls (Figure 4 C) and diphenyl ethers (Figure 4 G) also significant. Lignin also contains appreciable amounts of methoxyl groups, as well as smaller quantities of free phenolic hydroxyl, benzyl alcohol, and carbonyl groups [11]. The number of each group per 100 phenyl propane units are: 100-150 for methoxyl, 9-30 for free phenolic hydroxyl, 15-20 for benzyl, and 20 for carbonyl.

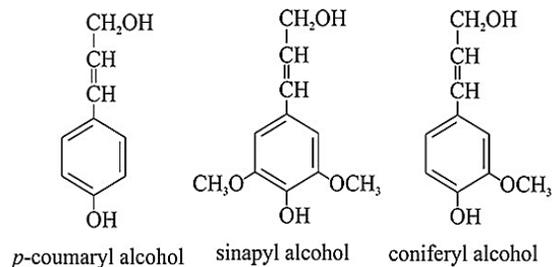


Figure 2. The primary lignin precursors

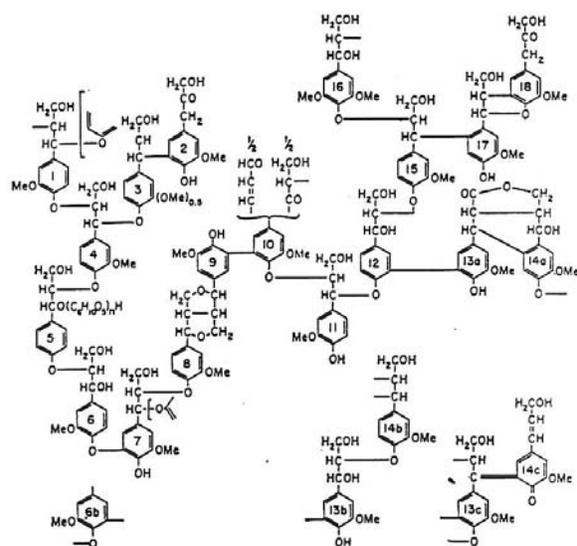
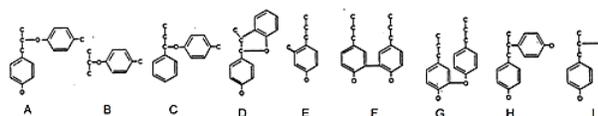


Figure 3. Freudenberg's lignin structure

Table 1. Percentages of Different Types of Bonds in Spruce and Birch Lignins

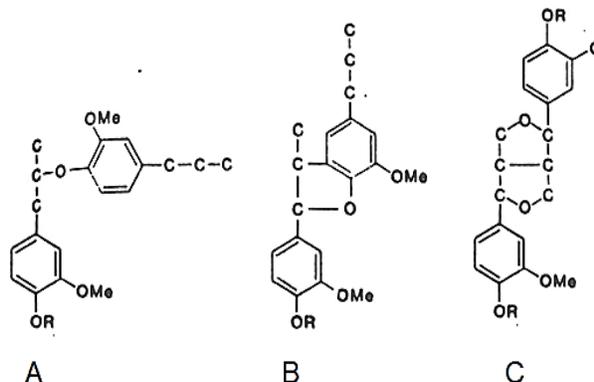
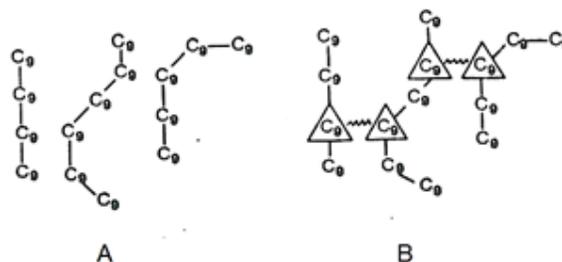
Bond Type*	Spruce	Birch
Arylglycerol- β -aryl ether (A)	48	60
Glyceraldehyde-2-aryl ether (B)	2	2
Noncyclic benzyl (α -aryl ether (C)	6-8	6-8
Phenylcoumaran (D)	9-12	6
2- or 6-Position condensed structures (E)	2.5-3	1.5-2.5
Biphenyl (F)	9.5-11	4.5
Diphenyl ether (G)	3.5-4	6.5
1, 2-Diarylpropane-1, 3-diol (H)	7	7
B, β -linked structures (I)	2	3

* Letters A-I refer to Fig. 4

**Figure 4.** The most common linkages between phenylpropane units in lignin

The structure of lignin can be described by units, linkages, and functionality defined as follows:

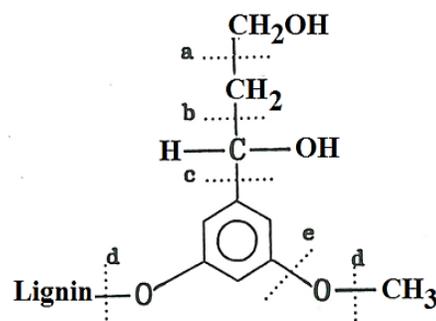
- The basic unit is a phenyl propane (C_9) unit. Each unit contains one phenolic hydroxyl group, which may be free bound (as aryl ether).
- Two C_9 units can be connected by only one C-C linkage, regardless of the number of bonds between them. Thus in Figure 5 A, a linkage contains one bond. The linkages in Figure 5 B and C, have two and three bonds, respectively.
- The units are linked mono-functionally and bi-functionally to form linear (primary) chains, as shown in Figure. 6 A.
- Non-terminal units in two linear chains may be cross-linked to form a "tree-like" polymer as shown in Figure 6 B.

**Figure 5.** Interunit linkages between lignin units containing (A) one, (B) two, and (C) Three chemical bonds**Figure 6.** Primary chains (A) before, and (B) after cross-linking

3. Lignin Depolymerization

For many years, a lot of methods have been developed in order to convert lignin, and other biomass wastes [12-16], into a more useful organic chemical with lower molecular weight. Particularly for those lignins which were obtained as by-products from the pulp and paper industries. By 1952, the Nouguchi Institute of Japan was successful in discovering a remarkable catalyst that was, used to convert lignin into substantial amounts of mono-phenols [17]. To improve such process, it is found that pretreatment is an important parameters. Number of pretreatments may be considered such as steam pretreatment, lime pretreatment, liquid hot water pretreatment and ammonia based pretreatments are found to be of high potential [18-21]. It is believed that liquefaction of lignin proceeds by a free radical mechanism [22]. It was postulated that the depolymerization of lignin occurs, in conjunction with Figure 7, by the following steps:

- The first step is the splitting of the ether linkages 'd' (see Figure 7). Products without methoxyl groups would be provided.
- The second step is the splitting of the side chains 'a', 'b', or 'c' into various free radicals, as long as the benzene nucleus remains unsaturated. The free radicals can then be hydrogenated giving methanol, ethanol, and other phenolic derivatives.
- The ether bond of the methoxyl groups, 'e', splits next, giving mono-phenols. The CH_3-O ether bond has low formation energy and its ease of scission probably accounts for high yield of CH_4 when lignin is pyrolyzed. Aside from aromatic rings, the most difficult bonds to split are the C-C bonds.

**Figure 7.** Mechanisms for the depolymerization of a lignin molecule at different bonds

Lignin was liquefied in phenol under a high hydrogen pressure using the Nouguchi catalyst, described earlier, at temperature of about 400 °C [17]. Conners et al. [23] were able to thermally degrade lignin in tetralin in order to provide more information about the use of tetralin as a hydrogen donor in place of the high hydrogen pressure. Significant amounts of liquid products were obtained at a temperature of about 400 °C. Meier and coworkers [24,25] have liquefied lignin in water in the presence of palladium as a catalyst. As high as 64 % oil yields were reported. In another study, Funazukuri et al. [26,27] have shown that during liquefaction of lignin sulfate, at 400 °C, in presence of subcritical or supercritical water, oil yields increased as the water density increased in the system. Enhancement in oil yields resulted with the addition of hydrochloric acid to the reaction mixture. Enhancements were reported with the addition of Na₂CO₃ + CO and water, compared to the oil yield obtained with the addition of Na₂CO₃ and just water.

Table 2. Top 20 Most Cited Lignin Processing Articles in Scopus Database

Rank	Reference	Cited
1	Moiser et al. [21]	2636
2	Sun and Cheng [20]	2475
3	Parton et al. [47]	2043
4	Baily et al. [48]	1820
5	Melillo et al. [49]	1450
6	Babel and Kurniawan [50]	1402
7	Hendriks and Zeeman [18]	1318
8	Yang et al. [51]	1292
9	Alvira et al. [19]	1074
10	Zakzeski et al. [52]	960
11	Alder [53]	886
12	Taherzadeh and Karimi [54]	776
13	Kim and Dale [14]	774
14	Olivier-Bourbigou et al. [13]	728
15	Hamelinck et al. [15]	722
16	Aerts [55]	720
17	Sanchez and Cardona [12]	717
18	Lin and Tanaka [56]	716
19	Lynd et al. [16]	716
20	Haritash and Kaushik [57]	705

Piskorz et al. [28] were able to produce 60-65 % hydrocarbon liquid fuels by liquefaction of lignin in a non-isothermal plug flow catalytic reactor. The light hydrocarbon liquid product was about 62 % aliphatic and 38 % aromatic with more than 50 % boiling in the gasoline range. Davoudzadeh et al. [29] liquefied lignin using a Lewis acid catalyst in tetralin, under high pressure. They have found that addition of guaiacol or phenol to the reaction mixture increased the liquefaction of lignin. Recently,

lignin pyrolysis plant was designed to produce 50 ton/day capacity [30]. Also, an efficient lignin depolymerization process was reported using metal chloride (MCl_x) to investigate its catalytic performances. The effect of reaction conditions on the lignin depolymerization and products distribution were also presented. The results showed that more than 35.4% yield of phenolic monomer including 7.8% phenols and 1.1% guaiacols could be obtained under optimized condition. And the product distribution can be efficiently controlled by the modification of the metal cation through different pathway of Lewis acid catalysis [31]. Also, thermal hydro-cracking of lignin enhances the liquefaction of other solid fossil fuels such as coal, by producing intermediates which then react further with coal producing lower molecular weight material, which is more desirable [32-46]. A lot of literature has been published on the processing of lignin. The most cited articles are listed in Table 2, which indicates that there are 3 articles with citations reaching 2000 and above [12-16, 18-21, 47-59].

4. Conclusion

It is evident that lignin can be used to produce liquid or gaseous fuels. It is best if the lignin goes through a thermal depolymerization process in the presence of hydrogen donor solvent. The heating process is responsible for splitting the carbon linkages, which then react with hydrogen atoms forming a lower molecular hydrocarbon compounds. These compounds are the formation of liquid or gaseous fuels.

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