

## Trends and Limitations of Lignin as a Starting Material

Laura G. Covinich, and María C. Area \*

This editorial envisions a future in which greater value is obtained from technical lignins. The currently available amounts of such lignins are immense, and the costs are often in line with lignin's fuel value. Key challenges are associated with lignin's complexity. When envisioning future prospects for lignin, it is important to consider any differences between different types of technical lignin as a starting material.

DOI: 10.15376/biores.19.1.6-9

Keywords: Technical lignins; Lignin valorization; Lignin complexity

Contact information: IMAM, UNaM, CONICET, FCEQYN, Programa de Celulosa y Papel (PROCYP), Félix de Azara 1552, Posadas, Argentina; \*Corresponding author: cristinaarea@gmail.com

### Value Opportunities

The conversion of each lignocellulosic component of biomass into high-value chemicals and biofuels can contribute significantly to the sustainability of its entire value chain. For many years, studies on the valorization of cellulose (40 to 45% of the raw material) and hemicelluloses (20 to 30% of the raw material) have abounded; furthermore, some of the technological processes have been developed, have reached a mature stage, and in some cases become industrialized.

On the contrary, lignin (25 to 30% of the raw material) is considered a by-product of the pulp and paper industry and cellulosic ethanol plants, with an application currently mainly limited to heat, energy, and fuel generation. Since lignin has an attractive market value, it is also considered a marketing product. The previously explained scenario implies that only about 5% of the lignin's potential as a chemical byproduct is being realized. Figure 1 shows the volume market and prices of different types of technical lignins.

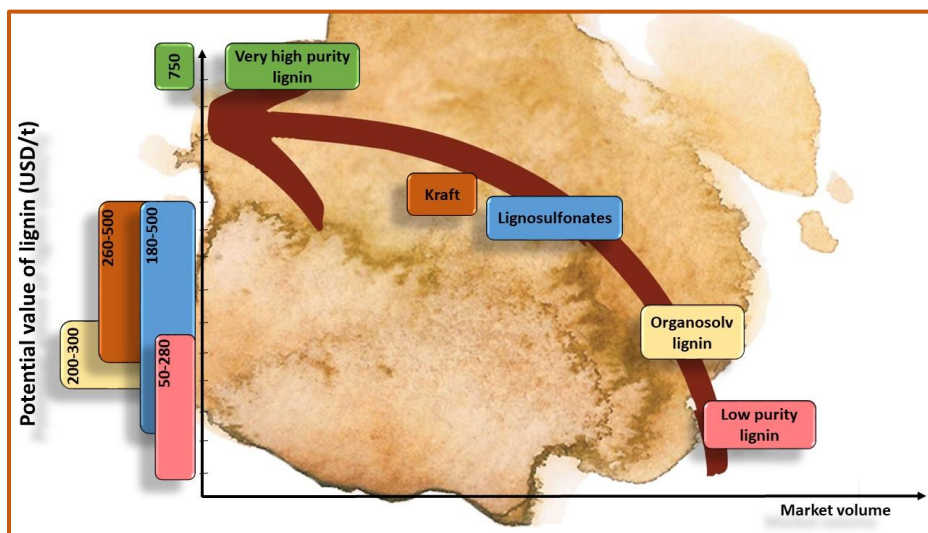


Fig. 1. Types, market volume, and prices of technical lignins

## Challenges and Complexities

Lignin's availability and its unique polymeric structure make it a raw material with great potential for several biochemical products and biopolymer synthesis.

**Table 1.** Main Features of Extracted Lignins (technical lignins) with Different Processes

Lignin Type	Properties Compared to the Native-Lignin Form	Potential Applications	Molecular Weight ( $M_w$ ); Polydispersity (PD); Ash (%); Sulphur (S%)
Kraft Lignin	Soluble in alkaline solutions and highly polar organic solvents. Increased 5-5 bonds between subunits, new functional groups, and bonds (stilbenes). Low sulfur content. 70-75% of the hydroxyl groups could be sulfonated. Sulfur, ash, and carbohydrates impurities.	Fertilizer and carrier of pesticides, carbon fibers, thermoplastic polymers, binders, resins, and activated carbon. Chemistry: vanillin, hydroxylated aromatics, quinine, aldehydes, and fatty acids.	$M_w$ : 1,500-25,000 PD: 2.5-3.5 Ash%: 0.5-3.0 S%: 1.0-3.0
Soda lignin	High content of phenolic hydroxy groups. Low glass transition temperature. Sulfur-free. Medium-high purity.	Dispersants, resins, animal nutrition, polymer synthesis.	$M_w$ : 1,000-15,000 PD: 2.5-3.5 Ash%: 0.7-2.3 S%: 0
Ligno-sulfonates	Soluble in acidic and basic aqueous solutions, highly polar organic solvents, and amines. High molecular weight. Incorporation of sulfonate groups in aromatic hydrocarbons. Compared to kraft lignin has low purity (higher ash content).	Colloidal suspensions, stabilizers, dispersants, detergents, adhesives and binders, surfactants, cement additives, feed components and complexing agents.	$M_w$ : 1,000-150,000 PD: 4.2-7.0 Ash%: 4.0-8.0 S%: 3.5-8.0
Organosolv lignin	Soluble in organic solvents with low boiling points. Higher phenolic hydroxyl groups. Sulfur-free. Quite a homogeneous structure. High purity. High chemical reactivity.	Additives for paint, varnishes, paints, dispersants, and carbon-based materials.	$M_w$ : 500-5,000 PD: 1.5 Ash%: 1.7 S%: 0-0.3
Pyrolytic lignin	Soluble in organic solvents but poorly soluble in water. The backbone of the C8 basic unit (instead of oligomers derived from C9) has a lower average molecular weight and frequently C-C bonds between subunits.	Pyrolysis products, chemicals, and liquid fuels.	-
Steam explosion lignin	High content of phenolic hydroxyl groups and low content of methoxy groups. Frequent C-C bonds between subunits.	Chemical products such as phenols, and biodiesel.	-
Acidolysis Lignin (hydrolyzed)	Few carbohydrate impurities. Low molecular weight. High amount of hydroxyl groups. Low content of ether and ester bonds. Medium-high purity.	Fire retardants and flocculants.	$M_w$ : 5,000-10,000 PD: 4.0-11.0 Ash%: 1.0-3.0 S%: 0-1.0

On the other hand, its highly irregular and complex polymeric structure represents the main challenge when selecting the most suitable conversion technology. One of the

main problems is the struggle to know this macromolecule's exact composition and structure due to its complexity and heterogeneity. This variability also originates from the source of biomass used, the season of the year, and various growth parameters. It is also relevant to consider that its polyphenolic structure can degrade and (or) undergo chemical and structural changes because of the type of pretreatments used to individualize each biomass component and its conditions. These effects will define the potential applications of lignin beyond combustion, as shown in Table 1.

### Development Strategies

Treatment approaches that are targeted as “lignin first” involve one-pot reductive catalytic depolymerization of all lignocellulosic components, avoiding condensation reactions that lead to a more recalcitrant lignin. Even if this is an interesting approach, the massive volume of lignin generated by the processes of producing cellulosic pulp justifies further research on the traditional methods of obtaining lignin from its precipitation from the black liquor that remains after the conventional pretreatments to valorize the carbohydrate fraction.

When kraft lignin is separated from black liquor, usually this is done by precipitation and filtration. The method highly depends on the black liquor concentration. There is a need to deodorize kraft lignin. Soda lignin can be separated by filtration and centrifugation, and there is no need to deodorize it. Lignosulphonates from sulfite pulping are recovered by ultrafiltration and are easier to separate than other lignins because of the higher molecular weight of the lignin fragments. Finally, organosolv lignin can be obtained by addition of a non-solvent, *e.g.* water.

### Prospects and Present Capacities

The lignin market includes relevant companies including Borregaard LignoTech, WestRock, Tembec Inc., Domtar Corporation, Domsjö Fabriker AB, Changzhou Shanfeng Chemical Industry Co. Ltd, Nippon Paper Industries Co. Ltd., UPMKymmene Corporation, Asian Lignin Manufacturing Pvt. Ltd., Lignol Energy Corporation, Green Value, and Liquid Lignin Company (LLC). Among the most efficient methods is the commercial LignoBoost™ process that isolates kraft lignin from black liquor with high purity by acidification of the liquor using CO<sub>2</sub>, and then the collected precipitate is washed with acid before filtration. Domtar's Plymouth plant (USA) and Stora Enso's Sunila factory (Finland) can produce 75000 t of kraft lignin/year using the LignoBoost process. Regarding lignosulphonates, the biggest producer is Borregaard LignoTech, with a capacity of about 500,000 t. Organosolv-type lignin is commercialized by FormicoFib, Organocell, ASAM, and CIMV, among others. In the case of pyrolytic lignin, reactors for the pyrolysis process are technology available commercially, but the obtained pyrolysis liquid is currently utilized mainly for energy generation.

The possibility of reaching economic benefits in the lignocellulosic biorefinery process increases the likelihood of industrial investment. Worldwide, the valorization of lignin through the formulation of high-value products have been essential as the basis of all technical-economic analyses of lignocellulosic biomass utilization schemes. In this sense, it becomes relevant to show that the chemical valorization of lignin could be competitive compared with the current energy use of 98% of the available lignin. However, the optimal pretreatment for the simultaneous valorization of biomass co-constituents has not been identified yet. Besides, suitable technologies that enable value-added applications

for lignin are not always available or ready for industrialization. Even if the options for lignin treatment and the variety of possible products are immense, it is necessary to find scenarios applicable on an industrial scale.

The costs associated with the development of these technologies must be offset by the maximum revenues expected for the specific lignin application. Furthermore, production volumes of the type of lignin for specific value-added applications must match market demand.