



# PYROLYSIS OF LIGNOFORCE™ LIGNINS FOR THE PRODUCTION OF VALUABLE CHEMICALS

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## INTRODUCTION

Brazil has one of the largest rates of forestry activities worldwide. With more than 7.84 million hectares of reforestation, forestry represents one of the segments with enormous potential for the construction of a green bioeconomy. It can provide clean energy using natural polymers such as cellulose, hemicelluloses, and lignin, and fulfill several gaps regarding bioenergy and bioproduct generation (IBÁ, 2017).

Global challenges such as poverty, inequality, peace, and social justice are strongly related to the effects of climate change and environmental degradation, and significant efforts must be made to address them. According to the United Nations (UN), the Sustainable Development Goals (SDGs) are the blueprint for achieving a better and more sustainable future for all<sup>1</sup>. Meanwhile, the 14th World Forestry Congress highlighted that forests are critical to achieving the 17 SDGs, and their sustainable management is key for this task<sup>2</sup>.

Lignin is the most widely available aromatic biopolymer in nature, and stands out as a timely and versatile raw material for a variety of industrial applications. Forests produce an equivalent to 150 billion tonnes of lignin per year, yet it remains a virtually unexplored renewable carbon source (Hu et al., 2018). This material binds cellulose and hemicelluloses in the plant cell wall and protects it against the action of water, radiation, and microorganisms by promoting hardness and strength properties in lignocellulosic materials (Vanholme et al., 2010). Its main constituents result from the radical coupling of cinnamic alcohol derivatives that produce an intricate network of monolignols whose structures are depicted in Fig. 1.

Several strategies have been developed to isolate lignin from the plant cell wall, such as: extraction techniques (e.g. organosolv), ionic liquids, and deep eutectic solvents. Acid,

<sup>1</sup> <https://www.un.org/sustainabledevelopment/sustainable-development-goals/>

<sup>2</sup> <https://www.un.org/sustainabledevelopment/blog/2015/09/forests-of-the-future-fundamental-to-achieving-sustainable-development-goals-un-agency/>



alkaline, and enzymatic hydrolysis are also known for sorting and allowing fractionation of the main biopolymers found in lignocellulosic materials (Ramos et al., 2020).

It is noteworthy that some of the applications for these technical lignins have already reached commercial scale, and are flourishing: lignin has been applied as a binder and dispersing agent in batteries, cement, and paving materials, as well as in animal feed and polymer chemistry (Suota et al., 2021).

At an industrial level, only pulp and paper and cellulosic ethanol production facilities can produce a significant amount of lignin for commercialization. The chemicals used to isolate cellulose fibers generate a black liquor with a massive amount of solubilized lignin daily (75,000 metric tons per year). The LignoForce™ process isolates kraft lignin in high purity by acid precipitation with CO<sub>2</sub>, and most of the black liquor produced worldwide is incinerated for energy and chemical recovery in the kraft process (Dessbesell et al., 2020). Since lignin is overproduced in some of these industrial sites, it may be seen as a sustainable source of aromatic compounds and other platform chemicals when isolated from the black liquor by precipitation.

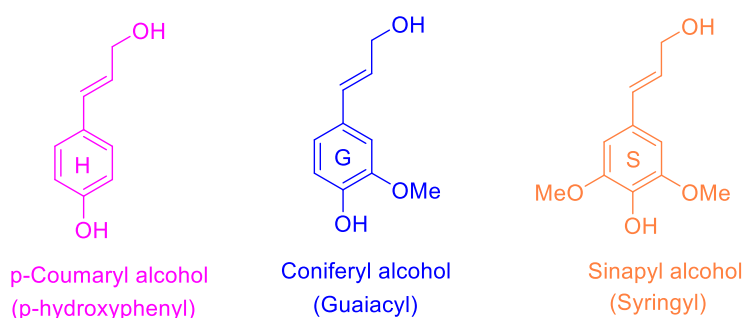


Figure 1 – Main monolignols of the lignin structure

Lignin depolymerization can be highlighted as another viable conversion process, since depolymerized lignin is a rich source of antioxidants, building blocks for chemical synthesis, and blends of aromatic compounds containing benzene, toluene, and xylene (BTX) (Nowakowski et al., 2010). Several techniques are available for lignin depolymerization, and they can be divided into oxidative, reductive, and thermal treatments.

Pyrolysis is a thermal conversion carried out without oxygen that turns solid lignin into liquid; this liquid contains monomers and oligomers, as well as carboxylic acids, alcohols, ketones, and aromatic compounds of the BTX family (Bridgwater, 2003). These small molecular mass compounds are useful for synthesizing phenol-formaldehyde resins, cosmetic and pharmaceutical formulations, antioxidants, and platform chemicals for the synthesis of a vast number of petrochemical derivatives, meaning that lignin is an outstanding candidate to decrease our dependence on petrochemistry.

In this study, lignin samples isolated from hardwood and softwood species by the LignoForce™ process were pyrolyzed at 550 °C to produce liquid small molecular mass compounds that were partially characterized by gas chromatography and mass spectrometry.

## MATERIAL AND METHODS

Softwood and hardwood LignoForce™ lignins (henceforth LFSL and LFHL, respectively) were used following the extensive characterization by Suota et al. (2021).

Pyrolysis was carried out in a 600 mL stainless steel tubular reactor equipped with two condensers in sequence. About 125 g of each sample were pyrolyzed in duplicate with a heating rate of 5 °C min<sup>-1</sup>, followed by an isothermal condition for 90 min at 550 °C. A nitrogen flow at 200 mL min<sup>-1</sup> kept the atmosphere oxygen-free.

After pyrolysis, solid (biochar) and liquid pyrolysis products were quantified in relation to the mass (wt.%) of the starting material, while the gaseous product was ignored. The liquid product was separated into two phases: aqueous and organic (bio-oil). The bio-oils were characterized by FTIR on KBr discs, using 32 scans and a resolution of 4 cm<sup>-1</sup>. Moisture content was determined using a coulometric module in an MKC-610-DT Karl-Fischer KEM EBU titrator (Kyoto Electronics Manufacturing, Tokyo, Japan). The acid value (AV) of bio-oils was determined using the ABNT NBR 14448:2013 standard.

The <sup>31</sup>P NMR provided the bio-oils hydroxyl profile following the protocol developed by Meng et al. (2019). Gas Chromatography analysis, coupled with Mass Spectrometry (GC-MS), was performed after solubilizing bio-oils in dichloromethane (DCM) at a concentration of 200 ppm. The aqueous fractions (5 mL of each) were filtered through a Hypersep C18 solid phase extraction cartridge (Hypersep™), and the retained components were eluted with 2 mL of DCM and diluted 1:3 (vol/vol). Then, these eluted fractions and the bio-oils were derivatized using N-O-Bis(trimethylsilyl)trifluoroacetamide (BSTFA) and chromatographed using a GC-MS containing a Varian VF-5 MS capillary column by injecting 1 µL in split mode (1:10).

The analysis started at 50 °C, held for 2 min, then increased to 280 °C with a heating rate of 5 °C min<sup>-1</sup> and held for 2 min. The ion source was maintained at 200 °C and the interface at 280 °C. Quantification was based on area normalization, and some components such as phenol, guaiacol, and vanillin were identified using primary standards.

## RESULTS AND DISCUSSION

Lignin pyrolysis yielded solid, liquid, and gaseous products. The liquid was separated into an organic phase (bio-oil) and an aqueous phase or pyroligneous extract (Table 1). Achieving high yields of pyrolysis liquids is challenging for biomass conversion processes. In fact, non-catalytic pyrolysis generates a range of reaction products with relatively low selectivity.

LFSL produced a slightly higher amount of biochar compared to LFHL, reflecting the differences revealed in the TGA assays of previous work (Suota et al., 2021). This result explains that lignins with more cross-linked structures (LFSL) have a peculiar behavior when heated, mostly degrading rather than melting during pyrolysis. In contrast, less condensed lignins (LFHL) undergo melting, followed by depolymerization (Han et al., 2019). In this process, there might have been an agglomeration of solids as well, favoring the formation of charcoal (Fan et al., 2017).

Table 1 – Yield of lignin pyrolysis products at 550 °C

Lignin	Biochar (%)	Gas (%) <sup>a</sup>	Liquids (%)	Bio-oil (%) <sup>b</sup>	Pyroligneous extract (%) <sup>b</sup>
LFSL	46.2	19.1	34.7	54.0	46.0
LFHL	43.9	16.8	39.3	55.5	44.5

<sup>a</sup> Calculated by difference;

<sup>b</sup> Based on the yield of the liquid phase.

FTIR of the bio-oils reproduced the classical vibrations for functional groups that are typically found in the original material (technical lignin). Among them, OH stretching at  $3400\text{ cm}^{-1}$ , C=O stretching around  $1700\text{ cm}^{-1}$ , and C-O in a range of  $1100$  to  $1300\text{ cm}^{-1}$  compose the main functional groups of bio-oil compounds. FTIR revealed that depolymerized lignins preserve their phenolic nature due to the aromatic ring vibration at  $1500\text{ cm}^{-1}$ .

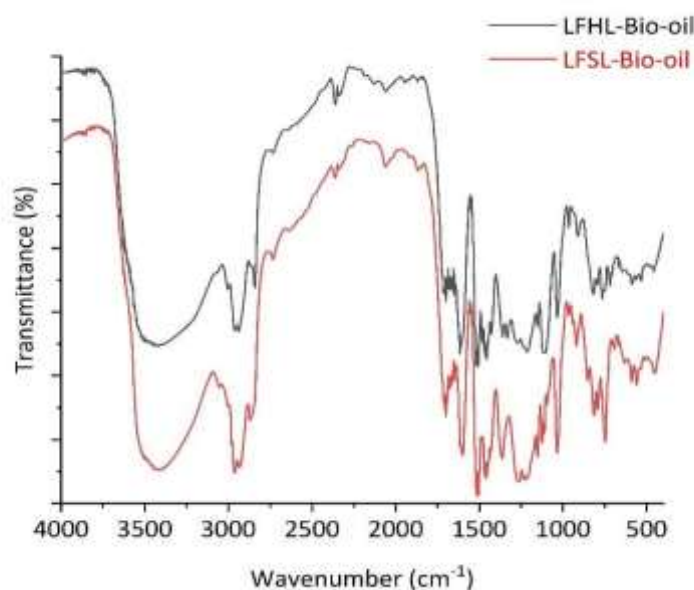


Figure 2 – Bio-oils FTIR spectra

Additional characterization of lignin bio-oils revealed a high total hydroxyl content and undetectable ash content (Table 2). This evidence shows that bio-oils are free from inorganic impurities and can be valuable in applications with high hydroxyl demand, such as green plastics, polyurethane foams, and resins. Although the organic samples had a low moisture content, which implies a particularly positive feature, the high acidity can hinder bio-oil oxidation and thermal stability (Table 2). The bio-oil acidity is a known property of bio-oils from lignocellulosic and triacylglyceride matrices that can be decreased by chemical modifications using techniques such as esterification (Suota et al., 2019).

Table 2 – Lignin bio-oil properties based on several analytical methods

Bio-oil properties (organic phase)	LFSL	LFHL
Ash content (%)	0	0
Moisture (%)	0.82	0.71
Acidy index (mg KOH g <sup>-1</sup> )	41.83	45.01
Hydroxyl content (mmol g <sup>-1</sup> )	13.72	10.28
Aliphatic	0.47	0.76
Phenolic total	12.47	8.74
Condensed syringyl and pyrogallol	1.61	3.93

Guaiacyl and catechol	10.85	4.81
Carboxylic	0.77	0.77

Typically, the bio-oil from lignin pyrolysis contains phenolic compounds derived from syringyl, guaiacyl, and *p*-hydroxyphenyl structures, whereas the aqueous phase comprises mainly water and water-soluble derivatives. In fact, these fractions—phenolics, alcohols, aldehydes, and mainly carboxylic acids—concentrate a significant amount of small molecular mass compounds.

Chromatograms of both LFHL and LFSL bio-oils and their pyrolygneous aqueous extract disclosed the presence of several well-resolved peaks, as shown in Fig. 3.

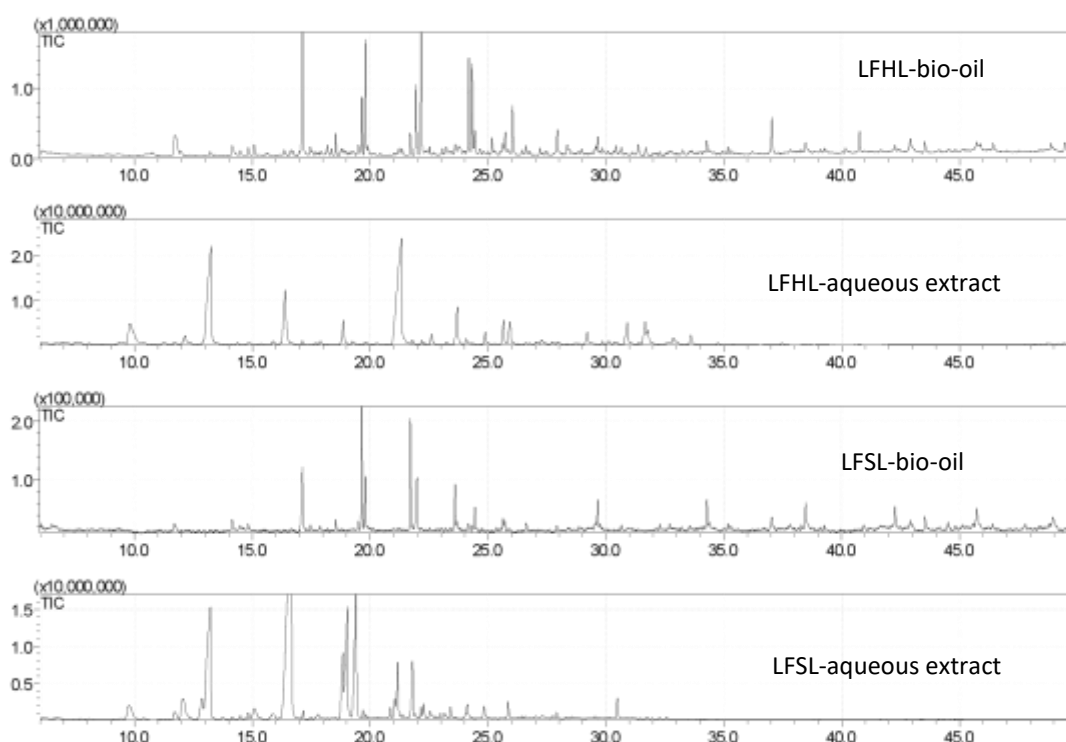


Figure 3 – Chromatogram of LFHL and LFSL bio-oils and respective aqueous phases obtained from GC-MS

There are at least 10 major compounds in each chromatogram, some of which were preliminarily identified by comparison with data from the NIST spectral library. Only 10% of the individual peaks were confirmed with proper analytical standards. Guaiacol was identified in bio-oil (8.8 wt.% in LFSL and 2.5 wt.% in LFHL) and aqueous samples (21.8 wt.% in LFSL and 12.1 wt.% in LFHL), and its presence was confirmed using a primary standard. Pyrolysis somehow led to demethylation as part of lignin degradation. Also, cleavage of  $\beta$ -O-4' linkages resulted in low molecular mass phenolic compounds. With a more intense degradation, pyrolysis produced simpler phenolics such as guaiacol, which was predominant in the aqueous fraction of LFSL (21.8% relative concentration). A literature review including the pyrolysis of lignins from various sources identified substituted guaiacols and syringols as the primary pyrolysis products of kraft lignins (Cheng & Brewer, 2017). Likewise, guaiacol and phenol appeared in all bio-oil samples but with a low relative percentage of 2–3%. These liquid compounds are promising starting materials for synthesizing polymers and coating agents and are potential precursors for renewable hydrocarbons such as green diesel and sustainable aviation fuels (Nowakowski et al., 2010).

Bio-oils may contain more than 300 components, but their identification and isolation is challenging (Bridgwater, 2012). Nonetheless, some prominent bio-oil components are commercially desirable due to their added value and potential applications. Catechol and pyrogallol fit well in this conjecture, and both were identified by  $^{31}\text{P}$  NMR (Fig. 4) and by GC-MS with high similarity by NIST.  $^{31}\text{P}$  NMR is the ultimate technique to identify and quantify hydroxyls in lignins and their derivatives. Moreover, the presence of catechol and pyrogallol in the bio-oil samples explains why they had a more elevated total hydroxyl content than the original material (Suota et al., 2021).

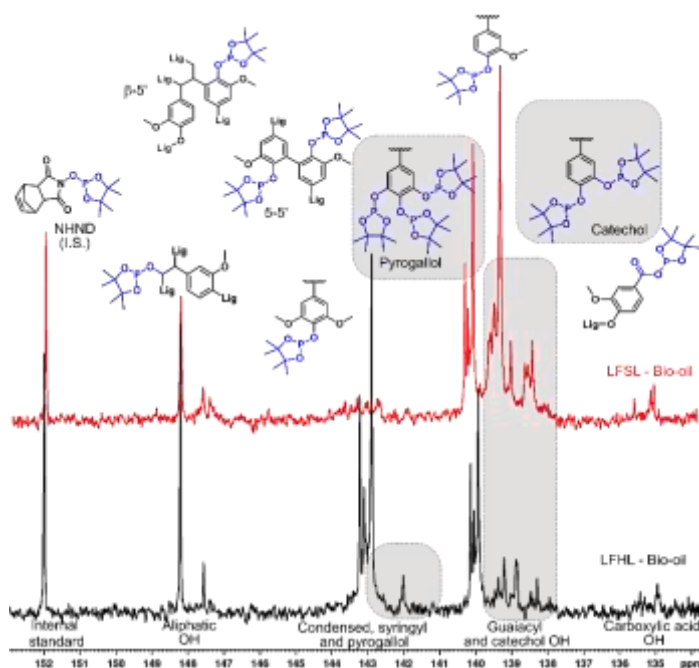


Figure 4 –  $^{31}\text{P}$  NMR spectra for lignin bio-oils

Catechol is an important precursor for the synthesis of pharmaceuticals and personal care chemicals, such as flavors and fragrances. The global catechol market size was US\$ 104.3 million in 2020, and it is expected to reach US\$ 155.4 million by the end of 2027, with a Compound Annual Growth Rate (CAGR) of 5.9% during 2021-2027.<sup>3</sup>

Pyrogallol—benzene-1,2,3-triol, according to the IUPAC nomenclature—is an oxygen-sensitive aromatic, white crystalline compound. Pyrogallol can be used in sensors for monitoring oxygen in the surrounding air since it can readily absorb oxygen, turning brown an originally colorless solution. Pyrogallol has also been known and used for its antiseptic properties<sup>4</sup>.

Therefore, lignin bio-oils are promising sources of valuable renewable compounds and biofuel precursors that can contribute to a lower dependence on fossil derivatives.

## CONCLUSIONS

Softwood and hardwood LignoForce™ lignins were depolymerized through conventional pyrolysis. The liquid products were separated into two phases and

<sup>3</sup> <https://www.openpr.com/news/2486491/global-catechol-market-growth-analysis-latest-trends>

<sup>4</sup> <https://www.vedantu.com/chemistry/pyrogallol>





characterized by GC-MS, FTIR, acid index (AI),  $^{31}\text{P}$  NMR, and Karl-Fischer titration. Formic and acetic acids, together with a wide range of phenolics, which included chemicals such as catechol, pyrogallol, and guaiacol, were identified in pyrolysis liquids. These monomers are essential precursors for the synthesis of fuel additives, platform chemicals, and renewable hydrocarbons. LignoForce<sup>TM</sup> lignins can also be used as a promising source of renewable carbon-based liquids after pyrolysis since phenolic compounds and aromatic structures are predominant components of pyrolysis liquids. Lignin applications go beyond the bioenergetic area and might contribute to decreasing petroleum dependence. Finally, lignin pyrolysis may offer an effective route to meet several important SDG goals, such as SDG 7 (clean and renewable energy), SDG 12 (responsible consumption and production), and SDG 13 (climate action), with an indirect contribution to SDG 2 (zero hunger), SDG 3 (good health), and SDG 15 (life on land). Thus, in the long term, lignin and lignin derivatives will have a significant role in sustainable development worldwide.

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