### SPECIAL FEATURE

**Lignin carbon fiber: The path for quality**

Qiang Li, Arthur J. Ragauskas, and Joshua S. Yuan

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### LIGNIN PRODUCTS

**Melt-blown compostable polyester films with lignin**

Wolfgang G. Glasser, Robert Loos, Blair Cox, and Nhiem Cao

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### LIGNIN CONVERSION

**Accelerated aging of bio-oil from lignin conversion in subcritical water**

Huyen Nguyen Lyckeskog, Cecilia Mattsson, Lars Olsson, Sven-Ingvar Andersson, Lennart Vamling, and Hans Theliander

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### LIGNIN CHARACTERIZATION

**An easy and reliable method for syringyl:guaiacyl ratio measurement**

Raquel Prado, Lisa Weigand, Shikh M.S.N.S. Zahari, Xabier Erdocia, Jason P. Hallett, Jalel Labidi, and Tom Welton

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### ECONOMIC ANALYSIS

**Analysis of economically viable lignin-based biorefinery strategies implemented within a kraft pulp mill**

Cédric Diffo Téguia, Rod Albers, and Paul R. Stuart
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Analysis of economically viable lignin-based biorefinery strategies implemented within a kraft pulp mill  
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TT NextPress, the new extended nip press, exceeds the standards of a traditional shoe press. Timely control of two rows of hydraulic pistons divided into six independently adjustable pressure areas affords perfect adaptability of the system to the Steel Yankee Dryer profile, ensuring optimal edge control. Additionally, automatic tilting adjustment allows managing the NIP curve in different operating modes.

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At its foundation, the chemical pulping industry was and is still centered around removal of lignin (Fig. 1) to produce high-quality cellulosic fibers. For sulfite pulping, the industry has well-established lignin isolation and conversion techniques to utilize lignin in several applications, including vanillin synthesis, binders, dispersion agents, emulsifiers, anti-corrosion agents, UV-absorbers, battery components, and anti-flammability agents in the future [2,3].

Challenging the status quo
Although the kraft industry has historically focused largely on pulp production and lignin for energy production, several developments have begun to challenge this convention from (a) enhanced energy efficiencies for pulp/papermaking [4], (b) lignin isolation technologies that can be incorporated into the kraft pulping platform [5,6], (c) an enhanced understanding of the structure of lignin during and after kraft pulping [7,8], and (d) new valorization conversion chemistries to convert kraft lignin to bio-derived chemicals, materials, and fuels [9,10,11]. In parallel, significant efforts are being directed to convert lignin from cellulosic ethanol plants to bio-derived products. In both cases, these efforts are being championed to garner greater value from lignin, enhance mill operations, and improve capital effectiveness.

Promising developments in lignin applications
Although the manufacturing platforms for kraft pulping and cellulosic ethanol are different, they will undoubtedly both benefit from lignin valorization studies. Even a brief review of lignin utilization efforts highlights several promising translational research outcomes, including:


1. Illustrative softwood native lignin structure [1].
Special TAPPI Journal issue: Lignin valorization

Although the cost of lignin as a bioresource remains important, additional factors are developing, including its natural anti-oxidant properties, sustainability, biodegradability, UV-absorbance, and as a unique resource for aromatic compounds. Equally important is the next generation of students and entrepreneurs dedicated to understanding the properties of lignin and, in turn, valorizing this unique polymer.

This special issue of TAPPI Journal is dedicated to the valorization of lignin and provides a sampling of lignin research studies going on globally. Please stay tuned for additional lignin research to appear in the April 2017 issue of TAPPI Journal.

LITERATURE CITED


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**Better drainage**
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**Reduced energy**
A core and tube producer wanted to increase production, have greater flexibility in its fiber selection and reduce energy use. Buckman applied Maximyze to the pulper, which conditioned the fiber faster with less refining energy, preserving fiber strength. Speed increased 10%. Refining energy decreased 30%. And tensile strength increased from 20 to 26 kgf/15mm.
Lignin represents an abundant biopolymer and a major waste from lignocellulosic processing plants, yet the utilization of lignin for fungible products remains one of the most challenging technical barriers for pulp mills and the modern biorefinery industry [1]. In recent decades, lignin has been sought after as a precursor polymer for carbon fiber due to the high carbon content (up to 60%). Lignin carbon fiber is expected to be compatible with the market size of the pulp and paper industry and may have transformative impact on petroleum-based carbon fiber [1].

CHALLENGES IN FABRICATING LIGNIN

Current strategies for fabricating lignin carbon fiber include blending lignin with other polymers served as plasticizers [2], reinforcing lignin carbon fiber using functional materials like carbon nanotube [3] and cellulose nanofiber [4], and modifying lignin phenolic hydroxyl groups (Ar-OH) through esterification [5,6]. Nevertheless, the quality and mechanical performance of current lignin carbon fiber are still too low to compete with commercialized petroleum-based carbon fiber, making lignin carbon fiber impractical for industrial application.

The real challenge of the poor quality lies in the heterogeneity of the lignin structure, which is caused by broad molecule weights, various interunitary linkages, and diverse functional groups. These inherent molecular characteristics could hinder the crystallite turbostratic carbon structure formation during the carbonization and graphitization of lignin carbon fiber. Thereby, the modification of lignin molecules toward more uniform structure could be the path for producing quality lignin carbon fiber.

TOWARDS HIGHER QUALITY LIGNIN CARBON FIBER

Two recent works have shed light onto the path for quality lignin carbon fiber. In the first work, Sun et al. (2016) [7] have shown the potential of organosolv lignin as the precursor of quality lignin fiber. Organosolv lignin is derived from organic solvent-based extraction of biomass and is purer than most other types of lignin due to less polysaccharide content and modified condensed structures [7,8]. In fact, the most abundant industrial lignin is currently generated from the widely-used kraft pulping process, namely kraft lignin. Most types of lignin, including kraft lignin, need to be purified and further fractionated to improve their uniformity before manufacturing carbon fiber toward high quality.

Recently, Li et al. (2017) [9] have shown that biochemical fractionation using an enzyme-mediator system can derive lignin fractions to produce carbon fiber with certain mechanical performance.
ical performance similar to some commercial carbon fibers. The carbon fiber derived from fractionated lignin improved spinnability, fiber morphology, and crystallite structure, all of which might have led to the improved mechanical performance and quality. The underlying molecular mechanisms for improved spinnability and crystallite structure could be due to the more uniform molecular weights, interunitary linkages, and functional groups. The detailed mechanisms are yet to be revealed.

**POTENTIAL OF A MULTI-STREAM INTEGRATED BIOREFINERY**

Despite the need for further studies, the recent work unveiled the potential of a multi-stream integrated biorefinery for bio-manufacturing enabled by lignin fractionation and utilization. As shown in Fig. 1, lignin fractionation could produce multiple lignin streams with different uniformity and chemical characteristics. The fractionated lignin streams could be used as starting materials for multiple biomanufacturing streams to make different final value-added products.

Basically, previous studies have demonstrated that low molecular weight lignin fraction is more suitable for bioconversion for lipid [10,11], bioplastics [12,13], and asphalt binder modifier [14], and high molecular weight lignin fraction could be better feedstock for carbon fiber, as demonstrated in the recent work [7,9]. The multiple lignin streams will inevitably enhance cost-effectiveness and sustainability for both the pulp and paper industry and lignocellulosic biorefineries.

**LITERATURE CITED**


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Nalco Water understands that achieving strength and basis weight targets can be a challenge for any papermaker, especially when lower quality fibers are part of the furnish mix. METRIX™ Dragon Technology for Strength and Productivity Improvement allows tissue, towel and paperboard manufacturers the ability to increase strength, lower basis weight, enhance production and improve sheet quality.
This report describes the first commercial application of industrially generated, chemically modified kraft lignin in melt-blown, environmentally degradable (compostable) polyester film products following hydroxypropylation. Lignin is the second most abundant natural (sustainable) polymer on earth. It is also the most abundant aromatic polymer in nature that serves land plants as matrix component in cellulose fiber-based composites; as modulus-raising copolymer with non-crystalline polysaccharides; and as natural defense against biological and atmospheric degradation [1,2]. Lignin is separated from the plant-biocomposite (mostly wood) in large quantities during papermaking. This resource, which is generated in amounts of approximately 0.5 ton per ton of pulp, is used primarily as in-house process fuel or as polymeric, water-soluble dispersant/surfactant (about 1,000,000 tons per year worldwide) [3]. Recent advances have improved the option of recovering lignin from the kraft pulping process, and this isolation method is beginning to be adopted on industrial scale [4]. Isolated kraft lignin is therefore considered a new resource for the development of sustainable and environmentally degradable polymeric materials on the scale of as much as 78 million tons per year worldwide [5]. In addition to kraft pulping, the emerging cellulosic biofuels industry is projected to potentially generate about 62 million tons of lignin by 2022 [5-8].

Lignin nature and sources
In its native state, lignin is insoluble (with the exception of minor fractions that are solvent-soluble, such as Brauns native lignin [1]), exhibiting typical network character. It is also thermally undeformable. Its insolubility has long been considered to be the result of its crosslinked network structure [1,2]. This has, however, been demonstrated to be mostly incorrect. In moist wood or other plant biocomposites, lignin does show a surprisingly low glass-to-rubber transition temperature (Tg), which signifies a loss in modulus in response to heating [9-11]. This Tg of lignin is in the same range as linear polystyrene. Under dynamic mechanical thermal analysis (DMTA), an analytical method typically used in polymer science to identify phase structure and compatibility of multi-phase materials in composites and blends, the mechanical response of moistened wood to heating revealed two distinct molecular phases [9]. This indicates that the amorphous matrix of the biocomposite consists of two molecular entities, each of sufficient independent size (sub-micron) to raise its own Tg, representing non-crystalline heteropolysaccharides (also called hemicelluloses) and lignin (Fig. 1, left) [9]. The Tg of lignin is in the same range as linear polystyrene.

The absence of network character necessitates an alternate explanation for the insolubility and thermal non-deformability of the non-crystalline matrix of the biocomposite. In the last 40+ years, this behavior has been attributed to block (or graft) copolymer instead of network architecture [12,13]. Figure 1 (right) shows a simplified view of its structure [13]. As a result of the copolymer structure, the two-phase amorphous matrix displays networklike properties, insolubility and thermal non-deformability, which necessitate hydrolysis of ether

ABSTRACT: Compostable films for such uses as packaging and agricultural soil covering materials were first produced on commercial scale from blends of biodegradable polyesters and a modified kraft lignin. The lignin consisted of an industrial product isolated according to the LignoBoost process. The lignin modification involved homogeneous phase reaction with propylene oxide, and the films were melt-blown from a pelletized compound consisting of up to a 30% blend of lignin derivative with commercial biodegradable polyester. The 12–93 µm thick films combined the characteristics of lignin as modulus-building and environmentally degradable polymer with those of the strength-building thermoplastic polyester. Although the modified lignin paralleled the behavior of native lignin in wood by resisting rapid and full conversion to carbon dioxide in a simulated composting environment, two thirds of the film mass biodegraded within 12 weeks of composting, with the remainder turning into (humus-like) water-soluble solids and particles <2 mm in size. The lignin derivatives suffered from the release of trace amounts of malodorous volatiles containing reduced sulfur when subjected to melt-blowing. The objectionable odor was virtually unnoticeable in injection-molded solid parts.

Application: The use of kraft lignin as a contributing thermoplastic polymer component of melt-blown film and injection-molded products from sustainable resources with environmental compatibility helps the kraft pulping process advance toward a multi-purpose biorefining technology with increased income potential.
bonds connecting lignin with carbohydrates for such matrix removal as needed for fiber liberation by pulping.

The lignin-carbohydrate complex has long been recognized as fragile (i.e., susceptible to hydrolytic cleavage) and renewable in the presence of moisture [14-19]. This behavior is considered the basis of the understanding of wood as an “intelligent composite material” [20-23]. The molecular basis of this reversibility (i.e., of hydrolytic depolymerization and repolymerization) revolves around the ease of forming reactive intermediates, quinone methides, that may recombine with carbohydrates and restore insolubility and non-deformability. This dynamic regeneration process of copolymer architecture is responsible for the need to apply lignin-degrading chemistry for obtaining bleached (lignin-free) pulp fibers, which has been corroborated by numerous studies over many years [14-19].

The isolation of the highly crystalline polysaccharide component (cellulose) from wood in fiber form, which requires the dissolution of the matrix (i.e., the delignification or pulping process) can be accomplished using aqueous solutions with pH levels ranging from very low (acid sulfite process) to very high (kraft process), or with organic solvents having solubility parameters resembling those of lignin (organosolv process). By these treatments, lignin becomes soluble (a) in aqueous medium in salt-form, sulfonate or phenolate (lignin sulfonate or kraft lignin), or (b) as organic solvent-soluble molecules with reduced (by hydrolysis) molecular weight (organosolv lignin). In addition to hydrolysis of the lignin-carbohydrate bonds, efficient delignification requires chemical action aimed at (a) raising the degree of modification with sulfonate groups through the use of aqueous solutions of sulfur dioxide or bisulfite salts (sulfite process), (b) effective hydrolytic cleavage (assisted by the addition of semi-catalytic sulfide salts) of alkyl-aryl ether bonds within lignin, causing a rise in phenolic hydroxyl group content (kraft process), or (c) mild hydrolytic separation of solvent-soluble lignin fragments with reduced molecular weight from the lignin-carbohydrate complex (organosolv process) [1,2]. Each process carries the risk for side reactions that typically result in an increase in the Tg of lignin [24,25].

The resulting solubilized lignins are distinct from each other while retaining their elevated molecular weight, their varied functional character, and their branched nature [11,24,25]. As sulfonated entities (i.e., lignin sulfonates), they remain water-soluble at any pH-level. As kraft lignins, they gradually lose their water solubility at pH levels below about 8-9. As organosolv lignins, they become insoluble when exposed to environments with adjusted solubility parameter (so-called non-solvents) and/or temperature. The separation of lignin from the native lignin-carbohydrate complex (i.e., the block copolymer) requires chemical action resulting in structural modifications of different types and degrees [24,25]. Unwanted side reactions involving necessary reactive intermediates, such as benzylic cations and quinone methides, may give rise to condensed structures with reduced solubility and reduced thermal deformability (i.e., raised Tg) while preserving their major varied functionality [24]. This change in structural character is more pronounced in sulfite and kraft lignins than in organosolv lignins. The latter, therefore, retain a high degree of solubility (in organic solvents) and a more moderate Tg.

Lignin sulfonates remain water-soluble polymers with high molecular weight. When isolated from associated inorganic salts and sugars by such processes as ultrafiltration, ion exchange, or spray drying, they are powerful surfactants and dispersants. These products have captured commercial markets in excess of 1 million tons per year worldwide [3].
Kraft lignins are rarely isolated in separated form and instead used mostly for fuel purposes after concentration by water evaporation. This process is designed to recover inorganic pulping chemicals (sodium hydroxide and sodium sulfate), plus steam for electric power. Much research effort has focused on the use of Kraft lignins in polymeric materials, with or without chemical modification, such as water-soluble surfactants, adhesive additives (phenolic resins and other thermosets), and in components of thermoplastics, mostly after some type of chemical modification aimed at overcoming the recognized molecular intractability based on the absence of solubility and thermal deformability.

Organosolv lignins have been much sought-after polymers for materials applications [8,26]. Their potential contribution to desirable properties paralleling those of lignin in the native biocomposite has been widely demonstrated in the laboratory and on a semi-industrial scale. However, this type of lignin is constrained by cost and availability factors. There are presently no known commercial suppliers.

This introduction is to emphasize that, while all isolated lignins preserve most of the inherent polymer properties, such as modulus, multi-functionality, sustainability, and biological degradability, significant differences exist between isolated lignins that invite strategies for developing materials applications in which the native properties are used for the benefit of the final product [27-29].

**Lignin modifications**

For lignins to make an effective entry into commercial materials markets, specialized isolation methodologies or chemical modification approaches must become practical. Numerous studies have demonstrated that lignin can be readily converted into a soluble, reactive, and thermally deformable polymer by chemical modification. This topic has been the subject of several recent reviews [8,29-31]. Among the many modification methods explored, one of the simplest, most property-altering, and most cost-effective techniques involves a reaction with alkylene oxides, especially propylene oxide [27-50]. As a component of thermoplastic and thermosetting materials, lignin is capable of contributing its inherent properties as modulus-builder and slow-degrading organic matter that is considered pre-humus. These characteristics have attracted the attention of such industrial polymer users and producers as IBM, for printed circuit boards [26]. However, the limited availability of isolated, water-insoluble lignins from industrial operations has deterred potential users. This situation, and on a semi-industrial scale. However, this type of lignin is constrained by cost and availability factors. There are presently no known commercial suppliers.

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The modification of lignin with propylene oxide (i.e., the formation of hydroxypropyl lignin [HPL] derivatives), which commenced in the early 1970s, transforms lignin into a thermoplastic (melt-deformable), (organic) solvent-soluble, functionally uniform aromatic polymer of (mostly) small size [32-50]. Its surprising $T_g$-lowering and solubility-raising effect that initially seemed to contradict the conventional understanding of lignin as a crosslinked polymer is consistent with the recent view of lignin as a compact aggregate of molecules assembled on the basis of non-covalent π-π interactions [51,52]. Just as esterification separates cellulose molecules sufficiently to create solubility by disturbing crystallinity (i.e., by creating distance between polysaccharide chains), hydroxypropylation of lignin seems to separate stacked aromatic structures sufficiently to render the modified product soluble in organic solvents and compatible with other macro-molecules [46-50]. Simple modification reactions capable of resolving non-covalent aromatic interactions, such as oxyalkylation, methylation [43], or esterification [30,31] are thus appropriate strategies for converting isolated lignins into important components of thermoplastic materials.

**MATERIALS AND METHODS**

**Lignin and polyester sources**

Isolated Kraft lignin was obtained from the Domtar Paper Company in Plymouth, NC, USA, (www.domtar.com/en/pulp/lignin/10387.asp), which uses primarily southern pine wood feedstock. The lignin composition was listed as 63%-66% carbon, 5.7%-6.2% hydrogen, 2%-2.5% sulfur, and <1.0% ash. The lignin was used as received for modification.

The BASF-supplied biodegradable polyester product, ecoflex F Blend C1200, is described as a statistical, aliphatic-aromatic copolyester based on the monomers 1,4-butanediol, adipic acid, and terephthalic acid (PBAT) in the polymer chain (www.basf.com) [53].

**Modification and structure analysis**

The oxyalkylation reaction was carried out as previously described [37] with modification to accommodate needs associated with the scale-up to the tonnage scale [44]. The resulting HPL product was filtered and washed, and used in dry powder form. It was analyzed by hydrogen-nuclear magnetic resonance (H-NMR) spectroscopy in dimethyl sulfoxide (DMSO) solution, as described previously [54].

**Compounding and melt blowing**

Melt processing was performed using pelletized blends composed of 0%-40% HPL in PBAT in a compounder with screw designed for filler dispersion, which allowed for superior mixing. The material was all fed at room temperature (zone 0). The temperature of the zones then varied from 110°C (zone 1) to 140°C for zones 3-10. Actual melt temperature was reached between 185°C–190°C at a screw speed of 200 rpm. A noticeable release of objectionable odor typical of Kraft pulping was recognized. Film blowing was performed on a small pilot film blowing line using an 80 mm die, a die gap of 0.8 mm, and a blow-up ratio of 3.5:1. Films were made in 12 µm, 25 µm, and 30–93 µm thicknesses. All films contained varying portions of gel (non-melt) particles that apparently resulted from incompletely fluidized HPL. These impurities created instability of the 12 µm film at higher HPL content, which tended to collapse.
Mechanical property testing
Film testing was performed at least 1 week after melt-blowing for the 12 µm films, according to ISO 527-3:1996 “Determination of tensile properties – Part 3: Test conditions for films and sheets,” at 23°C and 50% humidity using preconditioned strips with an effective measured length of 50 mm and a width of 10 mm. The results reported represent the median of five samples. The visual detection of some gel particles in the blown films indicated that the HPL sample used for the prototype films was incompletely homogenized, resulting in an apparent reduction in tensile strength.

Biobased/degradation/composting evaluation
The determination of biobased as opposed to fossil carbon composition by carbon dating was performed by Xceleron (Germantown, MD, USA). The results of percent-biobased have an uncertainty of +/- 3%, according to ASTM D6866 “Standard test method for determining the biobased content of solid, liquid, and gaseous samples using radiocarbon analysis.” The quantitative bio-disintegration of 43 µm film samples was evaluated by Organic Waste Systems (OWS; Gent, Belgium), in a pilot-scale aerobic composting test, according to ISO 16929 (2013) “Determination of the degree of disintegration of plastic materials under defined composting conditions in a pilot-scale test.” In brief, a sample of blended polymer composed of about 25% modified lignin, 15% calcium carbonate, and 60% PBAT was processed on a laboratory blown film line to produce a 43 µm film. This film was cut into 10 cm × 10 cm pieces and added in 1% concentration to bins of pure biowaste. Conditions remained at optimum levels of >60°C and <75°C for 1 week before the temperature dropped to >40°C for the consecutive 5 weeks. Tests were performed in duplicate and lasted for 12 weeks. Disintegration results were determined by sieving, in accordance with ASTM D 6400-12 “Standard specification for compostable plastics” and ISO 17088 (2012) “Specifications for compostable plastics.”

Film degradation by exposure to ultraviolet (UV) light radiation was conducted by BASF using an accelerated test protocol for 10 days.

Headspace analysis for volatiles
Headspace analysis was performed by the University of Dayton Research Institute (UDRI; Dayton, OH, USA) using the system for thermal diagnostic studies (STDS). This analysis is based on a temperature-programmable test section connected to an inline gas chromatography-mass spectrometer (GC-MS). An added sorbent trap was swept with about 10 mL/min of dry helium heated to 250°C at 20°C/min and held at 250°C for 10 min. Desorption of the trap produced a gas stream that was guided through the GC-MS. The resulting total ion chromatogram was analyzed using the National Institute of Standards and Technology (NIST) mass spectral library.

2. The plasticization effect of water (left) and hydroxyalkyl ether substituent content (C) (right) on the glass transition temperature of lignin (after Lora and Glasser [8]). $\Delta T_g$ represents $T_g$ – change in relation to control (i.e., unmodified lignin) according to the equation by Fujita-Nishimoto [8].

RESULTS AND DISCUSSION

Lignin modification
In dry state, all isolated lignins have high glass transition temperatures, often at or near the thermal degradation temperature of the polymer. However, thanks to their multi-functionality, lignins respond to plasticization (Fig. 2). Water (Fig. 2, left), which serves as such an effective plasticizer for non-crystalline polysaccharides (hemicelluloses), also has a great effect on lignin’s $T_g$, but its effect is limited to only the first 5-10 (wt.) % moisture (plasticizer) content. The alternate option to $T_g$-reduction is chemical modification, which amounts to internal plasticization (Fig. 2, right).

One of the most effective methods of altering the properties of lignin in terms of solubility and thermal properties involves reaction with alkylene oxides (Fig. 3) [32-37]. This reaction, which was first used in the early 1970s to synthesize lignin-based polyols for polyurethane foams [32-34], has evolved over several decades into a convenient technique for incorporating water-insoluble (non-sulfonated) lignins into...
polymeric materials with significant phase compatibility vis-
à-vis a range of manufactured thermoplastic and thermoset-
ting polymers [8].

Several factors, including reactivity, boiling point, and ease of handling, have contributed to a preference for propylene oxide (PO) as the modifying agent, although other epoxides were tested as well [31-33,54]. This chemistry has been the subject of considerable optimization throughout the research and development effort and the scale-up process [44]. Currently, the hydroxypropyl kraft lignin is manufactured economically in a batch process that produces multiple tons per batch. The resulting lignin derivatives proved to have glass transition temperatures that are 1.0°C–2.5°C/ % weight gain lower than the starting material. They were virtually mono-
functional and soluble in and compatible with a range of sol-
vents and polymers of common use, and their polydispersity was reduced over the starting material [37,54]. The complete removal of all phenolic functionality results in a derivative with a degree of substitution with PO of about 0.2 to 0.7 per phenylpropane lignin-repeat unit, depending on initial phe-
nolic hydroxide content and reaction conditions. H-NMR spectroscopy reveals a transformation of the phenolic hydroxyl groups (approximately 45% of total hydroxide groups in kraft lignin [24,25]) into aliphatic hydroxide and methyl groups (Fig. 4). Variability in degree of modification may result from a range of reaction parameters, especially pH, temperature,
time, and concentration, as well as product character, especially syringyl (S) and guaiacyl (G) ratio and functionality of the lignin source. This modification and analysis has developed into a state-of-art that is practiced in many laboratories and institutions world-wide. The resulting effects on solubility and thermoplasticity are well-documented.

Compounding and melt-processing

HPL in powder form was compounded in a 40 mm twin-screw extruder with the aliphatic-aromatic biodegradable polyester (PBAT) into pellets containing of 10%, 20%, and 30% HPL. The pellets were subsequently melt-blown into films of 12–14 µm (and greater) thickness. All melt-processing operations functioned without difficulties, except that the bubble became too unstable at the highest HPL concentration of 30% to allow for stable blowing operations. This was unique to the 12–14 µm films. At greater film thickness (60–90 µm), greater lignin contents were tolerated. Pellets with HPL contents as high as 50% were successfully melt-processed by injection molding without difficulties. Visually, the films provided no signs of separated phases; all (thin) films appeared transparent and with undiminished elongation at breakvalues. None of the films exhibited the embrittlement typical of blends with unmodified lignins.

Mechanical properties

The resulting films had the expected properties of increased modulus (and slightly enhanced elongation at break) and reduced tensile strength (Fig. 5) with HPL content. The degree to which modulus responded to HPL content proved to be somewhat dependent on degree of substitution of the lignin with propylene oxide. Desired properties were subject to film thickness and HPL content. Overall, the 12-14 µm films with HPL contents of up to 20% exhibited adequate performances during processing (compounding and melt-blowing) and mechanical testing. All required performance standards were met, especially if the lignin content remained below approximately 25%–30%.

Biodegradation

The analysis of biodegradation was performed in a simulated industrial composting test according to ISO 16929 (2013). The resulting data showed that under composting conditions, lignin and modified lignin (HPL) are essentially the same with regard to carbon dioxide (CO₂) production. The two degradation experiments were performed under very similar conditions. The results are consistent with wood biodegradation tests (provided by OWS, the contract laboratory), which revealed that wood with a 30% lignin content degraded quickly and reached a CO₂ production level of 70%–75% under conditions under which standard cellulose converts to CO₂ levels of 90%–100% (Fig. 6). These results indicate that, even given 1200 days of composting, the lignin content of the wood does not decompose into significant amounts of CO₂. Lignin in compost is degraded, but not primarily into CO₂. This is consistent with experiments with radio-labeled lignin [55] that

---

5. Mechanical properties of 12-14 µm films in relation to lignin content.
have shown that much of lignin is converted into carbon-14 labeled water-soluble fragments instead of CO2. Tuomela et al. [56,57] observed that lignin inhibits the degradation of carbohydrates and generates water-soluble degradation products that are mineralized or bound to humic substances and incorporated into humin or other insolubles.

In separate experiments, HPL in inoculated slurry designed to simulate a composting environment also produced a significant portion of dissolved aqueous lignin solids. After 33 days in an aqueous slurry at 60°C (at an initial pH of 7.5), along with cellulose and a commercial soil inoculant, 15.8% of the HPL sample had degraded into soluble lignin fragments, indicating that the modified lignin behaves comparably to unmodified lignin in a compost environment. The disintegration of the 10 cm × 10 cm film pieces into smaller particles proceeded well. After 10 weeks of composting the average size of the remaining pieces was approximately 1 cm × 2 cm. After 12 weeks the whole content of the bins, in which the simulated soil test was carried out, was used for sieving, sorting, further isolation and analyses, and a disintegration percentage was calculated. Disintegration is defined as a size reduction to <2 mm. Only some rather small pieces of film could be retrieved in the different fractions (Fig. 7). The major parts of these pieces were dark brown and fragile. By far the major part of the test material had disappeared. An average disintegration percentage of 94.0% was determined. This is well above the 90% pass level required by the ASTM D6400-12, EN 13432 (2000) “Requirements for packaging recoverable through composting and biodegradation-test scheme and evaluation criteria for the final acceptance of packaging,” and ISO 17088 (2012) standards for compostable plastics. Figure 7 gives a visual comparison of the <10 mm

6. Biodegradation results of cellulose and lignin under simulated composting conditions.

7. Illustration of the results of simulated composting tests with 93 μm-thick films. H3070E refers to sample designation by the contractor (Organic Waste Systems).
fraction of film subjected to test compost after 12 weeks. As a consequence of these results, the 30% HPL/polyester blend films have already been successfully certified in the United States as compostable materials according to ASTM D 6400-12.

The designation of compostable material hinges on both (or either) conversion to CO₂ (within time limits) and natural polymer source. Neither lignin nor HPL (nor wood, for that matter) fully meet those criteria. However, experiments involving radiocarbon analysis produced results distinguishing bio-based from fossil-based carbon in materials. The results shown in Fig. 8, which were obtained according to test standard ASTM D6866-12, reveal a bio-based carbon content of >95% for the HPL produced by cycleWood Solutions, Inc., and used in the tests described in this report. The missing designation as natural polymer prevents the film blends from being so-far recognized as compostable in Europe (according to EN 13432).

Photo-degradation

The initial evaluation of exposure of a prototype film (with 20% HPL content) to UV radiation was carried out in a test chamber simulating intense irradiation for 10 days. The film sample initially (within the first 7 days) responded well by displaying similar elongation at break compared with the pure polyester control sample, but the films showed distinct signs of photo-degradation by becoming totally colorless and transparent (Fig. 9) and severely brittle. It was obvious that the lignin component protected the polyester from being degraded until it lost its protective capacity by being degraded itself. This behavior parallels lignin’s function in the process of wood weathering [58,59], in which it serves as a guardian of the highly degradable (non-crystalline carbohydrate) portions of the biocomposite until the lignin itself has been converted...
to volatile (vanillin) and water-soluble degradation products, and its protective capacity has been exhausted.

Analysis of volatiles

Native lignin is an odorless polymer that protects the wood composite in many ways. Among them is a thermally induced charring at high temperature that involves some volatilization [60]. When lignin is removed from pulp fibers during kraft pulping, it is modified with reduced sulfur that results in a low level (<2.5% sulfur) of mercaptan (thiol) formation [2] at the benzylic carbon position. Exposure of kraft lignin and its derivatives to temperatures typically used in some melt-processing operations might therefore result in the release of malodorous volatiles. This was apparent with the melt-blown film samples, but much less so with more solid products generated by injection-molding at HPL contents as high as 50%. An analysis of the headspace of film samples stored in a closed container for an extended period for sulfur-containing volatiles produced the results summarized in Fig. 10 and Table I.

The analysis identified the usual compounds known to be associated with kraft pulping, plus a minor ingredient, propylene sulfide (#5 in Table I), that might originate from the release of propoxylated thiol groups.
LIGNIN PRODUCTS


ABOUT THE AUTHORS
Lignin is Earth’s most underutilized sustainable organic resource. It is separated from plant biomaterials in delignification processes leading, among others, to pulp and paper and cellulosic ethanol products. Its isolation as aromatic (brown) polymer of high purity has become technically and economically feasible worldwide. When re-purposed on the molecular level in such plastic commodity products as packaging films, it retains its native properties of high modulus (stiffness builder), biodegradability, and photo-degradability. This has been demonstrated in a series of commercial products described in this paper.

The first author (Wolfgang Glasser) has worked for 40+ years on the use of lignin in structural materials, mostly thermosetting and thermoplastic polymers of all types. One focus of this work was understanding of (a) lignin’s glass-to-rubber transition at target temperature levels by chemical modification, and (b) its flow, solubility, and compatibility properties in association with other macromolecules, natural and synthetic. The major obstacle to lignin use in structural materials has been its notorious intractability. This required (a) the development of an in-depth understanding of the structure-property-performance relationship that makes melt-blowing and blend compatibility possible, and (b) finding a modification method that is sufficiently simple and affordable to be used on tonnage scale.

One of the interesting challenges of this study was the process of transferring research explored (and demonstrated) on laboratory bench-scale to industrial scale within a short time.

Pulp and paper mills that are often limited by chemical recovery capacity can profitably extend this capacity by the recovery of isolated lignin (or its modified derivatives), which are useful in sustainable and biodegradable components of polymeric materials.

The next step in this research is to incorporate the process of isolation/modification into existing mill operations on-site, and to extend product use to other polymeric materials, thermosets (such as phenolics, epoxies and polyurethanes), and thermoplastics (other than biodegradable polyesters, such as polyolefins and PVC).

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Discovering viable alternatives to fossil fuels is imperative because of their shortage and environmental impact. It is, therefore, not surprising that a number of different thermal conversion processes, such as gasification, pyrolysis, and liquefaction [1], have been suggested for the production of bio-oil from various types of biomass. In the investigations of these conversion processes, it has been concluded that these bio-oils are promising supplements or alternatives to fossil fuels [2]. However, because of the varied methods and raw materials used, there are differences in composition and properties of the bio-oils produced.

In many applications, bio-oil requires storage for a long period at an elevated temperature; therefore, it is important that it be able to retain its original properties under these conditions. A number of studies can be found pertaining to the storage properties of various bio-oils in the literature [2-16]. It can be concluded that the properties of the majority of the bio-oils studied change considerably. The viscosity, molecular weight (mol. wt.), water, and insoluble fraction contents of biomass-pyrolysis bio-oil often increase significantly during aging. The changes in the physicochemical and chemical properties of this type of bio-oil were a function of aging temperature and time [5-8]. The increase in water content and mol. wt. after accelerated aging was mainly due to polymerization/condensation reactions leading to the formation of large molecules [9-12]. Joseph et al. [2] reported there was a major decrease in the ether soluble fraction and a substantial increase in both the low and high mol. wt. fractions during aging. Regarding changes in the chemical structure, Ben and Ragauskas [4] revealed that an increase in alkyl groups and a decrease in aromatic and methoxyl groups in the structure of biomass-pyrolysis bio-oil after aging was caused by the condensation reactions initiated by unstable organic peroxides via a radical mechanism. Structural information of bio-oil can be characterized using Fourier transform infrared spectroscopy (FTIR), gas chromatography–mass spectrometry (GC–MS), and nuclear magnetic resonance (NMR) [4]. They also showed that, by using 1H–13C heteronuclear single quantum coherence (HSQC) NMR analysis, deeper insight into the chemical structures of bio-oil with very high mol. wt. could be obtained as well as better understanding of the aging mechanism of bio-oil.

One promising bio-oil is obtained from the liquefaction of lignin using subcritical water [14-18], in which the catalytic system is a combination of base (potassium carbonate [K₂CO₃] and potassium hydroxide [KOH]) and solid zirconium oxide

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**ABSTRACT:** Accelerated aging of bio-oil derived from lignin was investigated at different aging temperatures (50°C and 80°C) and times (1 hour, 1 day, 1 week, and 1 month). The bio-oil used was produced by the hydrothermal liquefaction of kraft lignin, using phenol as the capping agent, and base (potassium carbonate and potassium hydroxide) and zirconium dioxide as the catalytic system in subcritical water. Elemental composition, molecular weight (by using gel permeation chromatography), and chemical composition (by using gas chromatography–mass spectrometry and 2D nuclear magnetic resonance [18.8 T, DMSO-d₆]) of the bio-oil were measured to gain better understanding of the changes that occurred after being subjected to an accelerated aging process. The lignin-derived hydrothermal liquefaction bio-oil was quite stable compared with biomass-pyrolysis bio-oil. The yield of the low molecular weight fraction (light oil) decreased from 64.1% to 58.1% and that of tetrahydrofuran insoluble fraction increased from 16.5% to 22.2% after aging at 80°C for 1 month. Phenol and phenolic dimers (Ar–CH₂–Ar) had high reactivity compared with other aromatic substituents (i.e., methoxyl and aldehyde groups); these may participate in the polymerization/condensation reactions in the hydrothermal liquefaction bio-oil during accelerated aging. Moreover, the 2D heteronuclear single quantum coherence nuclear magnetic resonance spectra of the high molecular weight fraction (heavy oil) in the aged raw oil in the aromatic region showed that the structure of this fraction was a combination of phenol-alkyl patterns, and the guaiacol cross-peaks of Ar₂, Ar₅, and Ar₆ after aging indicate that a new polymer was formed during the aging process.

**Application:** Pulp mill personnel can use this information when considering technology to extract lignin from black liquor and process it further into bio-oil.
LIGNIN CONVERSION

(ZrO₂), with phenol used as a capping agent. For this system, the yield of bio-oil and char were 69%–87% and 16%–22%, respectively. Furthermore, this bio-oil has the characteristics of low oxygen (15%–21%) and water (11%–19%) contents, making the oil advantageous for fuel application. Nguyen Lyckeskog et al. [14] investigated the storage stability (room temperature, 2 years) of this type of bio-oil (lignin-derived hydrothermal liquefaction [HTL] bio-oil) and reported some promising results. This type of bio-oil was found to be relatively stable: its low mol. wt. fraction (light oil) was found to be very stable. It was also suggested that the removal of the tetrahydrofuran (THF) insoluble fraction could be beneficial in enhancing the stability of the HTL bio-oil. However, to the best of the authors’ knowledge, few studies have been published on lignin-derived HTL bio-oil in a scientific journal. Therefore, it is important that the stability of lignin-derived bio-oil is evaluated, using elevated temperature to accelerate the aging process, so that the mechanisms of aging and ways of improving the quality of the oil can be identified.

The current work investigated the effects of temperature (50°C and 80°C) and time (up to 1 month) during the accelerated aging of lignin-derived HTL bio-oil. The properties of the HTL bio-oil were measured (i.e., water content, elemental composition, mol. wt. distribution, volatiles, and functional compositions) before and after aging. GC–MS and high-resolution ¹H–¹³C HSQC NMR (800 MHz, dimethyl sulfoxide-d₆ [DMSO-d₆]) analyses were used to provide new insights into the structural changes that occur in HTL bio-oil during an accelerated aging process.

MATERIALS AND METHODS

These method cannot fully address safety issues that might arise. The user is responsible for assessing potential safety issues associated with the given methods at its point of use and must consider all general laboratory safety precautions. In particular, the user must identify and implement suitable health and safety measures and comply with all pertinent regulations.

Production of the bio-oil

The bio-oil samples were obtained from the continuous conversion of LignoBoost (Invenntia AB; Stockholm, Sweden) kraft softwood lignin in subcritical water and have been characterized elsewhere [14-18]. In the experiment where the lignin-derived bio-oil was produced, the reactor temperature and pressure were kept at 350°C and 25 MPa, respectively. The dry lignin content was about 5.6% and the mass ratio of phenol to dry lignin was 0.70; the contents of K₂CO₃ and KOH were 1.6% and 0.4%, respectively. The heterogeneous catalyst used in this process was ZrO₂, manufactured by Saint-Gobain NorPro (Stow, OH, USA). The feed flow rate was 2 kg/h, the recycle-to-feed ratio was 4/5, and the steady-state period for sampling was 2 h and 40 min. Further details of the apparatus and procedure related to the production of lignin-derived bio-oil can be found in previous work by Nguyen et al. [17,18] and Belkheiri et al. [15,16].

Fractionation of the bio-oil

Figure 1 is a block diagram of the various steps involved in the solvent fractionation of lignin-derived bio-oil; the fractionation was performed according to a method described elsewhere [14]. The bio-oil (about 5 g) was first extracted by diethyl ether (DEE) using a solvent-to-feed ratio (S/F) of 20/1 and separated into DEE-soluble fraction (light oil) and DEE-insoluble fraction. The latter was extracted further by THF, with an S/F ratio of 20/1, into THF-soluble fraction (heavy oil) and THF-insoluble fraction (THF insolubles).
Accelerated aging of the bio-oil

The lignin-derived bio-oil produced by HTL was used in the investigation of accelerated aging at elevated temperatures (i.e., 50°C and 80°C). At 80°C, the large change in the properties of pyrolysis bio-oil can be expected [5,13], while at 50°C, the change can be used in comparison. The bio-oils were subjected to accelerated aging for periods of 1 hour, 1 day, 1 week, and 1 month. The aged bio-oil was fractionated into aged raw oil_light oil (aRO_LO), aged raw oil_heavy oil (aRO_HO), and aged raw oil_THF insolubles (aRO_TIS). The stability test was performed according to a procedure in Elliott et al. [19]; about 10 g of bio-oil were put into 10 mL Schott Duran bottles (with screw caps) and placed in a heating oven at different temperatures for different residence times. All bio-oil samples were weighed before and after accelerated aging to ensure there was no significant loss of water or other volatiles. The results showed that the samples of bio-oil were able to maintain a uniform phase, with only a minor loss in weight (~0.18%).

Characterization of the bio-oil

Water content

The water content of the bio-oil was determined in triplicate according to the ASTM E203-08 method [12]. About 0.5 g oil was dissolved in THF with an S/F about 20/1, and the water content was measured by using Karl Fischer volumetric titration using Hydranal-Composite 5 (Honeywell; Morris Plains, NJ, USA) and methanol. The titrant concentration was determined using the Honeywell Hydranal Water Standard 10.0.

Elemental analysis

The elemental composition of the bio-oil was determined at Mikroanalytisches Laboratorium Kolbe (Germany), which uses a CHNOS Analyzer (Elementar Analysensysteme GmbH; Langenselbold, Germany) to measure the contents of carbon and hydrogen, and an ion chromatography system (Metrohm; Herisau, Switzerland) to measure the sulfur content. The content of ash in the bio-oil was measured in triplicate according to the ASTM E1755-01 method [20], using a Labotherm Program Controller S27 (Nabertherm; Lilienthal, Germany). The oxygen content was calculated by difference; the higher heating value (HHV) was calculated using an elemental analysis by applying Doulong’s formula [7], as in Eq. (1):

\[
\text{HHV [MJ/kg]} = \left[338.2 \times \%C + 1,442.8 \times (\%H – \%O/8)\right] \times 0.001
\]

Molecular weight of the light oil, heavy oil, and THF insolubles (GPC analysis)

About 30 mg of each fraction of raw oil (light oil, heavy oil, and THF insolubles) at fresh state (LO, HO, and TIS) and aged state (aRO_LO, aRO_HO, and aRO_TIS) were dissolved in the mobile phase DMSO/LiBr (10 mM) and filtered with a 0.2 µm syringe filter. The sample solutions were analyzed for mol. wt. and mol. wt. distribution by means of gel permeation chromatography (PL-GPC 50 Plus, Agilent Technologies; Alpharetta, GA, USA) connected to refractive index and ultraviolet detectors (280 nm, Polymer Laboratories, Varian Inc.; Palo Alto, CA, USA). Two Agilent PolarGel-M columns and a guard column (500×7.5 mm and 50×7.5 mm, 8 µm) were coupled in series. A 10-point calibration curve with Pullulan standards (PL 2090-0100 polysaccharide calibrations kit, Varian) was used to determine the mol. wt. of the samples. The analyses were repeated in triplicate and the average value was reported. All of the samples were found soluble in the mobile phase (DMSO/LiBr). The same systematic error obtained from all of the samples (i.e., same concentration, solvent, analysis time) allows the average value of the mol. wt. determined by GPC for the oil to be compared.

Chemical composition of the light oil (GC–MS analysis)

About 0.5 g of raw oil in fresh and aged states were dissolved in DEE with an S/F of 50, and mixed with a known amount of internal standard (IST, syringol in DEE). This mixture was filtered through a 0.2 µm syringe filter and injected in the GC–MS system. The Agilent 7890A gas chromatograph used is coupled to an Agilent 5975C mass spectrometer operating in electron ionization mode. The analysers are separated in a chromatographic column HP-5MS (length: 30 m; internal diameter: 0.25 mm; thickness of stationary phase: 0.25 µm) by injecting 1 µL of sample via an Agilent7693A auto-sampler, using helium at 1 mL/min as the carrier gas. The injector temperature was set at 300°C and the temperature program of the gas chromatograph oven was 45°C for 2.25 min, 2°C/min up to 300°C, 300°C for 10 min. The mass spectrometer source and quadrupole temperatures were set at 250°C and 150°C, respectively. Spectral interpretation was carried out using the NIST MS Search program (version 2.0) operating on the NIST/EPA/NIH Mass Spectral Database 2011 (NIST 11). The contents of the main components were determined semi-quantitatively: each sample was analyzed in triplicate and the average value was then used.

Functional groups of the light oil, heavy oil, and THF insolubles (2D HSQC NMR analysis)

About 100 mg of each samples (LO, HO, TIS, aRO_LO, aRO_HO, and aRO_TIS) were dissolved in 0.75 mL DMSO-d6 using a small vial equipped with a stirring bar overnight to ensure that the samples were dissolved completely. The sample solutions were then analyzed by means of 1H–13C HSQC NMR (Bruker, 800 MHz). The correlation spectra were recorded at 25°C on a Bruker Advance III HD 18.8T NMR spectrometer (Rheinstetten, Germany) equipped with a 5 mm TXO cryoprobe. The HSQC spectra were recorded using a standard Bruker pulse sequence “hsqcehetgspsp2.3” with a 0.25-s 1H acquisition time, 5.3 ms 13C acquisition time, 3 s interscan delay, and 1JC–H coupling constant of 145 Hz, 8 scans; each spectrum was recorded for 4 h. The spectra were processed and analyzed using the default processing template of Mestrenova version 10.0.0 software (Mestrelab Research; Escondido, CA, USA), along with automatic phase and baseline correction.
LIGNIN CONVERSION

RESULTS

Fractionation and yields of the bio-oil

The raw bio-oil obtained from the lignin conversion in subcritical water was aged using a heating oven at 50°C and 80°C for periods of 1 hour, 1 day, 1 week, and 1 month. After aging, the raw bio-oil was fractionated into light oil, heavy oil, and THF insolubles to assess the compositional changes of the biooil. Table I presents the yield of each fraction after aging at different temperatures and periods, measured on a dry basis.

The yield of light oil decreased after aging whereas that of THF insolubles increased. In general, a higher aging temperature (80°C) and a longer aging time (1 month) result in larger changes in the yields of the bio-oils fractions; this is consistent with the findings of Jiang et al. [7], who studied the aging of biomass-pyrolysis bio-oil. In particular, the light oil decreased from 64.1% to 62.3% after 1 month of aging at 50°C and to 58.1% after 1 month of aging at 80°C. The THF insoluble, on the other hand, increased from 16.5% to 20.9% after 1 month of aging at 50°C and to 22.2% after 1 month of aging at 80°C. Various oligomerization/polymerization reactions of reactive compounds must thus have occurred not only in the light oil during aging, leading to a decrease in the yield of light oil and an increase in that of heavy oil, but also in the heavy oil, leading to a decrease in the yield of heavy oil and an increase in that of THF insolubles. The yield of heavy oil did not change significantly, which indicates that both the increase and decrease occurred simultaneously during aging. Compared with biomass-pyrolysis bio-oil [3,12], lignin-derived bio-oil from HTL is more stable at 80°C for up to 1 month.

Elemental composition of the bio-oil

Table II shows the water content and elemental composition of fresh and aged bio-oil at different aging temperatures and times, measured on a dry basis. The contents of water and oxygen of the lignin-derived bio-oil used in this study was about 4.8% and 14.1%, respectively, which is low compared to conventional biomass-pyrolysis bio-oil [21]. After aging, the water content of this bio-oil showed no systematic change; this indicates that the total water content had no dramatic effect on chemical reactions that are typical for producing water (i.e., condensations), and thereby differs to the biomass-pyrolysis bio-oil [12,15]. Moreover, the changes in the elemental composition of the bio-oil before and after aging were rather small. These results indicate that the chemical composition of the lignin-derived HTL bio-oil is very stable during the aging at 80°C for up to 1 month.

Determination of molecular weight of the bio-oil

The mol. wt. distribution curves of different fractions of fresh raw oil (light oil, heavy oil, and THF insoluble) are

---

**Table I**

<table>
<thead>
<tr>
<th>Aging Temperature, °C</th>
<th>Fresh</th>
<th>50</th>
<th>80</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aging Time</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Light oil</td>
<td>64.1</td>
<td>63.5</td>
<td>60.0</td>
</tr>
<tr>
<td>Heavy oil</td>
<td>19.4</td>
<td>17.0</td>
<td>19.6</td>
</tr>
<tr>
<td>THF insolubles</td>
<td>16.5</td>
<td>19.5</td>
<td>20.4</td>
</tr>
</tbody>
</table>

I. Yield (%) of each fraction before and after accelerated aging at different temperatures for different periods, measured on a dry basis.

**Table II**

<table>
<thead>
<tr>
<th>Aging Temperature, °C</th>
<th>Fresh</th>
<th>50</th>
<th>80</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water content, %</td>
<td>4.8</td>
<td>4.2</td>
<td>4.3</td>
</tr>
<tr>
<td>Elemental composition, %</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon</td>
<td>74.4</td>
<td>74.1</td>
<td>74.2</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>6.2</td>
<td>6.2</td>
<td>6.3</td>
</tr>
<tr>
<td>Sulfur</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Ash</td>
<td>5.0</td>
<td>4.5</td>
<td>3.8</td>
</tr>
<tr>
<td>Oxygen*</td>
<td>14.1</td>
<td>14.8</td>
<td>15.3</td>
</tr>
<tr>
<td>HHV (MJ/kg)**</td>
<td>31.6</td>
<td>31.3</td>
<td>31.4</td>
</tr>
</tbody>
</table>

* Oxygen was calculated by difference.
** HHV (higher heat value) was calculated using Dulong’s formula.

II. Water content and elemental composition of the fresh and aged bio-oil, measured on a dry basis.
shown in Fig. 2a. The mol. wt. distribution of the fresh light oil comprises a high amount of monomers (peak 1, ~60 dalton) and small amounts of dimers (peak 2, ~200 dalton) and oligomers (peak 4, ~2000 dalton). The mol. wt. distribution of the fresh heavy oil contains mainly oligomers with a low amount of peak 3 (~400 dalton) and a higher amount of peak 4 and 5 (~3600 dalton). The mol. wt. distribution of the fresh THF insolubles consists mainly of highly polymerized oligomers (peak 6, ~8600 dalton).

The mol. wt. distribution curves of light oil, heavy oil, and THF insolubles at aged state (aRO_LO, aRO_HO, and aRO_TIS, respectively) are shown in Fig. 2c–d. The mol. wt. distribution of all the aged raw oil fractions (aRO_LO, aRO_HO, and aRO_TIS) showed no major changes when compared with the fresh raw oil fractions (LO, HO, and TIS) after aging at 50°C for up to 1 month (1 hour, 1 week, and 1 month) and at 80°C for up to 1 week (1 hour, 1 day, and 1 week). However, when the bio-oil was stored for 1 month at 80°C, changes in the mol. wt. distribution of the bio-oil fractions could be detected. The mol. wt. distribution curve of the aged raw oil_heavy oil at 80°C for 1 month of aging (aRO_HO_80_1m) showed a significant shift toward signals characteristic of higher mol. wt. species. The weight-average molecular (\(M_w\)) of peak 5 increased from 3600 dalton to 5500 dalton after aging for 1 month at 80°C; this change was combined with a simultaneous reduction of the lower mol. wt. distribution fractions (peaks 1 and 3, Fig. 2c) in the aged raw oil_heavy oil (1 month, 80°C). Also, the mol. wt. distribution curve of aged raw oil_THF insolubles at 80°C for 1 month of aging (aRO_SS_80_1m) shows a major change (Fig. 2d), where the mol. wt. distribution curve shifts toward the higher mol. wt. region. In detail, \(M_w\) of peak 6 increased from 8600 dalton to 13700 dalton after aging at 80°C for up to 1 month. This indicates that the severest condition (80°C and 1 month) can alter the mol. wt. distribution of the bio-oil and thereby induce polymerization of the low-mol. wt. materials in the light oil and heavy oil to form high-mol. wt. materials (heavy oil and THF insolubles). Compared with pyrolysis bio-oil obtained from biomass [1,9,10,12], these changes are nevertheless small and indicate that the lignin-derived HTL bio-oil is more stable than biomass-pyrolysis bio-oil after aging at 80°C for 1 month.

**GC–MS analysis of the DEE solubles of bio-oil**

GC–MS analysis was performed to provide more detail of the chemical composition of the DEE soluble fraction. Table III shows the yield of the GC–MS compounds identified in the

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<thead>
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<tr>
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<td>Retene</td>
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* Ar = aromatic ring.

**III. Yields (%) of gas chromatography–mass spectrometry compounds identified from the diethyl ether solubles in the fresh and aged raw oil, measured on a dry basis.**
fresh and aged light oil, measured on a dry basis. The compounds were classified on the basis of structure, such as phenols (phenol and alkyl phenols), anisoles (anisole and alkyl anisoles), guaiacols (guaiacol and alkyl guaiacols), and catechols (catechol and alkyl catechols). As shown in Table III, the components that were detected include anisoles, phenols, guaiacols, catechols, phenolic dimers ($Ar-CH_2-Ar$) and some others, including 1,2-dimethoxybenzene, 2-acetylphenol, xanthene, and retene ($7$-isopropyl-1-methyl phenanthrene).

The results in Table III show that the only notable changes in yields are found for anisole, phenols, guaiacol, and phenolic dimers. For all other compounds, the changes in yield are small. After 1 hour of aging, the yield of anisole increased slightly from 5.8% to 6.3% (an increase of about 8.4%), whereas phenol decreased slightly from 16.0% to 15.0% (a decrease of about 6.2%) irrespective of aging temperature (50°C and 80°C). The clear simultaneous increase in anisole and decrease in phenol after 1 hour of aging may be explained by the formation of anisole from phenol. No other large changes in the yields of monomers were detected in the two shorter time samples (1 hour and 1 week) by using GC–MS.

At the severest condition in this study (1 month and 80°C), both the yields of anisole (6.3% to 5.7%) and phenol (16.0% to 14.1%) were found to be reduced. One possible explanation is that these monomers react with THF insolubles and that phenol, having no side groups, has a higher reactivity than other monomers (see Table III). Besides, the yield of guaiacol was decreased from 2.3% to 2.1% at this severest condition.

The yield of phenolic dimers with methylene ($Ar-CH_2-Ar$)
and ethylene (Ar–CH₂–CH₂–Ar) groups showed a large decrease in yield after being aged for 1 month: from 2.3% to 0.1% (a decrease of about 94.2%) and from 0.5% to 0.2% (a decrease of about 60.0%), respectively. This change was found to be independent of aging temperature (50°C and 80°C) and shows that the bridging phenolic structures have a high reactivity at the investigated conditions during aging. There are at least two possible routes these reactions can take: (1) the condensation reaction at the oligomerization/polymerization positions on the phenolic rings and (2) the nucleophilic substitution at the benzylic bridging methylene group [22]. Furthermore, our results indicate that an aromatic bridging methylene group (-CH₂-) has a higher reactivity compared with an ethylene group (-CH₂–CH₂-) during the accelerated aging of lignin-derived HTL bio-oil.

Consequently, the activity of the compounds identified by GC–MS in the bio-oil was in the following order: phenolic dimers (Ar–CH₂–Ar) > phenol > anisole > phenolic dimers (Ar–CH₂–CH₂–Ar) > guaiacol > alkyl phenols, alkyl anisoles, alkyl guaiacols, xanthene, catechol, and retene after aging at 80°C for 1 month. This trend in reactivity was found to differ slightly from our previous study of the long-term storage of lignin-derived HTL bio-oil at room temperature [14]. Xanthene in particular, having the methylene group (-CH₂-) in its structure but without a hydroxyl substituent, was shown to have a low reactivity in the present study. The reason for this is not fully understood, but a possible explanation might be that several different reaction paths occur in parallel and the influence of temperature on the reaction kinetics for the involved reactions differs. Summarizing, the GC–MS results indicate that lignin-derived HTL bio-oil is quite chemically stable at 80°C for up to 1 month.

**1H–13C HSQC NMR analysis of the bio-oil**

To gain deeper insight into the chemical changes that occur during the aging of raw bio-oil, the 1H–13C HSQC NMR spectra obtained for the bio-oil before and after it was subjected to the accelerated aging process were analyzed. The interpretation of NMR spectra is difficult for complex mixtures of bio-oil, so the NMR analysis was performed using different fractions, namely light oil, heavy oil, and THF insolubles. To achieve a more precise elucidation, 23 model compounds identified from GC–MS were recorded using 1H–13C HSQC NMR (800 MHz, DMSO-d₆) (Table A1 and Fig. A1 in the Appendix) together with NMR assignments found in the literature [23–30]. Figures A2–A4 in the Appendix show the aliphatic and aromatic regions in the 1H–13C HSQC NMR spectra of fresh bio-oil fractions: light oil, heavy oil, and THF insolubles. Signals corresponding to the aliphatic region, including aliphatic and ether/nonether connected groups, were observed between δ_C/δ_H 10–70/0–5 ppm. The chemical shift region belonging to the aromatic region of the respective subunits were detected in the range of δ_C/δ_H 105–135/5.7–6.2 ppm.

The major cross-peaks in the aliphatic region of the fresh light oil correspond to the alkyl groups (Ar–CH₃, Ar–CH₂–CH₃, Ar–CH₂–CH₂–CH₃), methoxyl groups (Ar–OCH₃), methylene and ethylene bridging groups (Ar–CH₂–Ar and Ar–CH₂–CH₂–Ar), aliphatic methylene groups (α/β–CH₂), and methylene groups adjacent to alcohol groups (β/γ–CH₂–OH/OR). The major cross-peaks in the aromatic region of the fresh light oil correspond to the aromatic C–H bonds at the α-, m-, and p-positions on aromatic rings. These findings are consistent with the results found in the GC–MS analysis of light oil. The fresh heavy oil and THF insolubles
structures, on the other hand, differ slightly from the structural motifs published previously by Mattsson et al. [26], in which the polycyclic aromatic hydrocarbon (PAH)-like structures (δ_C/δ_H 123–135/7.2–8.3 ppm), branched β-methyl groups (i.e., tert-butyl t-C_4H_9 or iso-propyl i-C_3H_7, δ_C/δ_H 29.7–30.9/1.1–1.3 ppm), and alkenes groups conjugated with aromatic structures were detected. Because heavy oil and THF insolubles contain higher mol. wt. structures, a lower signal intensity and peaks broader than that of light oil were found in the NMR spectra.

**Light oil**

The 1H–13C HSQC NMR spectra of the fresh light oil (LO) and aged raw oil_light oil at 80°C for 1 hour (aRO_LO_80_1h), 1 day (aRO_LO_80_1d), and 1 month (aRO_LO_80_1m) were analyzed for the aliphatic (δ_C/δ_H 10–70/0–5 ppm) and aromatic (δ_C/δ_H 105–135/5.7–8.2 ppm) regions of light oil (Figs. 3 and 4 and Figs. A5 and A6 in the Appendix). In the aliphatic region, no new cross-peaks were obtained; there was just a slight reduction in the existing structural motifs after aging at 80°C for 1 month. The aromatic substituents methyl (Ar–CH₃, Fig. 3a), methoxyl (Ar–OCH₃, Fig. 3b), and aldehyde (Ar–CHO, Fig. A6) groups were found to have a slight decrease in signal intensity after aging at 80°C for 1 month. This indicates that the aromatic rings, with substituents such as methyl (-CH₃), methoxyl (-OCH₃), and aldehyde (-CHO), have a higher tendency for participating in reactions during the accelerated aging of bio-oil at 80°C. Using our model compounds for 1H–13C HSQC NMR database makes it possible to detect nonoverlapping regions for the most dominating phenolic structures in the light oil [30]. For instance, the chemical shifts of the aromatic m–CH in phenol and anisole do not overlap with those of guaiacols and can thus be used to determine the changes in these structures (i.e., anisole with δ_C/δ_H 130.0/7.3 ppm, phenol with δ_C/δ_H 130.0/7.2 ppm, alkylated phenols [-CH₃–CH₃–CH₃], and phenolic dimers Ar–CH₃–Ar with δ_C/δ_H 6.9–7.1/125.6–127.8 ppm). Also, the chemical shifts of the guaiacol aromatic o–CH (Ar) with δ_C/δ_H 112.6/6.9 ppm are found not to overlap with those of other phenolic structures. Comparing fresh light oil with aged raw oil_light oil 1H–13C HSQC NMR spectra in the aromatic region (1 hour, 1 day, and 1 month), it can be concluded that phenol and anisole decreased slightly after aging at 80°C for 1 month, which corresponds well with the GC-MS data obtained in this study (Section 3.4). Previous studies on guaiacol and anisole structures have shown that the bond energy of the C–O bond in O–CH₃ (methoxyl groups) is low and reactions can therefore occur at this substituent during aging [23]. However, in the aged raw oil_light oil at the severe condition (i.e., 80°C and 1 month), it was possible to observe an increase in a cluster of peaks in the region with δ_C/δ_H 118–122/6.4–6.6 ppm and a specific cross-peak with δ_C/δ_H 117/6.6 ppm. In previous publications, this region has been interpreted as being catechol compounds [26], and our two examples of model catechol structures (i.e., catechol and 3-methylcatechol, Table AI and Fig. A1) also have resonance here [30].

**Heavy oil and THF insolubles**

**Figures 5 and 6** and **Figs. A7 and A8** show the 1H–13C HSQC NMR spectra of the fresh heavy oil (HO) and aged raw oil_heavy oil at 80°C (aRO_HO_80) for 1 hour, 1 day, and 1 month. When the fresh and aged raw oil_heavy oil are compared, the chemical changes that have occurred in the heavy oil structure can be clearly observed in the aromatic region; new cross-peaks, with a high signal intensity, are obtained (Fig. 6). In the fresh heavy oil fraction, the peak with the high-
est intensity is found in the region corresponding to the combined guaiacol Ar5/general region for aromatic C–H structures ($\delta_{\text{C}}/\delta_{\text{H}}$ 114.7–116.3/6.6–6.9 ppm). However, in the aged raw oil_heavy oil, cross-peaks with $\delta_{\text{C}}/\delta_{\text{H}}$ 115/6.7–6.8 ppm, 115/6.6–6.7 ppm, 119/6.6–6.8 ppm, 127/7.0 ppm, 130/7.1–7.2 ppm, and 131/6.9–7.0 ppm appear; this new pattern of peaks has clear similarities to that of the light oil monomeric fraction (Fig. 4). Correlation of our findings to the monomeric light oil fraction and the model database (Fig. A1) shows that these peaks correspond to $m$–CH in anisole ($\delta_{\text{C}}/\delta_{\text{H}}$ 115/6.7–6.8 ppm, 119/6.6–6.8 ppm, 127/7.0 ppm, 130/7.1–7.2 ppm, and 131/6.9–7.0 ppm appear; this new pattern of peaks has clear similarities to that of the light oil monomeric fraction (Fig. 4). 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were found to reduce in intensity with longer aging time, and finally disappeared in the aged raw oil/heavy oil after 1 month. This indicates that the aldehyde groups are involved in aging reactions, which is in agreement with the previous findings [2].

The new phenol-alkyl pattern signals obtained in the aged raw oil/heavy oil imply the formation of a new phenolic-polymer, the origin of which was investigated in another study by Nguyen Lyckeskog et al. [30]. In that study, the fresh bio-oil was separated into light oil and heavy oil fractions and these fractions were then aged at 80°C for 1 week. After aging, a small amount of the insolubles (DEE insolubles and THF insolubles) were separated and analyzed using 1H–13C HSQC NMR. It was confirmed that DEE insolubles (from aged light oil fraction) have a pattern similar to a phenolic-polymer found in the aged raw oil/heavy oil fraction detected in the present study.

Consequently, the structure of the aged raw oil/heavy oil obtained in the accelerated aging process used in this study is a combination of the DEE insolubles (from aged light oil) and THF solubles (from aged heavy oil) structures. This explained the observations made in this study of a new pattern of structural peaks in the aged raw oil/heavy oil (see Fig. 6). These findings were also supported by the results of the yield obtained of the various fractions after aging.

The THF insolubles (TIS) that were formed during aging at 80°C for different periods (1 hour, 1 day, 1 week, and 1 month) were found to be soluble in DMSO-d6 and investigated using 1H–13C HSQC NMR to discover any structural changes (Figs. A9 and A10). It was revealed that no structural changes could be observed during aging at the conditions used in this study.

Suggestions regarding the aging mechanism

On the basis of the GC–MS and 1H–13C HSQC NMR data, different pathways of the polymerization/condensation reactions that might occur in the HTL bio-oil can be proposed. One possibility is that the -CH2- group between two phenolic rings reacts to form a new carbon–carbon bond. No increase in Ar–CH was, however, found in the aliphatic region 1H–13C HSQC NMR spectra of the light oil and heavy oil (Figs. 3–6). Full substitution to quaternary carbon could nevertheless proceed; these types of carbon cannot be detected in 1H–13C HSQC NMR. Another possible pathway is the formation of new carbon–carbon linkages at the o- and p- positions in the phenolic nucleus, leading to a large network of phenolic structures. The findings of both an increase in the aliphatic methylene groups (Ar–CH2–Ar and...
LIGNIN CONVERSION

The accelerated aging of lignin-derived bio-oil was investigated at different temperatures (50°C and 80°C) and periods (1 hour, 1 day, 1 week, and 1 month). The lignin-derived HTL bio-oil was observed to be quite stable when aged at 80°C for 1 month compared with the biomass-pyrolysis bio-oil. In this study, phenolic dimers with methylene bridge (Ar–CH2–Ar) were found to be more reactive than corresponding ones with ethylene bridge (Ar–CH2–CH2–Ar). Xanthene, having a methylene group was, however, found to be relatively stable during aging. The fact that phenol and phenolic dimers (-CH2-group) were found to be mostly decreased indicates that the polymerization/condensation reactions differ in the oil during the accelerated aging in the presence of char/THF insolubles. The structure of the heavy oil fraction in the aged raw oil was found to be a combination of the light oil insolubles structures (phenolic polymers) that were formed and the heavy oil structures.

ACKNOWLEDGEMENTS
The authors gratefully acknowledge financial support from Chalmers Energy Initiative-LignoFuel Project, Valmet Power AB, the Swedish Energy Agency, and Ångpanneföreningens Forskningsstiftelse. The authors thank Maxim Mayzel for the NMR analysis at Swedish NMR Centre of Gothenburg University, Lars-Erik Åmand for the experimental support, and Tommy Friberg for the technical assistance.

APPENDIX
This appendix includes Table A1 and Figs. A1-A10.

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## LIGNIN CONVERSION

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<td>130.7/7.0, 119.5/6.7, 127.5/7.0, 115.5/6.8, 34.9/3.8, 115.5/6.7</td>
</tr>
<tr>
<td>2,2′-Methylene diphenol</td>
<td><img src="image5.png" alt="Structure" /></td>
<td>3, 4, 5, 5′, 6, 6′, 7</td>
<td>130.7/6.9, 119.4/6.7, 127.4/7.0, 115.4/6.8, 29.8/3.8</td>
</tr>
<tr>
<td>4,4′-Methylene diphenol</td>
<td><img src="image6.png" alt="Structure" /></td>
<td>2′, 6′, 3′, 5′, 7</td>
<td>115.7/6.7, 130.0/7.0, 40.1/3.7</td>
</tr>
<tr>
<td>Xanthene</td>
<td><img src="image7.png" alt="Structure" /></td>
<td>2, 2′, 3, 3′, 4, 4′, 5, 5′, 7</td>
<td>116.6/7.1, 128.3/7.2, 123.8/7.1, 129.7/7.3, 27.5/4.0</td>
</tr>
<tr>
<td>Naphthalene</td>
<td><img src="image8.png" alt="Structure" /></td>
<td>1, 2, 3, 6</td>
<td>126.4/7.5, 128.2/7.9</td>
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## LIGNIN CONVERSION

<table>
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<tr>
<th>Compounds</th>
<th>Structures</th>
<th>Positions</th>
<th>Chemical Shift $\delta_{C}/\delta_{H}$ (ppm)</th>
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<tr>
<td>Acenaphthene</td>
<td><img src="image" alt="Acenaphthene Structure" /></td>
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<td>128.3/7.5, 119.7/7.3, 30.3/3.3, 122.5/7.6</td>
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<tr>
<td>Phenanthrene</td>
<td><img src="image" alt="Phenanthrene Structure" /></td>
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<tr>
<td>Fluorene</td>
<td><img src="image" alt="Fluorene Structure" /></td>
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</tr>
<tr>
<td>Pyrene</td>
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<td>126.6/8.1, 127.8/8.2, 125.5/8.3</td>
</tr>
</tbody>
</table>

Al. $^1H-^{13}C$ HSQC NMR (800 MHz, DMSO-d$_6$) data of the model compounds.

![Diagram](image)

Al. $^1H-^{13}C$ HSQC NMR assignments (800 MHz, DMSO-d$_6$) of the model compounds.
A2. Aliphatic ($\delta_C/\delta_H$ 10–70/0–5 ppm) and aromatic ($\delta_C/\delta_H$ 105–135/5.7–8.2 ppm) regions in the $^1$H–$^{13}$C HSQC NMR spectrum (800 MHz, DMSO-d$_6$) of the fresh light oil (LO), and the highlighted characteristic signals. DEE = diethyl ether; THF = tetrahydrofuran.

A3. Aliphatic ($\delta_C/\delta_H$ 10–70/0–5 ppm) and aromatic ($\delta_C/\delta_H$ 105–135/5.7–8.2 ppm) regions in the $^1$H–$^{13}$C HSQC NMR spectrum (800 MHz, DMSO-d$_6$) of the fresh heavy oil (HO), and the highlighted characteristic signals. BHT = 3,5-di-tert-4-butylhydroxytoluene; THF = tetrahydrofuran.

A4. Aliphatic ($\delta_C/\delta_H$ 10–70/0–5 ppm) and aromatic ($\delta_C/\delta_H$ 105–135/5.7–8.2 ppm) regions in the $^1$H–$^{13}$C HSQC NMR spectrum (800 MHz, DMSO-d$_6$) of the fresh THF insolubles (TIS), and the highlighted characteristic signals. BHT = 3,5-di-tert-4-butylhydroxytoluene; THF = tetrahydrofuran.
A5. Aliphatic regions ($\delta_C/\delta_H 10–70/0–5$ ppm) in the $^1H$--$^{13}C$ HSQC NMR spectra (800 MHz, DMSO-$d_6$) of the (a) fresh light oil (LO), (b) aged raw oil_light oil at $80^\circ$C for 1 hour (aRO_LO_80_1h), (c) 1 day (aRO_LO_80_1d), and (d) 1 month (aRO_LO_80_1m), and the highlighted characteristic signals. DEE = diethyl ether; THF = tetrahydrofuran; Ar = aromatic ring; $\alpha$-, $\beta$-, and $\gamma$- = the aliphatic carbon from the aromatic ring.

A6. Aromatic regions ($\delta_C/\delta_H 105–135/5.7–8.2$ ppm) in the $^1H$--$^{13}C$ HSQC NMR spectra (800 MHz, DMSO-$d_6$) of the (a) fresh light oil (LO), (b) aged raw oil_light oil at $80^\circ$C for 1 hour (aRO_LO_80_1h), (c) 1 day (aRO_LO_80_1d), and (d) 1 month (aRO_LO_80_1m), and the highlighted characteristic signals. Ar = aromatic ring.
A7. Aliphatic regions (δ_C / δ_H 10–70/0–5 ppm) in the 1H–13C HSQC NMR spectra (800 MHz, DMSO-d_6) of the (a) fresh heavy oil (HO), (b) aged raw oil_heavy oil at 80°C for 1 hour (aRO_HO_80_1h), (c) 1 day (aRO_HO_80_1d), (d) 1 month (aRO_HO_80_1m), and the highlighted characteristic signals. BHT = 3,5-di-tert-4-butylhydroxytoluene; THF = tetrahydrofuran; Ar = aromatic ring; α, β, γ = the aliphatic carbon from the aromatic ring.

A8. Aromatic regions (δ_C / δ_H 100–160/5–10 ppm) in the 1H–13C HSQC NMR spectra (800 MHz, DMSO-d_6) of the (a) fresh heavy oil (HO), (b) aged raw oil_heavy oil at 80°C for 1 hour (aRO_HO_80_1h), (c) 1 day (aRO_HO_80_1d), (d) 1 month (aRO_HO_80_1m), and the highlighted characteristic signals. BHT = 3,5-di-tert-4-butylhydroxytoluene; Ar = aromatic ring.
A9. Aliphatic regions ($\delta_C/\delta_H$ 10–70/0–5 ppm) in the $^1$H–$^{13}$C HSQC NMR spectra (800 MHz, DMSO-$d_6$) of the (a) fresh THF insolubles (TIS), (b) aged raw oil_THF insolubles at 80°C for 1 hour (aRO_TIS_80_1h), (c) 1 day (aRO_TIS_80_1d), (d) 1 month (aRO_TIS_80_1m), and the highlighted characteristic signals. BHT = 3,5-di-tert-4-butylhydroxytoluene; THF = tetrahydrofuran; Ar = aromatic ring; $\alpha$, $\beta$, and $\gamma$ = the aliphatic carbon from the aromatic ring.

A10. Aromatic regions ($\delta_C/\delta_H$ 105–135/5.7–8.2 ppm) in the $^1$H–$^{13}$C HSQC NMR spectra (800 MHz, DMSO-$d_6$) of the (a) fresh THF insolubles (TIS), (b) aged raw oil_THF insolubles at 80°C for 1 hour (aRO_TIS_80_1h), (c) 1 day (aRO_TIS_80_1d), (d) 1 month (aRO_TIS_80_1m), and the highlighted characteristic signals. BHT = 3,5-di-tert-4-butylhydroxytoluene; Ar = aromatic ring.
CONTACT INFORMATION

Nguyen Lyckeskog is a doctoral candidate, Mattsson is a post-doctoral student, and Andersson, Vamling, and Theliander are professors at Chalmers University of Technology, Department of Chemistry and Chemical Engineering, Gothenburg, Sweden. Olausson is with Valmet Power AB, Gothenburg, Sweden. Email Theliander at hanst@chalmers.se.

ABOUT THE AUTHORS

Lignin valorization is an important step toward renewable liquid fuel and can simultaneously increase profit for the kraft mill. Our work differs from previous studies because we investigated a higher storage temperature. The biggest challenge we had to overcome was to conduct a proper analysis of the high molecular weight lignin-derived bio-oil structure.

We found that the stability of the lignin-derived bio-oil we investigated is very good. This information can help pulp mill personnel determine whether to investigate technology to extract lignin from black liquor and process it further to liquid bio-oil. Our next step is to refine the bio-oil further.

Nguyen Lyckeskog is a doctoral candidate, Mattsson is a post-doctoral student, and Andersson, Vamling, and Theliander are professors at Chalmers University of Technology, Department of Chemistry and Chemical Engineering, Gothenburg, Sweden. Olausson is with Valmet Power AB, Gothenburg, Sweden. Email Theliander at hanst@chalmers.se.
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Lignin structure elucidation is an important but difficult task for biorefinery research. Lignin has a complex structure composed of a variety of substituted aromatic rings and is the only known renewable source of aromatic compounds. When lignin is depolymerized, the obtained products can be valuable as platform chemicals for numerous processes and lignin itself can be used for many applications [1]. Lignin is biosynthesized by dehydrogenative polymerization from L-phenylalanine via coumaril alcohol, coniferil alcohol and sinapyl alcohol, whereupon phenoxyl radicals are created, initiating a radical reaction that finally forms the lignin [2]. This radical mechanism is responsible for the variability of final lignin structures that can be different for every unit. Several authors have also demonstrated that lignin structure changes during its extraction [3,4,5]. However, there are certain similarities among the types of biomass, such as the proportion of the types of linkages and the phenolic monomers. For example, the coniferil alcohol proportion is 90%-95% in softwood, around 50% for hardwood, and around 75% for grasses, and the proportion of β-O-4 linkages is around 46% for softwood and 60% for hardwood [6].

The syringyl (S):guaiacyl (G) ratio is one of the most widely measured characteristics for lignin samples, and it is indicative of its composition. It has been measured successfully by thioacidolysis [7], permanganate oxidation, and alkaline oxidation with nitrobenzene, commonly known as nitrobenzene oxidation [8,9]. These techniques take a long time and have complex processes, which involve lignin oxidation with dioxane or nitrobenzene (highly harmful chemicals), and the final step is a chromatographic technique, either gas chromatography (GC) or high performance liquid chromatography (HPLC), to determine and quantify the composition of the lignin. In the search for easier ways to determine the S/G ratio, spectroscopic techniques such as Fourier transform-infrared (FT-IR) and nuclear magnetic resonance (NMR) have been investigated, not only for saving reaction time but also to decrease the use of harmful chemicals following one of the principles of green chemistry [10], but this has proven difficult because of sensitivity problems with these spectroscopic techniques. With quantitative heteronuclear single quantum coherence-nuclear magnetic resonance (HSQC-NMR) spectroscopy, good agreement with the measurements obtained by the nitrobenzene oxidation technique was achieved [11]. Finally, pyrolysis-gas chromatography mass spectrometry (py-GCMS) is a promising alternative. It gives results very close to those obtained by nitrobenzene oxidation, and it is a well-established, reliable, and reproducible technique [12].

Chemometrics is a part of chemical science that uses algebraic calculation methods to extract quantitative or qualitative information from chemical data, particularly to identify trends. It is most commonly applied to spectral data [13]. Multivariate regression methods, such as principal component regression (PCR) and partial least squares regression (PLSR), have been designed to tackle situations in which there are many predictor variables and relatively few samples. They are widely applied, for example, in near infrared spectroscopy where the bands overlap and it is difficult to obtain quantitative information from the spectra. It is important to discard all the variations that are not related with the measurement conditions. When chromatography and spectral profiles are analyzed, it is necessary to normalize these to avoid the influ-

**ABSTRACT:** Lignin structure elucidation is one of the main targets for biorefinery related research. Because of its complexity, obtaining reproducible results in a straightforward way is very important. One of the values that is used to compare different lignins is the syringyl:guaiacyl (S/G) ratio, which has been measured in different ways. The most reliable result is obtained for nitrobenzene oxidation, but this involves a complex process. In this work, the S/G ratios measured by pyrolysis-gas chromatography mass spectrometry (py-GCMS) and heteronuclear single quantum coherence-nuclear magnetic resonance (HSQC-NMR) spectroscopy were compared with attenuated total reflection infrared (ATR-IR) spectroscopy results to establish a reliable, quick, and simple method for the measurement. To achieve this, two mathematical models were applied with multivariate data analysis software. A partial least squares regression model for py-GCMS gave the best result.

**Application:** This study describes an easy way to characterize lignin.

---

**An easy and reliable method for syringyl:guaiacyl ratio measurement**

RAQUEL PRADO, LISA WEIGAND, SHIKH M.S.N.S. ZAHARI, XABIER ERDOCIA, JASON P. HALLETT, JALEL LABIDI, AND TOM WELTON

**ABSTRACT:** Lignin structure elucidation is one of the main targets for biorefinery related research. Because of its complexity, obtaining reproducible results in a straightforward way is very important. One of the values that is used to compare different lignins is the syringyl:guaiacyl (S/G) ratio, which has been measured in different ways. The most reliable result is obtained for nitrobenzene oxidation, but this involves a complex process. In this work, the S/G ratios measured by pyrolysis-gas chromatography mass spectrometry (py-GCMS) and heteronuclear single quantum coherence-nuclear magnetic resonance (HSQC-NMR) spectroscopy were compared with attenuated total reflection infrared (ATR-IR) spectroscopy results to establish a reliable, quick, and simple method for the measurement. To achieve this, two mathematical models were applied with multivariate data analysis software. A partial least squares regression model for py-GCMS gave the best result.

**Application:** This study describes an easy way to characterize lignin.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Biomass</th>
<th>Treatment</th>
<th>Conditions</th>
<th>Py-GCMS</th>
<th>NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Willow</td>
<td>I onosolv</td>
<td>0.5 h, 120°C [Et$_3$NH][HSO$_4$]</td>
<td>1.28</td>
<td>1.59</td>
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<td>1.55</td>
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<td>2.28</td>
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<td>0.88</td>
<td>0.88</td>
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<tr>
<td>27</td>
<td>Rice straw</td>
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<td>4 h, 120°C [Et$_3$NH][HSO$_4$]</td>
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<td>1.32</td>
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<td>28</td>
<td>Mischantus</td>
<td>I onosolv</td>
<td>6 h, 120°C [Et$_3$NH][HSO$_4$]</td>
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<tr>
<td>29</td>
<td>Mischantus</td>
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<td>1 h, 150°C [Et$_3$NH][HSO$_4$]</td>
<td>1.39</td>
<td>1.40</td>
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<tr>
<td>30</td>
<td>Pine</td>
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<td>0.90</td>
<td>0.90</td>
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<tr>
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<td>0</td>
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<td>0.5 h, 170°C [Et$_3$NH][HSO$_4$]</td>
<td>0.13</td>
<td>0</td>
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<td>Baggasse</td>
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<td>2 h, 120°C [Et$_3$NH][HSO$_4$]</td>
<td>2.77</td>
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<td>40</td>
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<td>4 h, 120°C [Et$_3$NH][HSO$_4$]</td>
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<td>1.99</td>
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<tr>
<td>41</td>
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<td>Organosolv</td>
<td>1.5 h, 180°C EtOH</td>
<td>2.03</td>
<td>1.73</td>
</tr>
</tbody>
</table>

Py-GCMS = pyrolysis-gas chromatography mass spectrometry; NMR = nuclear magnetic resonance.

I. Samples used for the calibration.
LIGNIN CHARACTERIZATION

Excerpted from the text:

1. Attenuated total reflection infrared (ATR-IR) spectrum of willow lignin sample obtained by ionosolv process (120°C for 22 h).


ence of the size of the objects [14].

PCR and PLSR have been successfully applied to extract information in many instances. They are frequently used in medical chemistry, as in tumor classification and spatial analysis of brain images [15,16]. There is little difference between the use of PLSR and PCR; in most situations, similar results are achieved. However, PLSR normally requires fewer latent variables, so the model is better described and it is able to analyze correlated and noisy data, which can be very useful when spectral and chromatographic data are treated.

In this work, lignin from different sources (hardwood, softwood, and grass) and extracted by different processes (ionosolv and organosolv) from biomass were characterized to establish a model that relates attenuated total reflection infrared (ATR-IR) spectra with the S/G ratio measured by HSQC-NMR and py-GCMS. We compared both methodologies with the goal of finding a reliable, simple, and quick method to elucidate this ratio. This study will advance lignin structure elucidation and address the potential application of lignins as a source of process chemicals.

EXPERIMENTAL

Lignins from different species (willow varieties, pine, bagasse, rice husk, and Miscanthus), 41 different samples in total, obtained by different delignification processes (organosolv and ionosolv at different temperatures) (Table 1) were characterized by ATR-IR, HSQC-NMR, and py-GCMS. The lignins were characterized and the data were analyzed with The Unscrambler software (CAMO Software; Oslo, Norway).

Organosolv process

The organosolv pulping was carried out under the following conditions: 60% (v/v) aqueous ethanol solution, solid:liquid ratio of 1:4 at 180°C for 90 min. The resultant solutions were filtered and washed with distilled water. Lignin was precipitated from the black liquor by adding water acidified to pH 2 by adding H$_2$SO$_4$. Then the mixture was centrifuged at 4000 rpm for 15 min. Lignin was washed with acidified water and dried at 70°C for 16 h.

Ionosolv process

For the ionosolv process, biomass, water and ionic liquid (IL) were mixed in a mass ratio 1:2:8. Triethylamonium hydrogen sulfate [Et$_3$NH][HSO$_4$] and butylimidazolium hydrogen sulfate [Hbim][HSO$_4$] were used as the ionic liquids and mixtures were treated at different temperatures (120°C–170°C) and different times (0.5-22 h). Then the resultant solutions were filtered with Whatman 542 filter paper and washed with three volumes of ethanol (30 mL). The ethanol of the black liquor was removed by evaporation. Lignin was precipitated by adding 2 volumes of distilled water (20 mL) and then centrifuging at 4000 rpm for 15 min. Lignin was washed with distilled water and dried at 70°C for 16 h.

The ATR-IR spectra were collected by placing a particle of each sample onto the window of the ATR device. A background spectrum was measured before the sample spectrum (Fig. 1) [17].

S/G ratio calculation

The S/G ratio from py-GCMS was calculated by dividing the sum of the area of the syringol-related peaks (syringol, 4-ethylsyringol, 4-vinylsyringol, and 4-propenylsyringol) against the sum of the area of guaiacol-related peaks (guaiacol, 4-methylguaiacol, 4-vinylguaiacol, and vanillin) (Fig. 2) [12]. The G(C$_2$H$_2$) signal was used as an internal standard, with the following equation:

\[
\frac{S}{G} = \frac{S(C_2H_6H_2O)}{(G(C_2H_2) + G(C_6H_6))}
\]
LIGNIN CHARACTERIZATION

Figure 3 shows the HSQC-NMR of a representative lignin sample where S and G ring signals are detected. Where \( G_{(C=H)} \) was assigned to the 6.93-110.10 ppm peak, \( G_{(C=H_2)} \) was assigned to the 6.64–104.21 ppm peak, and \( G_{(C(H_2)} \) was assigned to the 6.77–119.13 ppm peak, all of these were integrated with \( G_{(C=H_2)} \) as the reference [18,19].

For the ATR-IR
The Unscrambler multivariate analysis software was used to establish the relationship between the ATR-IR spectra and the S/G ratio calculated by HSQC-NMR and py-GCMS. PLR and PLSR models were chosen for the multivariate analysis. Table II details the specifications of each model. Analysis of the data can lead to different conclusions as to which is the best model to be applied, if there is a good relation between IR spectra and S/G ratio, and which measurement has better correlation.

Instruments
All lignin samples were characterized by attenuated-total reflectance infrared spectroscopy (ATR-IR) by direct transmission in a single-reflection ATR system (ATR top plate fixed to an optical beam condensing unit with a zinc selenide lens) with a Specac (Orpington, UK) Golden Gate ATR accessory. Spectral data were acquired over 10 scans in the range of 4000–650 cm\(^{-1}\) and 4 cm\(^{-1}\) resolution.

HSQC-NMR spectra were recorded at 30°C on a Bruker (Karlsruhe, Germany) Avance 600 MHz NMR spectrometer equipped with a z-gradient BBI probe. Typically, 20 mg of sample was dissolved in 0.6 mL of dimethyl sulfoxide-d\(_6\). The pyrolysis device was a CDS Analytical (Oxford, PA, USA) Pyroprobe 5150. The pyrolysis temperature was set at 600°C for 15 s with a heating rate of 2°C msec\(^{-1}\). Helium was used as the carrier gas from the pyrolyzer to the GC.

GC-MS analysis was performed to identify the monomers in the lignin structure. After pyrolysis, the lignin monomers were transferred by the inner line and injected into an Agilent GC (7890A)-MS (5975C inert MSD with Triple-Axis Detector) (Agilent; Santa Clara, CA, USA) equipped with a HP-5MS capillary column ([5%-phenyl]-methylpolysiloxane, 60 m × 0.32 mm). The temperature program started at 50°C and was raised to 120°C at a rate of 10°C min\(^{-1}\), held for 5 min, raised to 280°C at a rate of 10°C min\(^{-1}\), held for 8 min, raised to 300°C at a rate of 10°C min\(^{-1}\), and finally held for 12 min. Helium was used as the carrier gas.

RESULTS AND DISCUSSION
Figure 1 shows the ATR-IR spectrum of one representative lignin sample. The bands were assigned as shown in Table III. This lignin spectrum was chosen as a general example to show the assignments of the bands to the different
aromatic structures present in the lignin and to highlight the bands specifically related to G and S rings. We observed that the bands assigned to G and S rings are found between 1400 cm⁻¹ and 800 cm⁻¹. Other bands related to aromatic rings in general were seen in the range of 1700 cm⁻¹ to 650 cm⁻¹.

In py-GCMS, the lignin is decomposed into its main monomers and other fragments that confirm its structure. The chromatogram is basically divided into three parts. The first is more related to the sugar fraction present in the lignin from 3 min to 11 min, the second is mainly composed of phenolic monomers from 9 min to 26 min, and the third is composed of complex aromatics and fatty acids from 26 min to 50 min.

**II. Multivariate analysis conditions.**

<table>
<thead>
<tr>
<th>X-variables</th>
<th>Y-variables</th>
<th>Number of components</th>
<th>Validation</th>
<th>Algorithm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spectra</td>
<td>S/G</td>
<td>10</td>
<td>Leverage correction</td>
<td>NIPALS</td>
</tr>
<tr>
<td>X-variables</td>
<td>Y-variables</td>
<td>Number of factors</td>
<td>Validation</td>
<td>NIPALS*</td>
</tr>
<tr>
<td>Spectra</td>
<td>S/G</td>
<td>10</td>
<td>Leverage correction/Cross validation</td>
<td>NIPALS*</td>
</tr>
</tbody>
</table>

NIPALS = non-linear iterative partial least squares.

| 816 | CH out of plane in positions 2, 5, and 6 of G units |
| 824 | CH out of plane deformation in 2 and 6 position on S ring and in all positions of H units |
| 912 | CH out of plane deformation |
| 1031 | C-O deformation, primary OH plus CO stretching in unconjugated ketones and aromatic CH in plane deformation |
| 1075 | CO deformation in secondary alcohols and aliphatic ethers |
| 1114 | Etherified G ring + S unit and secondary hydroxyl plus CO stretching |
| 1153 | Aromatic CH in plane deformation in the G ring |
| 1213 | G ring breathing plus C=O stretch |
| 1268 | G ring breathing with carbonyl stretching |
| 1323 | S ring and G ring condensed |
| 1362 | Phenolic OH and aliphatic CH in methyl groups |
| 1425 | Aromatic skeletal vibrations combined with CH in plane deformation |
| 1456 | CH deformation in methyl and methylene groups |
| 1514 | Aromatic skeletal vibrations |
| 1603 | Aromatic skeletal vibrations |
| 1724 | C=O stretch in unconjugated ketones, carbonyl, and ester groups |
| 2851 | CH stretching methyl and methylene |
| 2921 | CH stretching methyl and methylene |
| 3380 | OH stretching |

**III. Attenuated total reflection infrared (ATR-IR) spectroscopy bands.**

Figure 2 shows a typical lignin chromatogram, in which it can be observed that lignin is mainly composed of phenolic derived fragments. The peaks taken into account for the calculation of the S/G ratio have been marked. G itself is the peak at 9.78 min and S is the peak at 15.839 min, but other structures derived from these have been introduced in the calculation.

Figure 3 depicts a representative lignin HSQC-NMR spectrum. The signals needed for the calculation of S/G in accordance with Eq. (1) are marked in Fig. 3. The spectra can be divided into different sections for lignin, side chain region (δC/δH 50–95/2.5–6.0 ppm) and the aromatic region (δC/δH 95–160/5.5–8.0 ppm).
Multivariate analysis

The data treatment was accomplished using The Unscrambler software, which is widely used for multivariate analysis and design of experiments. PCR and PLSR models were independently applied to the data to decide which gave the best approach. PCR is generally considered to be a more robust model, whereas PLSR is often a better approach for spectra data analysis.

The data matrix was composed of 41 rows that are the lignin samples disposed in rows, two columns with the S/G ratios calculated by py-GCMS and HSQC-NMR, which are the response variables, and 837 columns of spectral data that are the predictor variables. The best model result was chosen according to the regression coefficient, the number of components for PCR and factors for PLSR, and the explained variance curve. The target is a model with a high regression coefficient, a low number of components, and low variance.

First, PCR was chosen as the model to apply to the data matrix with all the samples and the whole IR spectra with the S/G ratio measurements. Table IV shows the results obtained from the PCR model. The first row shows results for the initial approach. The best regression coefficient was obtained for the py-GCMS measurement. However, more components were needed to define the calibration than for HSQC-NMR. The predicted curve also did not match the model curve very well for more than three components. Hence, it was discarded.

To improve the results, the spectral range was reduced to cover only the aromatic ring-related part and was set from 1825 cm\(^{-1}\) to 650 cm\(^{-1}\). The second row of Table IV shows the results. Nevertheless, the result was contrary to that expected; more components were needed to have a good regression coefficient. Furthermore, the difference between the model curve and the predicted curve was higher; the predicted curve did not match the model at all. The obtained variance was not acceptable.

Finally, the softwood S/G ratio is very low because of the tiny concentration of syringyl in softwood lignin, making this ratio hard to measure, especially by NMR, resulting in outcomes with high standard deviations. The third row in Table IV shows the results of applying the PCR model to hardwood and grasses. As a result, the regression coefficient was substantially improved and the variance was acceptable up to five components (see Fig. 4 in which the predicted curve is depicted). Similar regression coefficients were obtained for NMR and py-GCMS measurements of the S/G ratio, but more components were needed to define the NMR calibration curve. To have less modification of the data and to give a better prediction, the aim is to reduce the number of components that define the model.

The PLSR model was applied in an attempt to improve on the results obtained by the PCR. The PLSR model was applied in the same way as the PCR to be comparable. The results of the application to the whole spectra are shown in the first row of Table V. The obtained regression coefficient improved in comparison to the ones obtained for the PCR model. The drawback was the number of factors needed in each case, which was eight for NMR and seven for py-GCMS. The best variance was obtained for two factors, as observed in the comparison of predicted curve with the modelled curve.

To reduce the number of factors in the final equation, the
Lignin was characterized by ATR-IR, py-GCMS, and HSQC-NMR for the calibration of S/G ratios with ATR-IR spectra. Using multivariate analysis, it was determined that the results obtained by py-GCMS had better correlation with the IR spectra and the best approach was obtained with the PLRS model. The regression coefficient was 0.97. The curve was defined with only three factors, with a good variance result. Hence, py-GCMS is a good characterization technique to determine the S/G ratio. In addition, it does not require manipulation of the sample, no solvent is required, and the quantity needed for running the experiment is very small compared with other techniques. Although this method is robust and reliable, the quantity of the original sample is usually not known. Therefore, the method can only give relative amounts and should be considered semi-quantitative. We have also demonstrated that ATR-IR can be calibrated with py-GCMS to obtain the S/G result. This information can be very useful in developing a sensor able to have a quick response. Lignin from different sources and processes can be initially characterized by py-GCMS and calibrated with ATR-IR to obtain the algorithm relating the S/G ratio with the spectrum. Further, lignins can then be characterized by simple ATR-IR alone by applying the obtained algorithm to give the S/G ratio.

**CONCLUSION**

**ACKNOWLEDGEMENTS**

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**LITERATURE CITED**


ABOUT THE AUTHORS

We chose this topic to research because I (Welton) have been dealing with the complexity of lignin characterization. The study will ease the way of samples characterization. The most difficult part of this study was organizing the data sheet. From the study, we learned that statistics are an important tool for characterizing complex structures. We were pleased to see a good correlation between py-GC-MS and ATR-IR.

We expect that mills will benefit from this new, facile way to characterize lignin. The next step could be the development of a new sensor.

Prado is researcher, Zahari is professor, and Welton is dean, Department of Chemistry; Hallett is senior lecturer, Department of Chemical Engineering; and Weigand is Ph.D. student, Department of Chemistry and Department of Chemical Engineering, Imperial College London, London, UK. Erdocia is doctor and Labidi is professor, Chemical and Environmental Engineering Department, University of the Basque Country, San Sebastian, Spain. Email Welton at t.welton@imperial.ac.uk.
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Analysis of economically viable lignin-based biorefinery strategies implemented within a kraft pulp mill

ABSTRACT: Many pulp and paper companies are considering implementing a lignin-based biorefinery to diversify their core business to new products and improve their longer-term competitiveness. The best strategy to achieve might not be obvious, considering the lignin extraction process and derivatives to be implemented over the longer term that meet market and business objectives, and provide competitive advantage. In this article, various lignin biorefinery strategies were considered in a case study involving lignin precipitation processes integrated within an existing kraft mill, and solvent pulping processes that would be implemented in parallel to the existing mill processes using additional hardwood. The analysis aimed to identify the conditions under which various strategies would represent suitable investments. Operating constraints in the case study mill limited lignin extraction to 85 metric tons/day from 15% of the mill’s black liquor, whereas 260 metric tons/day lignin could be extracted by solvent pulping 1500 metric tons/day of hardwood. The preferred strategies identified by the study were lignin precipitation to phenolic resins production, and solvent pulping to carbon fiber production. The first product-process strategy requires lower investment, provides high returns (internal rate of return [IRR] of 39% to 43%), and is more easily implemented in the near term. Solvent pulping resulted in reasonable profitability (IRR of 18% to 25%), with higher production volumes and a diversified product portfolio, and was considered more suitable as a longer-term strategy. Business model robustness and long-term competitiveness can be better assured by combining both strategies. It was shown that 1) government support to offset capital cost, and 2) high derivatives market prices positively influence lignin valorization strategies, which are sensitive to technology and market maturity.

Application: This study illustrates how a technical and economic analysis could be used to identify lignin-based biorefinery strategies that represent an attractive investment.

In recent years, certain segments of the pulp and paper industry have experienced stable growth, led by emerging markets in Asia and Latin America [1,2]. The forecasted trend is for a timid growth going forward [3]. These global numbers overshadow a more difficult situation for certain geographic and market segments, and most forestry companies today are actively pursuing transformation through product diversification to procure their competitive position in the longer term.

Biorefinery strategies related to the improved management of hemicelluloses, and from the sale of lignin either found in black liquor or extracted by wood fractionation processes, offer good potential for diversification, especially for kraft pulp mills that have traditionally focused on the sale of cellulose. Lignin is interesting as a basic chemical because of its complex chemical structure with aromatics, methoxyl groups, and a variety of other functional units [4]. As a result, lignin is being explored for a wide range of market applications [5], either by partially using it in a formulation or by exploiting specific functionalities. However, investment in a lignin-based biorefinery strategy is not obvious because of a number of factors. These include 1) technology maturity – especially for the case of solvent pulping, 2) uncertainty in the understanding of the linkage that exists between lignin properties and specific market applications, and 3) uncertainty around the reproducibility of lignin-based product properties, etc.

The purpose of this paper is to evaluate lignin-based biorefinery strategies implemented in retrofit to an existing kraft pulp mill. The defined product-process strategies, implemented using a phased approach over several years, consider technology and market risk mitigation. A techno-economic analysis is performed to identify lignin-based biorefinery strategies that represent an attractive investment. In this project, we addressed the following objectives:

1. Characterize the lignin biorefinery in terms of extraction processes and downstream derivatives.
2. Define a set of promising product-process combinations that could be integrated to an existing kraft pulp mill using a phased implementation strategy.
3. Evaluate the economic performances of the strategies, and analyze critical factors for their success.

THE LIGNIN-BASED BIOREFINERY

Lignin extraction processes

The common nomenclature used for generic lignin types recognizes the difference between native lignin, as it forms in
plants, and technical lignins, as obtained from diverse industrial processes. It is practical to classify technical lignins based on physical and chemical conditions in the extraction processes that lead to the final structure and functionality of the lignin [6].

Agbor et al. [7] present an extensive review of existing biomass fractionation processes. They did not, however, define the technologies reviewed with the specific purpose of isolating lignin. Biomass fractionation processes can be classified according to comminution (i.e., mechanical size reduction) and biological, chemical, and physical-chemical characteristics. Comminution methods are mainly used to increase the specific surface area of wood before digestion. Biological processes are currently less practical at the industrial scale because of the long residence times required. Physical-chemical pretreatments include most of the fractionation processes that have been developed (steam explosion, dilute acid pretreatment, and ammonia fiber expansion) and the use of organic solvents (organosolv) for pretreatment, among others. In this category, organosolv pretreatment appears promising for lignin extraction, especially for those processes where the operating and separation conditions produce minimum damage to the lignin structure. The mixture of water and organic solvent (often ethanol) used in organosolv pulping leads to a purer lignin than do processes that use sulfurous solvents. Organosolv lignin is recognized as a high-purity, low molecular weight lignin [8,9].

Valuable products can be obtained from hemicelluloses and extractives present in pulping spent liquors. The low proportion of extractives renders economies-of-scale complex to establish, whereas hemicelluloses isolation can be achieved using membrane filters [10]. In kraft black liquor, lignin is kept in colloidal form by repulsion forces that the charged phenolic and carboxylic acid groups create between lignin particles. Disrupting black liquor’s properties, such as pH, temperature, or ionic strength, can reduce repulsion forces and lead to lignin precipitation. The most common method consists of acidification using carbon dioxide, sulfuric acid, or a combination of both to lower the pH of the black liquor from 13–13.5 to 9–10. The resulting precipitated lignin must be filtered and washed [11,12].

The first commercial scale plant for lignin precipitation from black liquor was implemented by Domtar in its mill in Plymouth, NC, USA, using the LignoBoost technology developed by Innventia in association with Chalmers University of Technology and supplied by Valmet (Fig. 1) [13]. In this technology, the acidification is followed by an initial filtration of lignin. Following a re-slurry of the lignin cake in dilute sulfuric acid, a second filtration step is then performed. More recently, the LignoForce technology has been introduced by FPInnovations, commercialized by NORAM (Vancouver, BC, Canada) (Fig. 2), and recently implemented at the West
Fraser mill in Hinton, AB, Canada [14,15]. This technology introduces an oxidation step before the acidification and uses a press filter in a single filtration washing step.

**Lignin conversion into added-value derivatives**

Black liquor is combusted in the kraft pulp mill recovery boiler to produce steam and green liquor. Lignin can be separated from the black liquor to the extent that acceptable combustion conditions can be maintained, or when lignin is produced by fractionating wood using an organosolv process. Lignin separated from black liquor can be used for numerous fossil-based products, among which phenol-formaldehyde (PF) resins and carbon fibers appear as promising [16,17].

Because of their affinity for wood and wood fibers, liquid phenolic resins are used for the specialty wood adhesives industry. Wood bonding applications such as particleboard, medium-density fiberboard, or waferboard/ply wood have traditionally used phenolic resin binders. The interest in lignin for use in phenolic resins resides in its high substitution potential for phenol. The substitution level for phenol can potentially be higher than 50% [18], but 30% remains a practical maximum tested at the commercial scale to meet a range of board processing and product requirements (e.g., bond strength, hardening time, and the mechanical properties of panels). Lignin can essentially be directly mixed with phenol and formaldehyde to formulate PF resins. Currently, this method is limited to a relatively low percentage of lignin because of the amount of reactive sites in the lignin structure. A chemical modification of lignin, such as phenolation, can be used to overcome this limitation [19]. Phenolation requires mixing lignin with phenol to improve its reactivity, before blending with formaldehyde or additional phenol.

Lignin also has potential as an inexpensive and abundant replacement of polyacrylonitrile (PAN), which is the most conventionally used carbon fiber precursor. Higher production volumes and a wider use of carbon fibers are currently limited by the feedstock cost, which can contribute to more than half of production costs and has high market price volatility [20]. Recent research by Oak Ridge National Laboratory in the United States has focused on melt-spun PAN, polyolefins, and lignin as low-cost alternative precursors, targeting structural (e.g., vehicles, aerospace, infrastructure) and non-structural applications (e.g., thermal management, electronics). Lignin usage challenges remain regarding production at higher scales and the mechanical properties of the resulting fibers [21].

The conventional carbon fiber manufacturing process consists of four main steps: 1) fiber spinning, 2) stabilization, 3) carbonization, and 4) surface treatment. In some applications, carbonization is followed by a graphitization step [22]. A study by Kadla et al. [23] demonstrated the potential to manufacture carbon fibers via melt spinning using organosolv and hardwood kraft lignins. However, softwood kraft lignin failed to pass the spinning step (it charred at temperatures above 140°C). Eckert and Abdullah [24] demonstrated that charring could be prevented by acetylation of lignin such that its acetyl content is at least 16% before spinning. Acetic anhydride is a suitable acetylating agent for that purpose. More recent work by Norberg [25] shows another alternative, which is to separate the kraft black liquor into two molecular weight fractions using an ultrafiltration membrane before...
acidification, and to use the lower molecular weight fraction for carbon fiber manufacturing. This method has been successfully used with hardwoods, softwoods, and combinations of the two feedstocks.

**Phased biorefinery implementation**

Every biorefinery strategy implies technology and business risks to different extents, and should incorporate implementation approaches that mitigate risk to the extent possible. Such an approach has been introduced by Chambost et al. [26] and further applied by Jeaidi et al. [27] to the context of mechanical pulp mills (Fig. 3). They suggest a phased implementation of biorefinery strategies, nominally over three phases. The longer-term phases (II and III) are defined first, and these determine the near-term implementation phase. Phases I and II are where technology disruption mainly occurs, while phase III implies mainly business disruption. Phase II represents the longer-term evolution of the product portfolio, while phase I represents the risk mitigation stage(s) implemented to gradually achieve the longer-term goals.

To invest, companies expect that their biorefinery strategy should result in high returns and an enhanced competitive position, considering the integration of new bioproducts within the existing product portfolio. Phase I in the near-term (typically <5 years) should involve the implementation of low to no-risk technologies that would be part of the overall process in the long run. Ideally, these technologies lead to the production of building blocks or intermediate products to provide early profits in the development of the biorefinery. Besides technology and business risk mitigation, an advantage of the sequential implementation is that it can potentially provide flexibility to change the orientation of phase II as processes and markets evolve in the bioeconomy, in case a more valuable strategy is identified during the phase I implementation period.

The timeline for each phase is case-specific. In many cases, the timelines for the later phases will depend on the ability of the pulp and paper company to create partnerships, capture market share, and reach targeted production and sales volumes before switching from one phase to the next. The case study developed in this article focuses on the assessment of biorefinery implementation in phases I and II, with additional analyses of the effect of the length of phase I on the overall economic return of the project.

**CASE STUDY**

The case study considers an existing kraft pulp mill producing 1500 air-dried metric tons/day of softwood pulp. In addition to black liquor from the kraft process, potential feedstock for the biorefinery includes unused biomass in the forest management area owned by the mill, of approximately 1500 moisture-free metric tons/day of hardwood sawlogs. Lignin extraction from black liquor is limited to the extent that would maintain suitable burning properties of the black liquor, thus ensuring good operation of the recovery boiler. A major concern for the pulp mill was to maintain the quality and amount of pulp because of existing long-term agreements with customers.

**METHODOLOGY**

Lignin-based biorefinery strategies were defined by combining process and product possibilities, as well as their phased-approach for implementation. To avoid affecting the existing mill pulping process by hardwood chips, strategies were separated into two categories: 1) integrated processes that would use black liquor as the main feedstock, defined as the lignin precipitation (LP) strategy, and 2) non-integrated hardwood conversion processes defined as the organosolv or more specifically, solvent pulping (SP) strategy.

Relevant information was collected for the completion of
mass and energy balances, and combined in a large-block analysis [28] to obtain comparable capital and operating costs estimates for each phase of the strategies defined. Energy balance simulations of some process units were carried out using Aspen Plus (AspenTech; Bedford, MA, USA) chemical process optimization software. Other calculations relative to mass balances, process economics, and cash flows were made using Microsoft Excel software.

**Definition of product-process combinations**

The LignoBoost process was considered the most mature of the lignin precipitation technologies and was selected as the base case (LP base case) (Fig. 1). The LignoForce process is the main comparison alternative (LP1), and differences in economics were estimated (Fig. 2). A second alternative consists of incorporating ultrafiltration technologies before black liquor acidification in conjunction with the LignoForce process (LP2), and using only the lower molecular weight fraction in subsequent operations (Fig. 4). This strategy is interesting because of its implication for the production of carbon fibers. Not having to pretreat the kraft lignin before spinning increases savings in capital and operating costs, and affects the overall profitability. For the LP process alternatives, estimates were based on a lignin production capacity of 85 metric tons/day. Lignin recovered in the first two strategies (LP base case and LP1) was defined as “kraft lignin” and lignin from LP2 was defined as “ultrafiltrated kraft lignin.”

Phenolic resins and carbon fibers are the only two lignin derivatives assessed in the case study. They would be produced in phase II. Lignin was converted either into a PF resin or a carbon fiber precursor and sold to a manufacturer downstream on the value chain during phase I to mitigate market risks. For PF resin applications, lignin was phenolated before sale to resin manufacturers as a phenol replacement. For carbon fiber applications, kraft lignin was acetylated and sold as a PAN replacement; ultrafiltrated kraft lignin was sent to the market without any additional modification.

The organosolv process, as developed by Alcell and further improved by Lignol [29], was defined as the base case for solvent pulping (SP base case) (Fig. 5). Solvent-based fractionation and the conventional pulping of wood chips have many similarities. This makes it easier to adopt the new technology at the mill and mitigates certain risks associated with technology disruption. Although there are several potential lignin extraction spots along the SP process, the differentiation between lignin grades was not considered in the process evaluation. All the lignin collected was assumed to be mixed into a single stream identified as “organosolv lignin.”

To make the biorefinery strategy comparisons consistent, the sequence of business phases for the sale of lignin derivatives is the same for the LP and SP alternatives. In the case of carbon fibers production, and similarly with ultrafiltrated kraft lignin, organosolv lignin was considered to not require any pretreatment and sold as-is during phase I. Because the focus of the case study is on lignin, products identified as “preferred derivatives” have been selected for cellulose and hemicellulose conversion, considering a minimum risk approach.

Although ethanol production through C6 sugar fermentation is well established in North America, the current trend is toward replacing ethanol with butanol, as the latter provides several advantages (e.g., higher energy content, better compatibility with automobile systems, higher blending potential with gasoline [30]). Companies such as Gevo and Butamax have developed processes for converting existing ethanol production plants into butanol plants [31], and several projects are expected in the coming years. Two approaches have been considered for butanol production: 1) implement the organosolv process for ethanol production in phase I and convert the cellulose line into a butanol plant during phase II, or 2) implement the acetone-butonal-ethanol (A-B-E) process [32] (com-
6. Block flow diagram of SP1 strategy, incorporating hot water extraction.

7. Block flow illustrations of SP base case and SP2 strategies in phase II.
monly used to produce butanol, with ethanol and acetone as byproducts) and start butanol production during phase I. Butanol from the A-B-E process (n-butanol) would be used for chemical applications; butanol from retrofitting ethanol processes (isobutanol) would target biofuel applications.

Furfural has been selected among possible hemicellulose derivatives for its market potential [33] and the maturity of processes for its manufacturing. Formic and acetic acids are co-products. The implementation approach proposed for this strategy consists of converting hemicellulose into a C5 sugar syrup to be sold as animal feed in phase I, before converting sugars into furfural during phase II. In the pulp and paper industry, hemicellulose extraction processes are increasingly used as pretreatment units to isolate C5 sugars and convert these into higher-value products [7, 34]. This strategy is considered as an alternative in the case study, by implementing a hot water extraction process [35] before the organosolv reactor (Fig. 6).

Overall, four strategies were defined for the SP category combining the implementation approaches for butanol and furfural (Table I). Figure 7 represents the evolution of the SP base case to isobutanol and furfural production in phase II, and the alternative strategy producing n-butanol (SP2).

**Process techno-economics**

Techno-economic estimates involve determining a realistic value for capital and operating costs, and for expected revenues that depend on future market prices. The techno-economics for most biorefinery projects is most sensitive to the latter, around which there is high uncertainty.

Equipment costs were estimated by assessing comparable processes in the literature, including projects and equipment similar to those for which estimations were being made. Cost data were scaled to the capacity required for the case study and actualized using cost index factors. Commonly used design heuristics were used to estimate components of direct and indirect capital costs for the LP processes. For the SP processes, after equipment costs were obtained, the Lang method [36] was applied. This method uses factors to obtain order-of-magnitude estimates of capital investment from equipment.
costs. This method was considered appropriate because detailed cost information on the organosolv process was scarce. Different Lang factors have been applied to operating units of the SP processes, as summarized in Table II. For cash flow calculations, a 2-year construction period was assumed for each of the implementation phases. Two cases were considered for the internal rate of return (IRR) calculations for each product-process strategy:

- IRR for phase I was calculated as though run for 20 years (“Phase I” in the figures).
- IRR for phase I was calculated for 5 years, then phase II is implemented and run for 20 years (“Phase I + Phase II” in the figures).

Table III summarizes other main assumptions of economic calculations. Regarding lignin derivatives, specific discounts were applied to assumed market prices to reflect market penetration strategies. Discounts applied vary from 10% to 20% for different lignin types and applications, based on judgement.

**Scenarios definition and sensitivity analysis**
Based on the results of the preliminary profitability assessment, a scenario representing the preferred strategy was developed. A sensitivity analysis was performed on this scenario, considering five parameters identified as critical to the profitability of the case study strategies: 1) capital cost subsidy, 2) process scale, 3) the length of phase I, 4) the market price of phenol, and 5) the market price of carbon fiber.

Capital cost subsidy considered the minimum of 1) 50% of phase I capital requirements, and 2) $100 million. Subsidies are considered only for phase I.

The effect of process scale was assessed on the SP processes for biomass procurement capacities of 1) 500 metric tons/
day (i.e., the same lignin production capacity as lignin precipitation [LP] producing 85 metric tons/day of lignin), and 2) up to 2335 metric tons/day (inventory of pulp logs and sawlogs in the forest) on a dry basis.

The length of phase I was evaluated from 3 years (2-year construction + 1-year production) to 27 years (2-year construction + 25 years of the “Phase I + Phase II” scenario).

**RESULTS**

With 1500 metric tons/day of hardwood supply, 260 metric tons/day of lignin can be extracted for the SP base case process, whereas only 85 metric tons/day are recovered from the acidification of 15% of the mill black liquor. This amount of lignin results in the production of 178 metric tons/day of resin precursor in Phase I and 410 metric tons/day of PF resin in Phase II, for the case of LP strategies. The same conversion yields apply to organosolv lignin. In the case of carbon fibers production, a yield of 42% is estimated for organosolv lignin and ultrafiltrated kraft lignin, and a 53% yield is assumed for kraft lignin. This difference is because of the mass increase that occurs during acetylation of kraft lignin.

**Techno-economic performance**

Figures 8 and 9 summarize the results of cost and revenue estimates for each phase of the production of PF resins and carbon fibers, respectively. These results are specific only to the case study mill because they take into consideration integration and other costs that are related to the existing processes (e.g., materials handling, power island, and wastewater treatment plant). Costs and revenues are much lower for LP strategies than for SP processes; however, direct comparison between LP and SP categories is difficult because of the magnitude of the scale difference between the two types of processes. Regardless of the lignin extraction process, carbon fibers appear more costly to produce than PF resins.

Figures 10 and 11 present the IRR estimates for “Phase I” alone, and “Phase I + Phase II” for PF resins and carbon fibers production, respectively. For PF resins production, LP strate-
gies are generally more profitable than SP ones, at each phase of biorefinery implementation. Results are more balanced in the case of carbon fiber production, for which ultrafiltrated kraft lignin (LP2) presents substantially better results. The production of PF resins is more interesting in the “Phase I + Phase II” scenarios, while in the case of carbon fibers, the production of precursors (“Phase I” scenarios) are more profitable.

**Scenarios analysis**

Lower investment requirements, a more mature technology, and a good IRR result in LP processes and PF resins production being the most promising in the short-term. In the longer term, SP processes will become preferred because higher production volumes are required for capturing market share and added-value lignin-based products are manufactured from differentiated lignin. Furthermore, SP processes result in a better IRR for carbon fibers production. Therefore, the strategy selected for the scenarios analysis combined LP and SP processes as follows:

- **Phase I** — Lower risk phase
  - LP2 integrated to existing mill, producing PF resins precursor.
  - SP base case demonstration plant (300 metric tons/day of hardwood) for carbon fiber development.
- **Phase II** — Commercial scale development
  - LP2 evolves to carbon fiber precursor production.
  - SP base case commercial scale plant implemented (1500 metric tons/day), producing carbon fiber precursors, ethanol, and sugar syrup.
- **Phase III** — Full implementation of the product portfolio
  - Carbon fiber manufacturing strategy evolves from precursors to carbon fiber production.
  - Ethanol and sugar syrup units evolve, respectively, to isobutanol and furfural production.

*Figure 12* presents the results of the sensitivity analysis applied to this “LP+SP strategy.” The allowance of capital cost subsidy, or a higher carbon fiber price, make the strategy...
much more attractive. As well, a higher phenol price benefits short-term profitability. From another perspective, a low-capacity commercial scale or a longer-than-expected phase I reduces the profitability of the strategy.

**DISCUSSION**

Although the estimates for biorefinery implementation are context-specific and have high uncertainty, some generalities can be extrapolated from the case study.

For this case study, obtaining PF resins from lignin precipitation processes was the preferred strategy for the short term. Revenue from this strategy is limited by capacity constraints of the kraft mill recovery cycle. SP strategies performed better when combined with carbon fiber production.

Solvent pulping processes are capital-intensive. Considering their level of risk, especially during scale-up, this is a significant discouraging factor to their implementation in the near term. Further, depending on the existing mill power island and the process steam demand, the integration of SP processes into existing mills might require the purchase of a new boiler and adapting the chip handling system or the wastewater treatment facility. Nonetheless, the resulting diversified product portfolio can potentially provide significant additional revenue streams in the early years of an implemented project if the market conditions are realized.

Combining LP and SP processes into a single strategy provides the opportunity to develop a unique competitive advantage regarding lignin markets, and the production of high-value derivatives in the longer-term. At the same time, short-term risks are mitigated by more developed applications...
such as phenol replacement in PF resins. A vertically integrated company that owns forest management areas, pulp mills, and plywood manufacturing plants would have a considerable advantage in this regard. Capital cost subsidy significantly enhances the profitability of the transformation strategy, and should be considered essential to mitigate short-term risk.

**CONCLUSIONS**

Beyond the need to generate positive cash flows in the short term, pulp and paper companies have the opportunity to define their long-term biorefinery strategy through substantial volumes of added-value product streams. In this project, the context of the lignin-based biorefinery implemented at a kraft pulp mill has been considered, for which integrated lignin precipitation and parallel solvent pulping strategies were assessed for the production of PF resins or carbon fiber. These strategies would be implemented using a phased approach, where phase II involves the manufacture of added-value products, and phase I is defined to mitigate short-term risks in a way that supports the transition to phase II. This analysis shows that 1) PF resins production from lignin precipitation and 2) carbon fibers production from solvent pulping are profitable strategies. Lignin precipitation, including ultrafiltration of black liquor before acidification, is a promising alternative for carbon fiber production. Two important drivers are technology maturity and the ability to match production volume with market demand, which will depend on the speed to market maturity. In this regard, combining lignin precipitation and solvent pulping for the production of PF resins in the short-term and carbon fiber in the longer term appears to be a competitive and robust strategy. TJ

**ACKNOWLEDGMENTS**

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**LITERATURE CITED**


**Sensitivity analysis for the “LP+SP” lignin-based biorefinery strategy.**

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<th>Scenario</th>
<th>Subsidy on Phase I</th>
<th>Commercial Scale Capacity</th>
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ECONOMIC ANALYSIS


ABOUT THE AUTHORS

The lignin biorefinery is emerging as a business consideration, but companies need to consider strategies that are implemented incrementally to create competitive advantage over the long term. This report provides practical research intended to inspire mills considering the lignin-based biorefinery. The report organizes the conceptual ideas and provides a quantitative analysis as illustration for those in the field.

The most difficult part of developing this analysis was in making the broad assumptions needed for the techno-economic analysis. This was addressed through databases and discussions with experts. As part of the study, we found that companies investing in the lignin-based biorefinery have ambitious long-term plans! We were impressed by the high rates of return possible with the lignin-based biorefinery, but also note the high level of uncertainty around this outcome. From here, we intend to extend these scenarios to a multi-criteria decision-making (MCDM) panel.

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