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A Preparation Method of Softwood Lignin Derivatives: US9347177B2 Patent Evaluation †

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Abstract: This study, in the form of a patent evaluation, which is a technique for studying the information present within and attached to patents, describes the state of the art by introducing what has been patented in relation to softwood lignin derivatives. Inventors have described and claimed, through the US9347177B2 patent, a method for the preparation of derivatives of native lignin from softwood sources that have a certain aliphatic hydroxyl content. The invention covered by the patent concerns the processes of treating or compounding macromolecular substances and compositions of lignin-containing materials, as well as lignin and products derived therefrom. To prove the concept of this invention, recovery of lignin derivatives has been carried out from three softwood species. Samples of each softwood biomass feedstock were treated using an acid-catalyzed ethanol organosolv pulping process under different conditions. As a result, the recovered lignin derivatives may have an aliphatic hydroxyl content of 2.5−7 mmol.g^{-1}, a phenolic hydroxyl content of 2−8 mmol.g^{-1}, a molecular weight that varies in the range of 200−4000 g.mol^{-1}, and any suitable polydispersity of 1−5. These features result in a product with more consistent antioxidant activity. Furthermore, these recovered lignin derivatives may be advantageous when formulating such compositions, making these materials highly desired for wide applications.

Keywords: softwood; lignocellulosic material; lignin; polymer; patent

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1. Introduction

Lignin is one of the three major biopolymers of the lignocellulosic biomass, accounting for 10−25% *w*/*w* of its composition and about 30% *w*/*w* of the organic carbon in the biosphere [1,2]. It consists of inter-unit linkages of three repeating phenyl-propane monomers, termed sinapyl alcohol (S), coniferyl alcohol (G), and p-coumaryl alcohol (H) (Figure 1) [3]. Other monolignols may be present in infinitesimal concentrations [4]. The proportions of these monomers may vary depending on the type of plant species (e.g., hardwoods, softwoods, annual plants, etc.), and environmental conditions [1,5]. This endows lignin macromolecules with a diverse range of molecular weights and polydispersity [6]. Due to its composition and structure, lignin can serve as an environmentally friendly, biodegradable, antimicrobial, and antioxidant substance to develop high-value products with potential applications in the chemical, pharmaceutical, cosmetic, and food fields [7].

Lignin can be isolated in various forms by different extraction processes, which can be classified into two major categories, namely sulfur and sulfur-free processes (Figure 2) [3]. Generally, extracting native lignin from lignocellulosic biomass results in lignin fragmentation into numerous mixtures of irregular components [8,9]. Several pre-treatment methods classified into chemical, physicochemical, and enzymatic pre-treatments have been developed to investigate and allow the isolation and recovery of lignin from wood [10]. In addition, a number of alternative wood lignin extraction processes have been developed but not yet industrially introduced. Among them, four major organosolv pulping methods tend to produce highly purified lignin mixtures and are defined as [11]:

1. Alcell® process: This method involves the use of ethanol and solvent pulping;
2. ASAM process: This method involves pulping with alkaline sulfite anthraquinone methanol;
3. Organocell process: This method uses methanol pulping followed by methanol, NaOH, and anthraquinone pulping;
4. Acetosolv process: This method uses acetic acid, hydrochloric acid, or formic acid pulping.

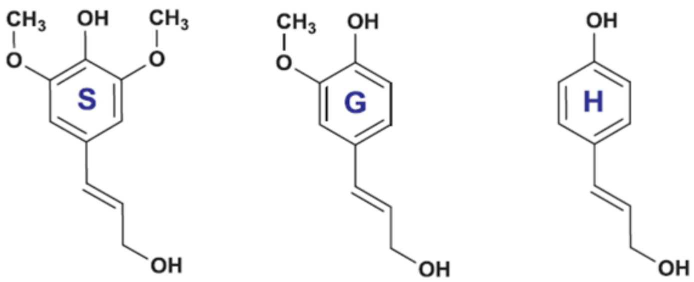

Figure 1. Chemical structures of different lignin monomers: sinapyl alcohol (S), coniferyl alcohol (G), and p-coumaryl alcohol (H) (Adapted with the permission from Ref [3]. Copyright © 2019 Elsevier Ltd.).

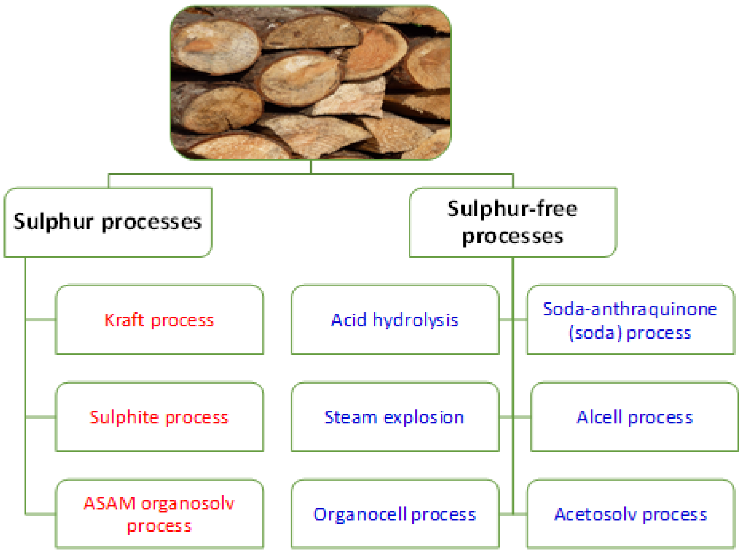

Figure 2. Different processes for the isolation of lignin from lignocellulose wood matrix (Adapted with the permission from Ref [3]. Copyright © 2019 Elsevier Ltd.).

These four commercially registered organosolv pulping methods (i.e., Alcell®, ASAM, Organocell, and Acetosolv) can yield lignin derivatives with excellent performance characteristics such as structural optimization, low inorganic impurities, and low molecular weight, thereby opening up new potential applications [11,12]. The commonly adopted solvents for organosolv pulping are ethanol, methanol, acetic acid, and formic acid, which are usually mixed with water and mineral acids as catalysts [7]. Taking into account all of the above, organosolv pulping processes tend to be the most practical technique used to recover lignin material from biomass feedstock.

Research on lignin and its derivatives is developing rapidly through the innovation and improvement of raw materials, chemical synthesis, methods of preparation, and formulation. Nevertheless, to promote the sufficiency of lignin in potential applications, several researchers have investigated pathways to enhance lignin properties to meet physicochemical and biological requirements. Compared to the use of cellulose, which has been commercialized for centuries, commercial applications of lignin use are rare. That is why there is a great interest in developing future strategies for lignin utilization, especially for softwood lignin.

This study, in the form of US9347177B2 patent evaluation, which is a technique for studying the information present within and attached to patents, describes the state of the art by introducing what has been patented in relation to methods used to recover derivatives of native lignin with a certain aliphatic hydroxyl content from softwoods as biomass raw materials. Both regarding preparation methods and applications, this study suggests a summary of the incorporation of recovered lignin derivatives in different polymer compositions for the purpose of providing additional functionality, such as enhancing their antioxidant property. Furthermore, samples of hybrid spruce trees, radiata pine, and loblolly pine were studied under various conditions to demonstrate the concept of the present invention.

2. Patent Analysis

The studied patent was invented by Balakshin et al. and it was filed by the company Fibria Innovations Inc. (Burnaby, BC, Canada) in 2015. The earliest priority date of this patent was 28 May 2009, with 64 patent families [13].

The jurisdictions of the 64 related patent documents (i.e., patent applications and granted patents) correspond to the United States (27 patents), Canada (11 patents), Europe (eight patents), China (eight patents), Brazil (five patents), and the global system for filing patent applications (five patents), known as the Patent Cooperation Treaty (PCT) and administered by the World Intellectual Property Organization (WIPO) [14]. The evolution of patent documents, related to the US9347177B2 patent, as a function of application filing year, granted year, and publication year, is presented in Figure 3.

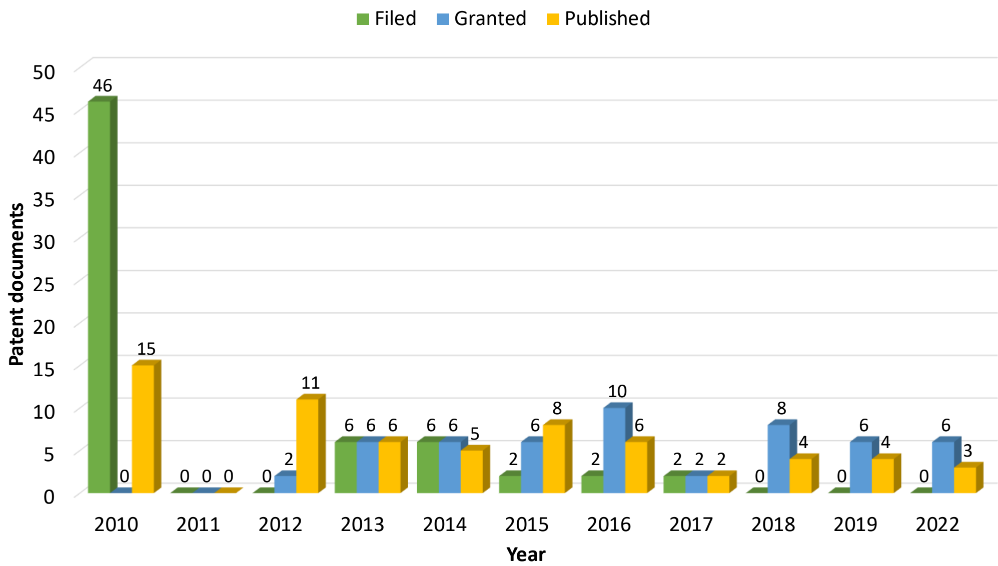

Figure 3. Filed, granted, and published patents concerning the 64 related patent families of the US9347177B2 patent [15].

The International Patent Classification (IPC) is a hierarchical system in the form of codes, which divides all technology areas into a range of sections, classes, subclasses, groups, and subgroups. It is an international classification system that provides standard information to categorize inventions and evaluate their technological uniqueness [16]. The relevant IPC codes concerning the studied US9347177B2 patent are presented in Table 1.

Table 1. Relevant classifications of the US9347177B2 patent [16].

IPC Codes	Description
C07G1/00	Low-molecular-weight derivatives of lignin
C08H7/00	Lignin; modified lignin; high-molecular-weight products derived therefrom
C08J3/00	Processes of treating or compounding macromolecular substances
C08K5/13	Use of organic ingredients and oxygen-containing compounds such as phenols and phenolates
C08L23/02	Compositions of homopolymers or copolymers of unsaturated aliphatic hydrocarbons with only one carbon-to-carbon double bond not modified by chemical aftertreatment
C08L57/00	Compositions of unspecified polymers obtained by reactions only involving carbon-to-carbon unsaturated bonds
C08L97/00	Compositions of lignin-containing materials
C09K15/06	Antioxidant compositions containing organic compounds such as oxygen
D21C11/00	Regeneration of pulp liquors
D21H11/00	Pulp or paper, comprising cellulose or lignocellulose fibers of natural origin only

3. Patent Evaluation

3.1. Materials and Methods

The properties of lignin materials differ greatly depending on the lignocellulosic feedstock (e.g., hardwoods, softwoods, annual plants, etc.), and the method used to isolate them from other biomass components, for which several processes have been suggested (Figure 1). Through the US9347177B2 patent, the inventors described and claimed a method for producing lignin materials from softwoods that have a specific content of aliphatic hydroxyl groups, resulting in a product with a predictable level of antioxidant activity. The claimed method includes pulping the fibrous biomass, heating the biomass, isolating the lignin-rich material from the cellulosic pulp, and recovering lignin derivatives that have an aliphatic hydroxyl content ranging from 2.5 to 7 mmol.g^{-1}.

The invention was based on the principles of the organosolv pulping processes for obtaining lignin derivatives with specific characteristics from softwoods. The inventors proposed, at first, different values of pulping conditions, including temperature and pressure, which can vary between 100–300 °C and 5–150 atm, respectively, under a reaction duration that varies between 1 and 300 min. Furthermore, the pH of the pulp liquor can vary between 1.5 and 5.5. Furthermore, the liquor-to-biomass weight ratio may take different values, such as 5:1–15:1, 5.5:1–10:1, and 6:1–8:1. Therefore, the adopted method at the end allows the pulping of the biomass feedstock with an aqueous solution of an organic solvent (30% w/w or greater). The obtained liquor shows a pH value of 1–5.5. It was then heated to about 100 °C or greater. Simultaneously, the pressure of the reaction medium was raised to about 5 atm or greater. These conditions were maintained for one minute or longer, in order to separate the biomass feedstock constituents and recover the derivatives of native lignin.

In order to prove the concept of the invention, recovery of the lignin derivatives was carried out from three softwood species, including hybrid spruce trees, radiata pine, and loblolly pine grown in Canada, Chile, and the United States, respectively. A total of four samples of each softwood biomass feedstock were treated using an acid-catalyzed ethanol organosolv pulping process under different conditions (Table 2).

After pulping, the isolation of the lignin derivatives was performed as follows: first, the liquor was separated from the solids by pressing the pulped materials in a press to squeeze out the liquid. The resulting liquor was then filtered through a coarse silk screen to separate the chip residue from the liquor stream. Thereafter, the liquor stream was filtered through fine filter paper to recover the lignin derivatives that are referred to as self-precipitated lignin derivatives (SPL). However, another part of these materials still remaining in the filtered liquor is thus precipitated through dilution with cold water; this is referred to as precipitated lignin (PL). The relative yield of each lignin derivative was determined in reference to its original lignin (i.e., the sum of acid-insoluble lignin and acid-soluble lignin), and the PL yield (% w/w) was calculated for each sample.

Table 2. Pulping conditions for the three softwood species at a 6:1 liquor-to-wood weight ratio.

Softwood Species	pH	Sulfuric Acid (% *w/w*)	Time (min)	Temperature (°C)	Ethanol (% *w/w*)
Hybrid spruce trees	1.81–2.18	0.9–2.5	33–55	175–184	47–78
Radiata pine	1.92–2.63	0.23–1.9	33–110	179–194	44–61
Loblolly pine	1.83–3.2	0.13–2.1	39–79	170–199	42–73

3.2. Results and Discussion

Benefiting from the chemical structure of the obtained lignin derivatives, including phenolic and aliphatic hydroxyl content, they can be exploited in various polymer compositions. They can comprise, in addition to the lignin derivatives, a polymer-forming component and other ingredients such as adhesion promoters, dispersants, fillers and extender, fire and flame retardants, stabilizers, ultraviolet light absorbers, and viscosity regulators. Based on the results, the inventors confirmed that the recovered lignin derivatives may have an aliphatic hydroxyl content of 2.5–7 mmol.g^{-1}, a phenolic hydroxyl content of 2–8 mmol.g^{-1}, a molecular weight that varies in the range of 200–4000 g.mol^{-1}, and any suitable polydispersity of 1–5. These features are correlated to the antioxidant capacity of lignin derivatives, which has been evaluated by the Radical Scavenging Index (RSI) by using the 2,2-diphenyl-1-picrylhydrazyl (DPPH) assay. The inventors confirmed through the invention that the normalized RSI (NRSI) value can range from 5 to 40.

3.2.1. Hybrid Spruce Trees

For the hybrid spruce wood chips, the yield of PL lignin derivatives varies in the range of 40.42−71.84%, for which the content of the aliphatic hydroxyl groups was assessed, ranging from 2.60 mmol.g^{-1} (sample 1) to 3.04 mmol.g^{-1} (sample 4). In addition, the antioxidant activity of the analyzed PL lignin derivatives was evaluated by measuring their radical scavenging capacity. For the hybrid spruce trees, the NRSI values vary in the range of 26.23−30.64 (Table 3).

Table 3. Pulping conditions for different wood chip samples at 6:1 liquor-to-wood weight ratio and characterization of the precipitated lignin.

Samples	Hybrid Spruce Trees				Radiata Pine				Loblolly Pine			
	1	2	3	4	1	2	3	4	1	2	3	4
pH	1.95	2.18	1.81	2.12	1.92	2.23	2.5	2.63	1.83	2.52	2.5	3.2
Sulfuric acid (% w/w)	1.9	0.9	2.5	1.2	1.9	0.9	0.47	0.23	2.1	0.35	0.38	0.13
Time (min)	33	55	36	41	33	55	57	110	39	79	73	53
Temperature (°C)	179	184	175	181	179	184	194	191	170	198	189	199
Ethanol (% w/w)	57	47	78	68	57	47	61	44	46	42	54	73
PL yield (% w/w)	63.89	40.42	71.84	70.59	48.76	38	48.55	27.01	29.8	16.4	39.3	23.3
Aliphatic hydroxyl contents (mmol.g^{-1})	2.60	2.66	2.75	3.04	2.80	3.31	3.66	3.78	2.65	2.90	3.42	3.81
NRSI	27.43	28.15	26.23	30.64	36.97	28.28	27.19	29.76	27.78	27.95	27.78	24.56

3.2.2. Radiata Pine Wood

As seen in Table 3, the yield of PL lignin derivatives of radiata pine wood chips is lower than that of the previously mentioned hybrid spruce wood chip samples. It varies between 27.01% and 48.76%, for which the aliphatic hydroxyl content of each sample was determined. These contents ranged from 2.80 mmol.g^{-1} (sample 1) to 3.78 mmol.g^{-1} (sample 4). The antioxidant activity was also evaluated and showed NRSI values ranging from 27.19 to 36.97.

3.2.3. Loblolly Pine Wood Chips

For this material, the yield of PL lignin derivatives varies between 16.4% and 39.3%, for which the aliphatic hydroxyl content ranged from about 2.65 mmol.g^{-1} (sample 1) to 3.81 mmol.g^{-1} (sample 4). In addition, the NRSI value showed low variety in the range of 24.56 to 27.95 (Table 3).

4. Conclusions

Lignin has gained huge interest due to its attractive properties such as its biodegradability, non-toxicity, sustainability, and antimicrobial and antioxidant properties. Through the US9347177B2 patent, the inventors have successfully validated a method for the production of lignin derivatives from softwood species with a specific amount of aliphatic hydroxyl groups, which is correlated to the antioxidant property. Based on patent classification, the invention covered by the patent concerns the processes of treating or compounding macromolecular substances and compositions of lignin-containing materials, as well as lignin and products derived therefrom. The proposed method, which is based on the principles of the organosolv pulping processes, was used to obtain derivatives of native lignin from hybrid spruce trees, radiata pine, and loblolly pine, resulting in a high yield of lignin derivatives with significant antioxidant activity. The stable antioxidant activity of these recovered lignin derivatives may be advantageous when formulating such compositions, making these materials highly desired for wide applications, including, among other things, nutritional supplements, inks, pigments, surfactants, oils, films, coatings, and adhesives.

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Conflicts of Interest: The authors declare that they have no conflict of interest.

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