



(REVIEW ARTICLE)



## An overview: Importance of lignin and different analytical approaches to de-lignify it from plants

Zeyad Fadhil <sup>1,2,\*</sup>, Dheaa Shamikh Zageer <sup>1,3</sup>, Abbas Hasan Faris <sup>4</sup> and Mohammed H Al-Mashhadani <sup>1</sup>

<sup>1</sup> Department of Chemistry, College of Science, Al-Nahrain University, P. O. Box: 64021, Baghdad, Iraq.

<sup>2</sup> College of Pharmacy, University of Thi-Qar, Thi Qar, Iraq.

<sup>3</sup> Forensic DNA Center for Research and Training, College of Science, Al-Nahrain University, Baghdad, Iraq.

<sup>4</sup> Directorate of Materials Research, Ministry of Higher Education and Scientific Research, Baghdad, Iraq.

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### Abstract

In this short review, it is going to discuss the chemical structure of lignin. Hence the chemical structure of lignin is phenolic high crossed linking polymer so this type of polymers has high rigidity and not so easy to decay. Thus Lignin is insoluble in most organic solvent and water but slightly soluble in basic solutions. Mono-lignols are monomers to form crosslink polymer (lignin) and there are three main types (paracoumaryl, coniferyl and sinapyl) of these monomers. Lignin's separation process is called delignification which is the procedure of extraction lignin from botanical source. Several analytical methods have been reviewed of delignification process and the most two common approaches are kraft pulping process by utilizing alkaline solution and organosolv pulping process by utilizing organic solvents.

**Keywords:** Lignin; De-lignification process; Coniferyl; Lignin linkages; Kraft pulping

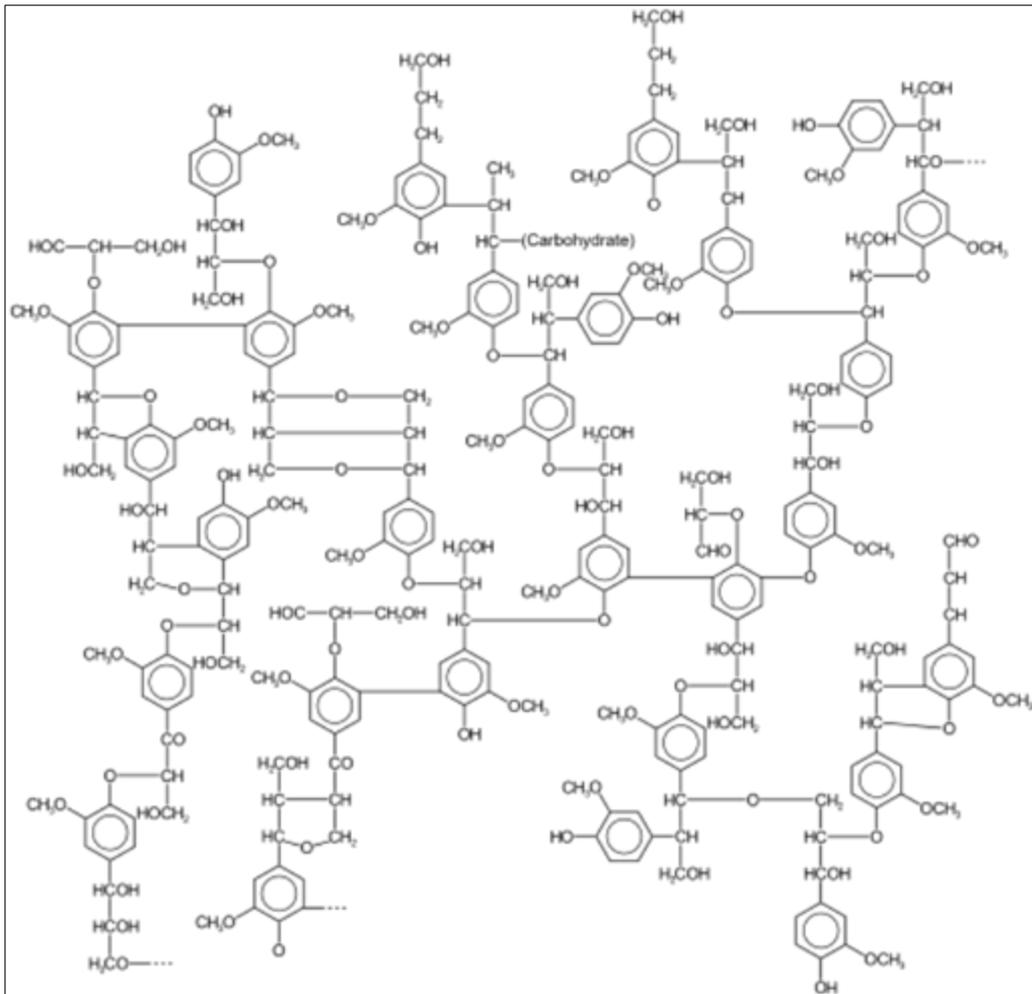
### 1. Introduction

Majority of plants contain lignin in their support tissue structures as lignin is an organic polymer [1]. Hence the chemical structure of lignin is phenolic high crossed linking polymer so this type of polymers has high rigidity and not so easy to decay. Therefore lignin is significantly important in the cell walls of wood to give them rigidity [2]. Figure (1) shows the possible chemical structure of lignin and showing the high cross linking of polymer between aromatic rings and phenol groups.

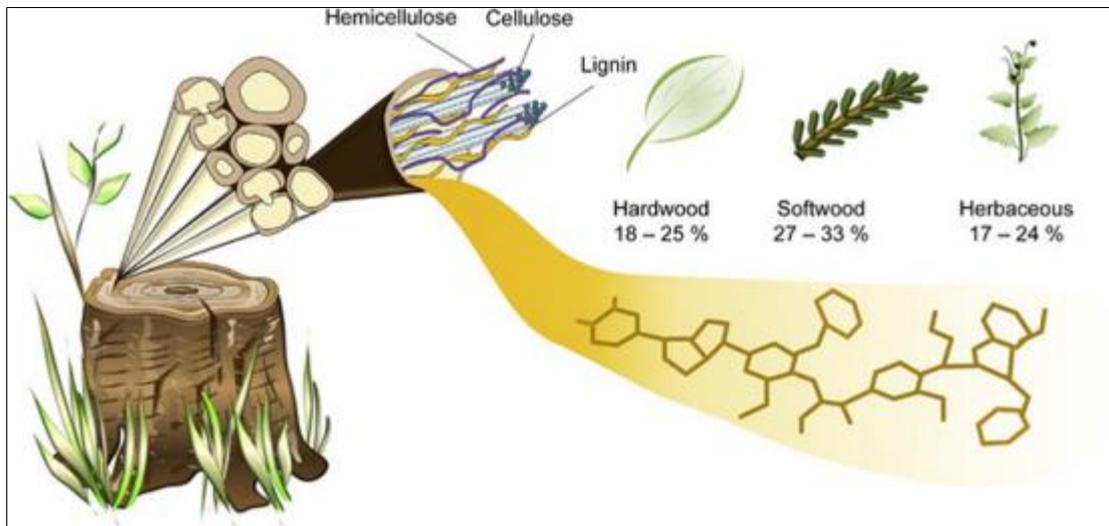
The first scientist discussed lignin was Candolle (Swiss botanist) in 1813 when he described it as a fibrous in his book [3]. Lignin is insoluble in most organic solvent and water but slightly soluble in basic solutions. Moreover, lignin can be precipitated by adding acidic solutions to its mixture. Lignin name was derived from Latin work lignum which means wood by Swiss botanist Candolle [4]. Lignin is considered as one of the major rich natural polymer around the world as about 30% of dry wood is lignin [5], lignin is also found in red algae [6]. Figure (2) shows the components of wood and existence of lignin in nature. Thus it consists mainly from lignin, hemicellulose and cellulose [7].

\* Corresponding author: Zeyad Fadhil

Department of Chemistry, College of Science, Al-Nahrain University, P. O. Box: 64021, Baghdad, Iraq.



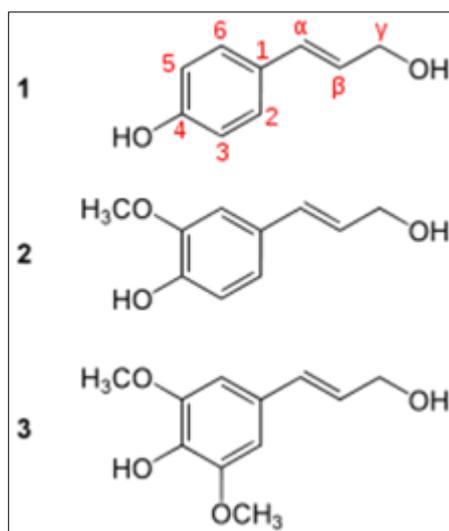
**Figure 1** Possible chemical structure of lignin as an organic cross linked polymer



**Figure 2** Animated graph of wood components [7]

### 1.1. Lignin structure

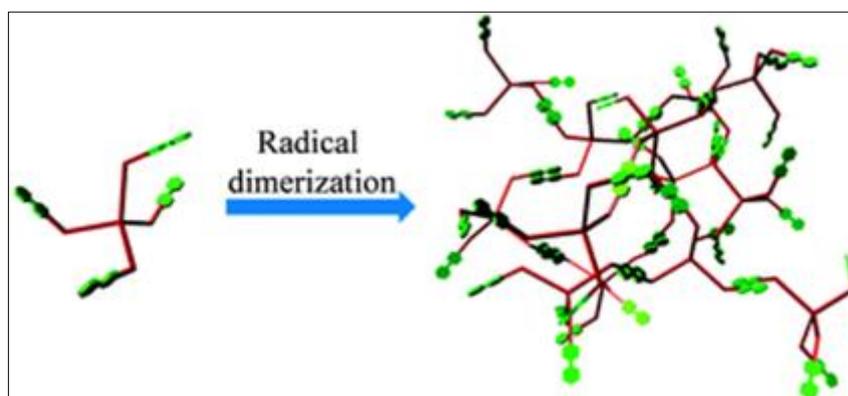
One of significant structural properties of lignin is its cross-link in different ways so it is very heterogeneous cross-linked polymer. Mono-lignols are monomers to form crosslink polymer (lignin) and there are three main types (paracoumaryl, coniferyl and sinapyl) of these monomers as shown in Figure (3) [8].



**Figure 3** Chemical structure of main mono-lignols monomers. 1) paracoumaryl. 2) coniferyl. 3) sinapyl

The type and amount of lignols is verity to form lignin according to the part and type of plant such as sinapyl and coniferyl moieties are rich in hardwoods and grass but, in softwoods coniferly moieties are more available. Because of lignin chemical structure has a lot of aromatic segments, it is hydrophobic (insoluble in water) and its molecular weight sometimes exceeds ten thousands units [9]. It is hard to determine the polymerization degree of lignin because it is a random co-polymer with various moieties. Thus several lignins were studied depending on their isolation approach [10]. Non-woody plants have small amount of lignols linked to other modified monomers [11].

By free radical reaction of above mentioned monomers, the matrix of three dimensions cross-link polymer (lignin) is formed as shown in Figure (4). The main feature of lignin is the rigidity to external physic-mechanical performances, prominent to shear the distortion and stress. Thus high flexibility of lignin chemical structure to rearrange their bonds is very important to give more compressed materials. Researchers consider lignin as insoluble biopolymers but till now there are many studies regarding lignin chemical structure and biological activity [12].

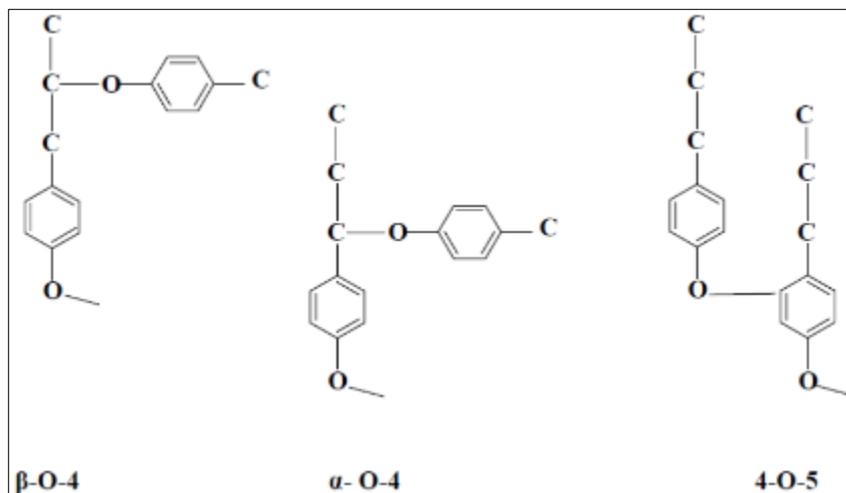


**Figure 4** Animated graph of free radical polymerization reaction

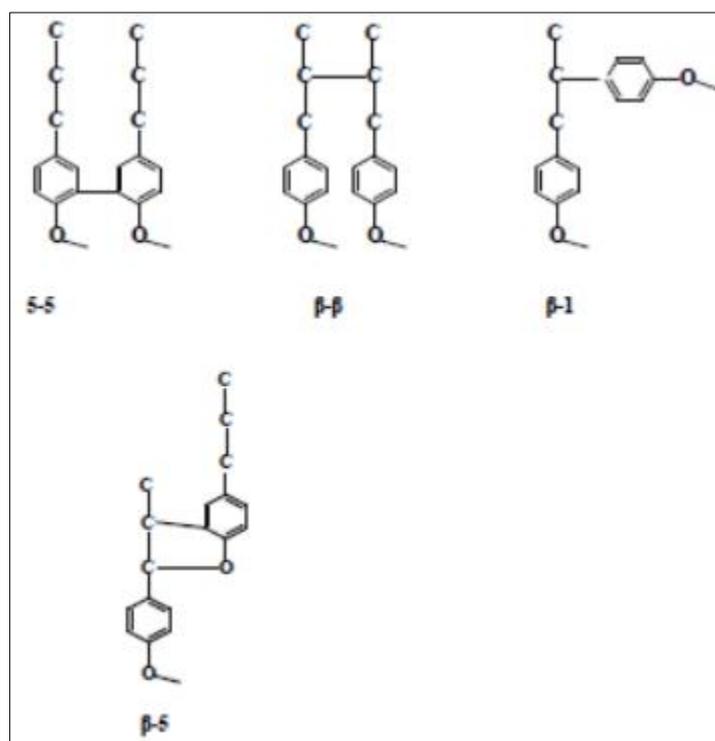
### 1.2. Lignin linkages

Lignol units can make four types of bonds C–C bond, hydrogen bond, C–O–C (ether bond), and ester bond to form cross-link polymer lignins. Therefore the monomers units are linked to each other by these bonds to form the polymers chains and this linkage is called intra-polymer linkage. In addition these bonds are in charge about forming bonds between the

polymer chains to get cross-linked polymer this linkage is called inter-polymer linkage [13]. Ether bonds (C–O–C) and carbon-carbon bonds (C–C) are the major bonds link the lignols monomers to form lignin. Hence ether linkage is about 70% of the total connections between the monomer units within the polymer structure, although the rest 30% is belong to C–C bond linkages [14]. Figures (5) and (6) shows the most famous linkage (C–O–C and C–C) between lignin's moieties which have been demonstrated by researchers [15, 16]. Even though there are more than twenty minor linkages have been discovered till the date of writing this report [17].



**Figure 5** The most common ether linkages



**Figure 6** The most common carbon-carbon linkages

Till now several linkage functional groups between lignin polymeric chains have been discovered which is match the industrial desires [18-19]. Generally the efficiency of lignin relies on the phenol, aliphatic and sometimes carboxylic groups too. Both extraction process and source of lignin determine the percentage of these groups and type of linkage. Furthermore the type of functional groups and their linkage limit the solubility of lignin. Due to the acidic features of

lignin, hence it has phenolic and carboxylic properties, so it is good soluble in alkaline media [20]. Almost of hydroxyl phenol groups make ether linkages with adjusting series and about 13% of them form linkages phenyl propane units [21]. The most reactive position within lignin chemical structure toward chemical modifications is phenol groups [22].

### 1.3. Delignification of wood

In the production of papers and bioethanol, lingo-cellulosic is obtained as by-products which contain lignin see Figure (7). The last is separated from mixture by chemical and physical processes. Lignin's separation process is called delignification which is the procedure of extraction lignin from botanical source. Thus the plant source controls lignin features and delignification procedure influence the structure and purity of lignin [23]. Several analytical methods have been used to delignification process and the most two common approaches are kraft pulping process by utilizing alkaline solution and organosolv pulping process by utilizing organic solvents. Next sections we are going to discuss these methods in more details [24].



**Figure 7** Manufacturing of paper (woodchips)

### 1.4. Kraft pulping analytical process

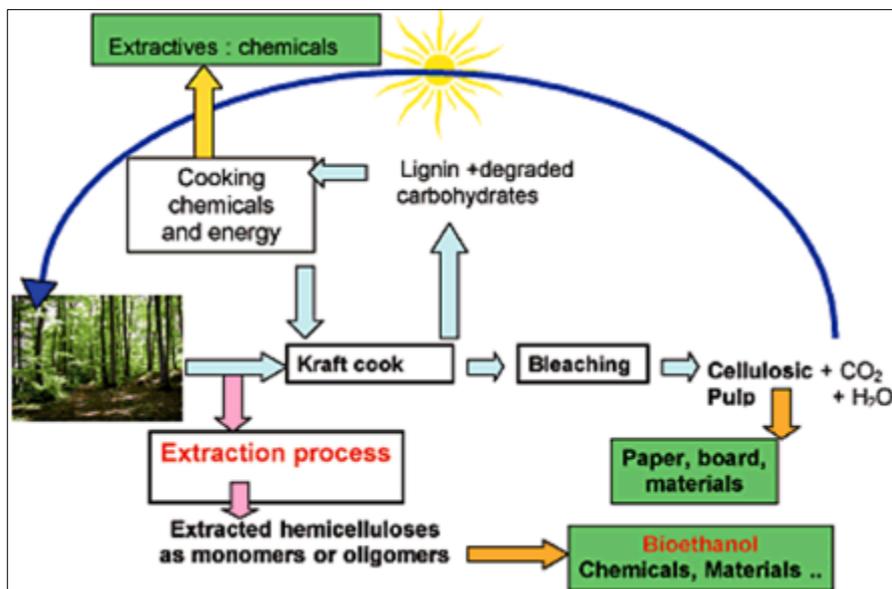
Pulping is an analytical method to take away lignin from wood by delignification; hence various approaches have been followed regarding that. However, kraft pulping process is the most famous analytical process to remove lignin from wood around the world [25]. Kraft or alkaline pulping procedure is very common in industrial applications such as manufacturing of papers see Figure (8).



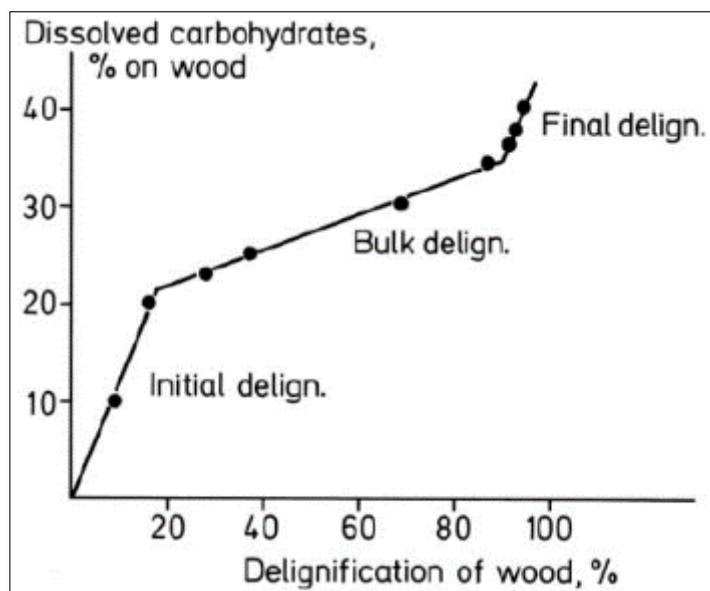
**Figure 8** A kraft paper roll

In this process, sodium sulfide is added to wood under basic and high temperature conditions to dissolve lignin then get rid of it. There are two main analytical ways to delignification of wood by kraft method. The first way is by degradation the lignin into smaller series through splitting polymer chains which happens *via* cleavage the inter-bonding linkages between lignin's polymer chains [26]. The second way is introducing hydrophilic units to modify the chemical structure

of lignin and make it water soluble [27]. In the first way, the phenol linkages are broken to make phenol groups which have acidic properties so it can react with alkaline as acid-base reaction to form organic salts which is soluble in water. Thus C–C linkages are still survived after alkaline or kraft pulping process [28]. Throughout alkaline process more than 95% of phenol (C–O) linkages are cleavage to form lignin with different molecular weights [29]. As the color of the mixture resulting from kraft process is deep brown; hence the hemicellulose still linked to the lignin. Figure (9) shows the extraction process of wood components include lignin and how to produce different useful materials by kraft cook such as chemicals, paper, board materials, and bioethanol [30].



**Figure 9** Schematic of kraft pulping process of wood [30]



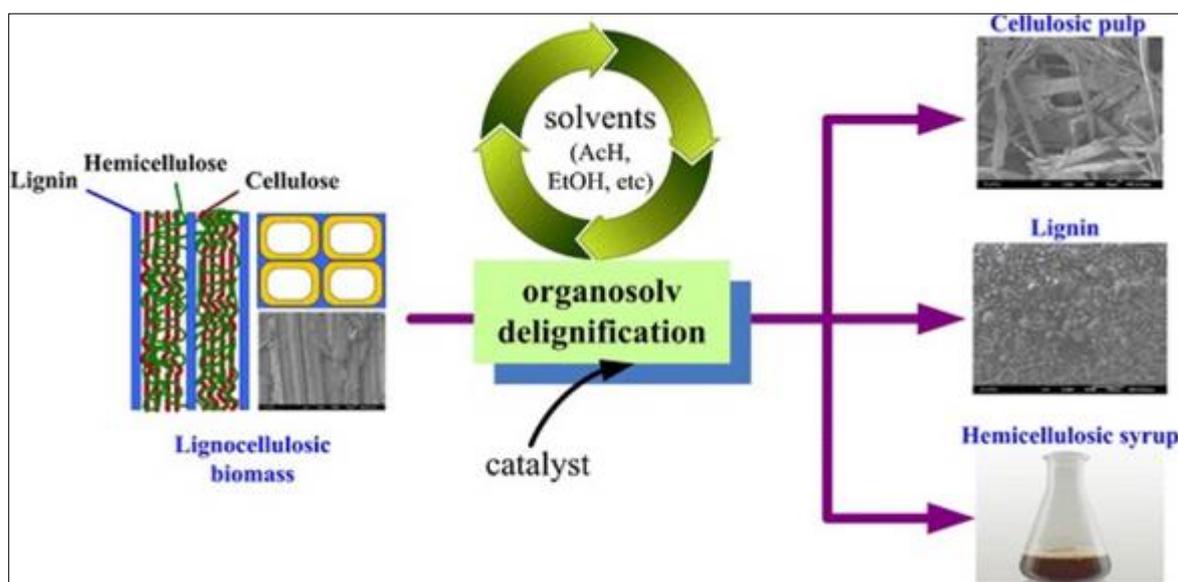
**Figure 10** Delignification of wood in three phases in kraft process to remove lignin and carbohydrates [31]

The delignification of wood occurs in three phases in kraft process to remove lignin and carbohydrates as shown in Figure (10). In the first phase about only 20% of lignin are dissolve in alkaline solution when the temperature is less than 150 °C. Although more than 90% of lignin are dissolved after increasing the temperature up to 150 °C with very good selectivity without dissolving extra carbohydrates. Even though increasing the temperature up to 170 °C lead to

dissolving the rest of lignin and dissolving large amount of carbohydrates. Therefore the time and temperature are very important two factors to control lignin purity and quantity [31].

### 1.5. Organosolv pulping analytical process

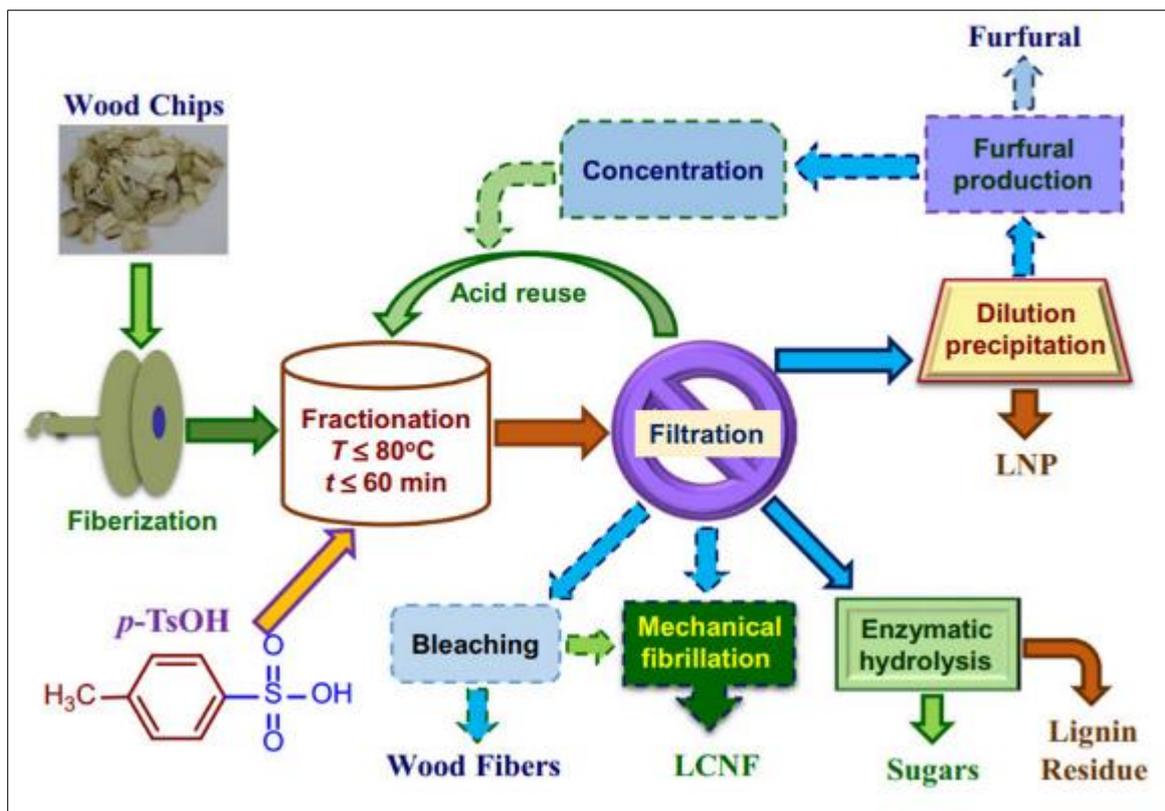
Organosolv is an analytical process to remove lignin and hemicellulose components from wood by utilizing organic solvents such as ethanol, methanol, butanol, acetic acid, acetone, formic acid, and ethylene glycol [32-36]. However, in some new researches it has been used some unpopular organic solvents such as xylene [37] to delignification of wood. In 1968, Theodor Kleinert was the first scientist invented the organosolv analytical process to delignification of wood as an eco-friendly process [38, 39]. There are many advantages of organosolv analytical process in compare to kraft analytical process. For example, obtaining lignin in better quality otherwise it is considered as a waste. The other advantage is removing of organic solvent is so easy by vacuum distillation. Furthermore, the utilizing of organosolv analytical process reduces the creation of sulfated byproducts, which are eco-unfriendly materials. Figure (11) shows animated diagram of the organosolv analytical process to delignification of wood using acetic acid and ethanol as a solvents to dissolve lignin [40].



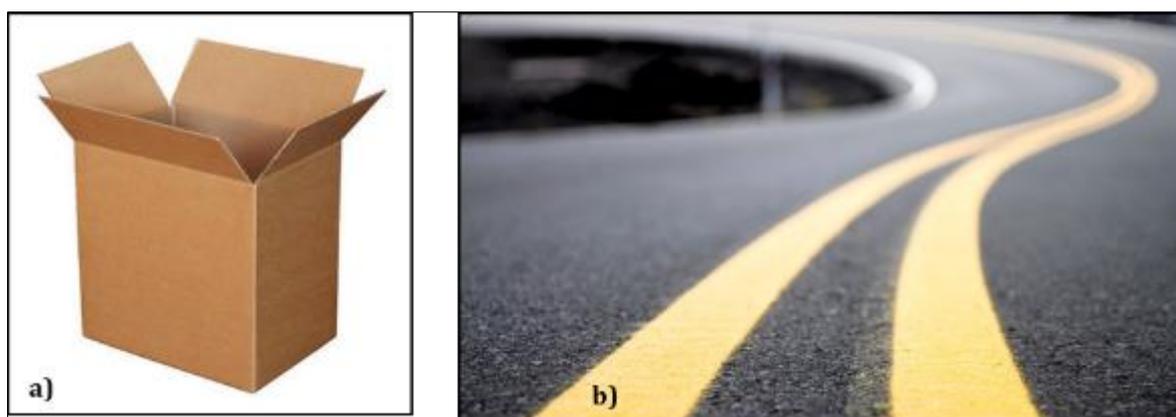
**Figure 11** Schematic diagram of Organosolv analytical process [40]

Recently Zhu's group has used aqueous p-toluenesulfonic acid to delignification of wood. They have also demonstrated that using p-toluenesulfonic acid can reach almost completely solubility of lignin at reasonable temperature equal or less than 80 °C and for only 20 min. Figure (12) shows schematic diagram describe the separation process of wood chips components [41].

Mostly lignin is found in the cells of wood as it is considered the most plentiful natural polymer around the world after cellulose [42]. Annually, more than 50 million tons of lignin is produced around the world as a waste from paper manufacturing [43]. Therefore, it is necessary to find ways to consume lignin in useful applications. Last few decades, many researches in both academic and industrial field have tried to use lignin in different application such as papers, biofuel, some important chemicals, concrete, board binder, asphalt, foams, plastics, carbon fiber, adsorbent surface ..etc [44-48]. Figure (13) shows brown paper box made from lignin and using lignin as a crack filling with asphalt.



**Figure 12** Schematic diagram of separation wood components utilizing p-Toluenesulfonic acid for manufacture of fibers [41]



**Figure 13** a) Brown paper box made from lignin. b) Asphalt contains lignin as a crack filling materials

## 2. Conclusion

To conclude, lignin has been extensively investigated as a useful material in industry. Even though, lignin has not investigated enough to get large scales of valuable outcomes, so this paper recommend lignin to be investigated by researchers and focus on two main important applications. Number one is utilization of lignin as adsorbent surface to remove pollutants from water. Number two is utilization of lignin as a photo-stabilizer of plastic polymers to stop the photo-degradation of them.

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## Compliance with ethical standards

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### *Disclosure of conflict of interest*

All authors of the manuscript have no conflict of interests to declare.

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