

DIFFERENT INDUSTRIAL APPLICATIONS OF LIGNIN AS A SUSTAINABLE MATERIAL

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REZUMAT. Această lucrare își propune să stimuleze interesul asupra ligninei industriale și să ofere o imagine asupra utilizării ei în industrie. Lignina este, după celuloză, cel mai des întâlnit polimer natural, iar în ciuda acestui fapt, nu este utilizată pe măsură. În procesul de fabricare a hârtiei, lignina este eliminată din lemn și devine un co-produs. Doar o parte nesemnificativă este folosită în produsele de specialitate, restul servește drept combustibil pentru producerea de energie termică. Există diferite tipuri de lignină, care diferă funcție de resursa naturală din care sunt realizate (lemn sau recolte agricole), dar și funcție de protocolul de fabricare. Un material special, bazat pe o matrice de lignină, este Arboform. Fabricat din biopolimeri puri materialul termoplastice este potrivit la turnarea prin injecție. Lignina este de asemenea un combustibil excelent, deoarece are un randament energetic mai mare la ardere decât celuloza.

Cuvinte cheie: lignina, bioplastic, biopolymer, biomass, materiale regenerabile

ABSTRACT. This paper aims to revive the interest of industrial lignin and to show its current applications in industry. Lignin is second to cellulose as the most abundant natural polymer and in spite of this fact it is a vastly under-utilized material. During the pulp and papermaking operations lignin is discarded from wood and becomes a co-product. From here only an insignificant part is used in specialty products, the rest serves as fuel for thermal energy generation. There are different types of lignin regarding the plant resource they are made of (wood or agricultural harvest) but also depending on the isolation protocol. A special material based on a lignin matrix is Arboform. Made from pure biopolymers this thermoplastic is suitable for injection molding. Lignin is also an excellent fuel, since lignin yields more energy when burned than cellulose.

Keywords: lignin, bioplastic, biopolymer, biomass, renewable material

1. INTRODUCTION

In the search of a renewable and sustainable material that can be a substitute for materials based on crude oil, lignin might be the answer.

Industrial lignins are mostly obtained as co-products of the manufacture of cellulose pulp during paper making and biomass fractionation. Although the amount of lignin reaches 50 million tons per year [1] only a small amount, up to 2%, is recovered and used in a wide range of chemical products or materials, such as Arboform [2]. The rest of the 98% are restricted to serve as fuel for the paper mills. Yet there are enough reasons and solid arguments to put this promising source of materials and chemicals in our daily applications.

Lignin is a complex chemical compound, cross-linked polymer that forms a large molecular structure. Most commonly derived from wood or crops it is an integral part of the cell wall where it forms a tridimensional structure, a matrix, which gives mechanical strength to wood, basically supporting the tree's structure. Lignin is formed by photosynthesis and makes up about 15-25% of the substance of every wood or plant (depending on the variety) as shown in Figure 1. Depending on this

content, lignin has a various structure from hardwood to softwood and even more from agricultural crops. It also varies regarding the different method of isolation that are used.

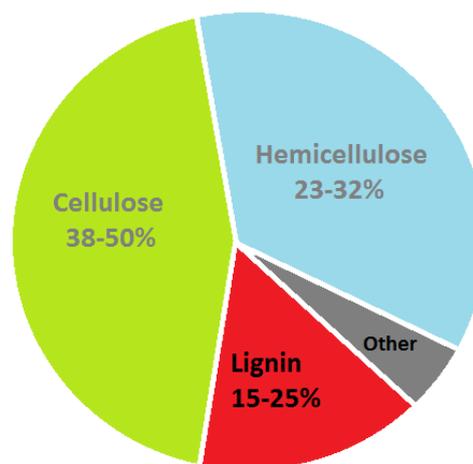


Fig.1 Simplified structure of wood

2. MATERIALS

Considering the molecular complexity of lignin it makes all isolation and identification processes difficult [3] and, consequently is not possible to

define the precise structure of lignin as a chemical molecule [4]. All lignins show a certain variation in their chemical composition. One of the difference of the lignin is given is given by the wood content, depending if it 's softwood o hardwood. In Figure 2 there are shown the monomeric buildings of lignin: Guaiacyl which is predominant in softwoods and Syringyl which is predominant in hardwoods.

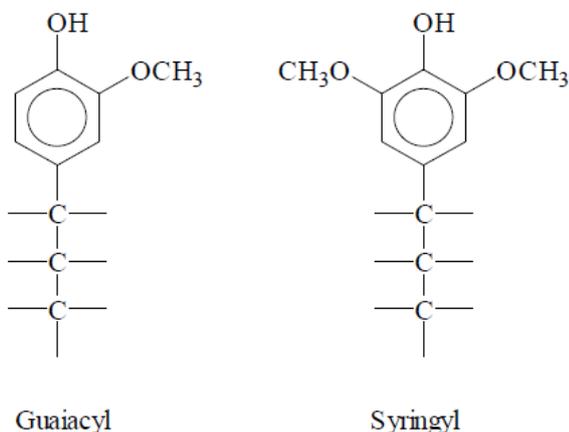


Fig.2 Building units of lignin

But as far as applications are concerned, this differences are minor. The major differences are between lignins are given by the isolation method that is being used. By the method that is being used we can differentiate two principal categories of lignin: those which are sulphur bearing and those which are sulphur-free. The most widely spread are the sulphur bearing lignins which are being commercialized for various applications. The sulphur free lignins have resemble more closely to the structure of native lignin.

Among the sulphur bearing lignin we differentiate:

- Kraft lignin
- Sulphite lignin
- steam explosion lignin

Sulphur free lignins can be obtained through following processes:

- Biomass Conversion Technologies
- Solvent pulping
- Soda pulping

2.1 Kraft lignin

The Kraft process is the most predominant pulping process worldwide, especially for the papermaking industry. The process (Figure 3) entails treatment of wood chips with a mixture of sodium hydroxide and sodium sulfide, known as white liquor, that break the bonds that link lignin to the cellulose. It basically converts wood or non-wood material into pulp. Pulping processes range from purely mechanical processes, in which the wood is ground into fibers by disk refiners or grindstones, to

chemical processes, in which the fibers are separated by using chemicals that degrades and dissolves the lignin that binds them together in the living tree. Mechanical pulping is energy intensive, while the dominant chemical process, the Kraft process, uses a solution of sodium hydroxide and sodium sulfide (i.e, hydrosulfide) to dissolve the lignin [6].

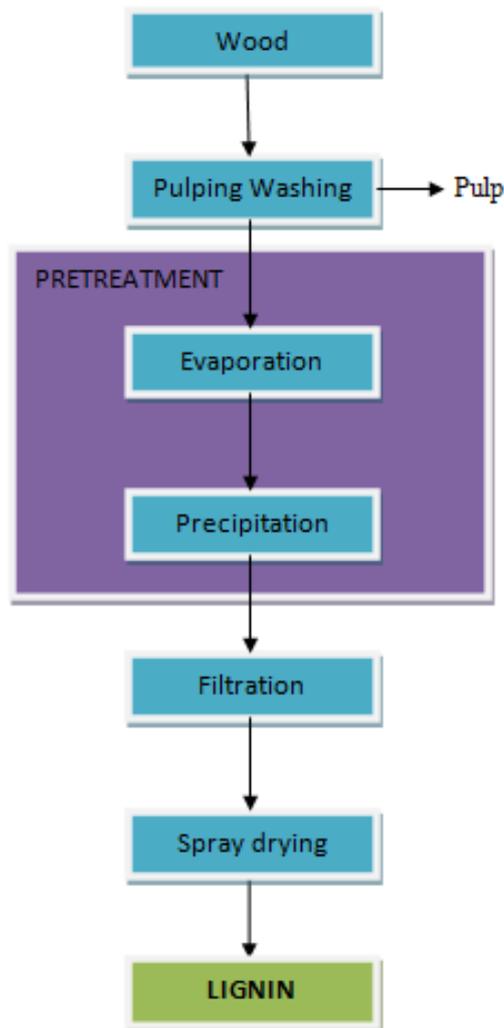


Fig.3 Schematic kraft process for obtaining lignin

Kraft pulp mills have evolved into very large facilities that are integrated with a highly engineered system for recovery of pulping chemicals and energy which is based on the combustion of the spent pulping liquor (black liquor). The recovery system is essential to the economic and environmental performance of the kraft pulp mill and its use simplifies the business model of pulp and paper producers, allowing them to concentrate on their core paper business. Therefore, relative to sulphite lignin, the quantity of kraft lignin recovered for chemical use is rather small; worldwide only one company is currently practicing it on an industrial basis. This situation may change in the near future, since due to steady efficiency improvements, a modern kraft pulp mill nowadays may generate an

excess of energy relative to its needs. In addition, the ability to implement incremental kraft pulp production is a desirable goal. Thus, the extraction of lignin has been proposed as a strategy to allow pulp capacity expansion and keep energy production and consumption in balance within the mill. The extracted lignin can then be used inside the mill to generate exportable electricity or outside the pulp mill for energy or other uses.

2.2 Sulphite lignin

The most abundant type of commercial lignin available is Sulphite lignin because traditionally this was the most used type of pulping process [7]. At first it was developed based on the use of calcium bisulphite, an inexpensive pulping chemical. The lack of suitable technology for the regeneration of this chemical from the spent pulping liquor precipitated the development of uses for calcium lignosulphonate. The sulphite pulping technology evolved to encompass the use of other sulphites and bisulphites, such as magnesium, ammonium and sodium. With time, the sulphite pulping process started to be replaced by the kraft pulping, which is more versatile and produces stronger pulps, and has a robust chemical recovery process. Thus, the days of sulphite pulping dominance are long gone and sulphite pulp production has declined from nearly 20 million tons in the 1980s to about 7 million tons nowadays. Current trends are for sulphite pulp production to decrease, since no interest in building new sulphite mills has been shown. In spite of this trend, sulphite lignin production has managed to remain relatively stable, meeting a worldwide demand in which recent declines in consumption in Western Europe, North America and Japan have been offset by increases in China, India and other parts of the world.

In the sulphite pulping process, wood is digested at 140–170 °C with an aqueous solution of a sulphite or bisulphite salt of sodium, ammonium, magnesium or calcium. The type of salt and its solubility and association characteristics determine the pH of the digestion. For instance, the pulping medium is highly acidic when calcium bisulphite is the pulping agent, but is practiced in highly alkaline environment when using sodium sulphite. During the digestion process, several chemical events take place, including the cleavage of linkages between the lignin and the carbohydrates, the scission of carbon–oxygen bonds that interconnect lignin units, and the sulphonation of the lignin aliphatic chain. The latter reaction is the most critical in sulphite pulping and gives sulphite lignin its main characteristics. This reaction is the result of the attack of the negatively charged sulphite or bisulphite ions on the lignin structure.

2.2 Steam explosion lignin

With this method the wood or other biomass is subjected to high temperature steam treatment, followed by a rapid pressure release, the fibrous mass is ‘ exploded ’ and liberated fibres together with fibre bundles are formed. Different degrees of wood polymer modification and degradation can be achieved by adjusting the time and temperature. Although the process is not commercial at present, it has gained much attention as a possible means for simple and cheap separation of wood polymers (e.g . for the production of micro-crystalline cellulose and bio-based ethanol). In particular, hardwood species such as aspen are suitable raw materials, since the lignin portion can be extracted, to a large extent, by either aqueous alkali or by organic solvents leaving a residue highly enriched in cellulose [8].

In a pure steam explosion process without any added chemicals, the reaction conditions are weakly acidic, due to the release of acetic acid from the hemicellulose. Thus, the major reaction types are similar to those present in acidic sulphite pulping, viz. hydrolysis of polysaccharides and hydrolysis and condensation of lignin. In addition, due to the high temperature usually employed (approx. 200°C), homolytic cleavage reactions can be assumed to take place. Altogether, these reactions result in a highly heterogeneous lignin structure containing both degraded lignin fragments and recombined fragments through condensation reactions.

2.3 Sulfur-free lignins

Although not very popular and hardly even commercialized to date, sulfur-free lignins are a type of lignin that are getting more and more attention and interest. Having a very similar structure to the one of native lignin it opens the road to new fields of utilization.

Lignin can be obtained by the conversion of biomass technologies that are typically using a hydrolytic pretreatment. These treatments are the ones that generate sulfur free lignin. From the pretreated biomass the lignin must be extracted with an organic solvent and from the resulting solution lignin is recovered normally by precipitation. The recovered lignin is largely insoluble in water under neutral or acidic conditions. The converting of biomass to ethanol is only at its early stages but it has the potential to become a source of sulfur free lignin.

Another alternative to kraft and sulfite pulping is solvent pulping being also a more environmentally friendly solution. Lignin is recovered from the spent solvent by precipitation but furthermore other co-product chemicals are recovered [9]. These lignin

have high solubility in organic solvents and are very hydrophobic, they are practically insoluble in water. They also have a low glass transition temperature and exhibit flow when heated.

Sulfur-free soda pulping of non-wood feedstock such as straw, sugar cane bagasse, etc., is already practiced around the world and therefore could be a more readily available solution. Recovery of these lignins is based on precipitation followed by the separation of the solid from liquid and drying. One of the main disadvantages of this technologic process is that when applied to nonwood fiber sources soda spent pulping liquors often contain silica, which may co-precipitate with the lignin which gives a lower quality. In the meantime companies have claimed to have solved this problem and to have obtained soda lignins with low ash and silica content.

3. CONCLUSIONS

New applications are emerging for specialty, sulfur-free lignins in diverse areas, principally as sustainable alternatives to nonrenewable products, such as phenolic and epoxy resins, and isocyanates. This is in addition to industrial efforts that aim at using lignin as the principal component of thermoplastic materials. The latter represents an activity for which little published information exists so far. The ability for lignin to make significant impact in these areas, however, depends on its availability in industrial quantities as a high-purity product, preferably in a sulfur-free form.

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