A Perspective of Lignin Processing and Utilization Technologies for Composites and Plastics with Emphasis on Technical and Market Trends

Marcel Kropat, Mochen Liao, Hyeonji Park, Khandoker S. Salem, Shelly Johnson, and Dimitris S. Argyropoulos *

This effort is focused on work completed publicly and privately within academic research and industrial sectors on the utilization of lignin to produce thermosets, thermoplastics, foams, hydrogels, and rubbers. The size of the plastics market and the current and projected influence of lignin on it were evaluated. Further, an analysis of patent activity was employed to show the direction of and interest for lignin in these markets. The market trends documented in the literature, when coupled with detailed patent research, offer a new approach to evaluate potential markets and future directions. The analysis of the commercial market sizes of bioplastics and segmentation showed low penetration of actual lignin-based bioplastics. This exposed the contradiction between the abundance of technologies for lignin-based materials and their little practical use. In addition, this finding highlighted a severe gap between lignin research and development and the actual market.

*Contact information: Department of Forest Biomaterials, North Carolina State University, 2820 Faucette Drive, Raleigh, North Carolina, 27606, USA; *Corresponding author: dsargyro@ncsu.edu*

INTRODUCTION

Global environmental awareness and sustainability efforts have gained momentum, which has increased the need for environmentally friendly primary resources for chemicals, materials, and energy. Thus, the concept of biorefinery has stemmed from the research and development of biomass products to tackle such key societal and technological challenges (Passoni *et al.* 2016). International Energy Agency Task 42 coined a formal definition for biorefinery as "the sustainable processing of biomass into a spectrum of bio-based products (food, feed, chemicals, and/or materials) and bioenergy (biofuels, power, and/or heat)" (Jungmeier *et al.* 2015). Biorefinery can be a concept, a facility, a process, a plant, or even a cluster of facilities that provide a sustainable approach to valuable products. It can improve biomass processing economics and environmental impact (*e.g.*, greenhouse gas savings) if a fully integrated concept is developed.

Among the various products of biorefinery, lignin is an indispensable and valuable component. Both renewable energy and renewable chemical practices must be adopted for a sustainable economy based on biorefineries. However, due to the current low price of oil, biorefineries require improved profitability to compete with fossil fuels. This can be accomplished by manufacturing diversified products and effectively utilizing byproducts for materials applications (Ho *et al.* 2018). Petroleum-based chemicals have been the primary feedstock for the production of commodity plastics since the 1940s. Due to limited

petroleum resources, the focus has shifted towards the identification of renewable feedstocks as substitutes for the currently used non-renewable petroleum-based materials.

In an effort to increase sustainability, the U.S. Department of Energy and the U.S. Department of Agriculture are strongly committed to expanding the role of biomass for the energy and chemical industry. An increase in the proportion of commodity chemicals and materials made from renewable feedstocks from 5% in 2005 to 25% in 2030 is predicted (Perlack *et al.* 2005). Lignocellulosic biomass can be utilized for a variety of different materials, such as chemicals and biofuels, and it is the most accessible renewable carbon-based feedstock (Upton and Kasko 2016).

The three main components of lignocellulosic biomass are cellulose, hemicellulose, and lignin, whereby the mass percent composition is dependent on the plant species. Cellulose, a polymer of glucose, incorporates 30% to 50% of the biomass. Hemicellulose, a heteropolymer of various monosaccharides, represents a smaller portion of 20% to 35%. The remaining 15% to 30% of the lignocellulosic biomass consists of lignin. Lignin is a cross-linked heteropolymer that promotes structural integrity in the bio-composite. The aromatic-based amorphous polymer consists of various phenyl propane units linked by carbon-carbon and ether bonds. As the second most abundant natural polymer, lignin accounts for approximately 30% of organic carbon in the biosphere. According to Tuck *et al.* (2012), as lignin is the only scalable renewable feedstock composed of aromatic units, it is highly underutilized. In 2010, only 2% of the 50 million tons of lignin produced in pulp- and papermaking processes was utilized for specialty products. The largest proportion (48%) was used as low-value fuel (Upton and Kasko 2016). This underutilization indicates a need to develop processes to efficiently isolate lignin from biomass and engineer lignin-based products with increased commercial value.

However, the purity and consistency of the products obtained from petroleum-based starting materials are redeeming qualities. Though lignin is a bio-based product that contributes to more renewable and sustainable products, its heterogeneity is a major technical drawback. Furthermore, the established infrastructure and favorable economics of petrochemical feedstocks inhibit the ability of lignin to be considered as a viable substitute. In this analysis, the patent search and subsequent market analyses were solely based on lignin and current commodity polymers. Overall, this work did not examine the uses of lignin as direct replacement molecules (of monomeric or oligomeric nature as would be derived by catalytic lignin degradation approaches). Further, this approach, if technically and economically resolved, could be a substantial contributing factor to the emergence of "lignin-to-polymer" products.

To comprehensively explore these issues, this review examined the various stages of development in using lignin in different polymer markets, which included the full range from laboratory-scale to industrial, commercial, and market considerations.

LIGNIN PRODUCTION AND MODIFICATION

Current Production of Lignin

The heterogeneity of lignin offers extreme difficulties for technical processes that require a uniform lignin product (Argyropoulos 2014). For example, polymerization processes often require precise stoichiometry that cannot be met by "unrefined" technical lignins. This can be attributed to the fact that the pulping processes are aimed at creating paper or other products, not lignin. The use of a variety of feedstocks, process conditions,

bioresources.com

manufacturing processes, and pulping sequences, *etc.*, tends to deliver heterogeneous lignin products (Cui *et al.* 2014). This is further compounded by the fact that the delignification statistics cause the inherent production of lignin fragments, whose molecular weights and distributions (M_w/M_n) are governed by the Flory-Stockmayer equations that contain critical exponents. Such exponential processes are very hard to precisely control (Argyropoulos and Bolker 1987a,b,c). This situation results in tremendous structural, polymeric, and functional group variations that need to be addressed prior to any successful implementation of value-added processes with lignin. In this respect, one may cite a variety of efforts of lignin utilization within the confines of the enumerated variations (Pan *et al.* 2013; Du *et al.* 2014; Duval and Lawoko 2014; Laurichesse and Avérous 2014; Thakur *et al.* 2014; Mendis *et al.* 2015; Kun and Pukánszky 2017; Tribot *et al.* 2019). However, recently, a welcome review has appeared in the literature that precisely addresses the various fractionation processes available (Gigli and Crestini 2020).

Because lignin is a major bio-based aromatic material, its importance and relevance to the petrochemical-based industrial economy are immense. Most valorized lignins include materials produced from the following processes: lignosulfonate, kraft, organosolv, and soda. Other methods include steam explosion and processes using various catalysts, which are called catalytic processes. The first step in isolating lignin from the native biomass is delignification, which involves the separation of the lignin from the cellulose, hemicellulose, and extractives. After delignification, the modification or lignin fractionation stage follows. Each pathway in a process influences the quality and purity of the lignin product. The following sections of the review summarize the delignification and the ensuing modification stages.

Delignification

The delignification stage is used to separate lignin from the other biomass components, which are mainly cellulose and hemicellulose. The pulp and paper and bioethanol industries are large-scale operations that use commercially proven techniques. The delignification methods differ based on the active species and process conditions used. The soda and kraft processes each treat the biomass at high temperatures (ranging from 155 °C to 175 °C) for up to 5 h under basic conditions (OH^-) for the soda process and a combination of OH^- and SH^- nucleophiles for the kraft process. The sulfite process operates under reaction times and temperatures similar to the soda and kraft processes but under acidic conditions using acid bisulfite or bisulfite as the reactants. Steam explosion is a process that treats the biomass with steam before explosively decompressing the biomass/steam mixture. Finally, the organosolv process uses polar solvents, such as ethanol, methanol, formic acid, and/or acetic acid, at elevated temperatures. Common to all methods is the final lignin precipitation stage. Each of these processes results in an extracted lignin product with a large variety of average molecular weights, polydispersity indices (PDI = M_w/M_n), and functional groups depending on the nature and the intensity of the delignification process applied, which exemplifies various heterogeneity concerns (Argyropoulos 2014; Cui *et al.* 2014).

Chemical Modification of Lignin

Various lignin modification stages have been proposed and mainly developed to address its compatibility with synthetic polymers *via* improving the mechanical and thermal stability characteristics (Figueiredo *et al.* 2018). Such lignins have seen utilization

as fuels (Wang *et al.* 2015; Cheng and Brewer 2017), fuel additives (Chuck *et al.* 2013; Ogunkoya *et al.* 2015), chemicals (Schutyser *et al.* 2018), and polymers (Pan *et al.* 2013; Su *et al.* 2013; Mendis *et al.* 2015).

The functional groups of lignin (hydroxyl, methoxyl, carbonyl, carboxyl groups, *etc.*) are usually targeted to create various lignin derivatives. The precise modification is generally decided depending on the intended application, the reactivity of the functional groups, and the type of lignin used in the reaction. The chemical modification of lignin usually offers enhanced solubility for the modified lignin in organic solvents, makes the lignin production process more straightforward, and decreases the brittleness of the polymer with lignin. Therefore, lignin has emerged as a possible precursor to a variety of polymer applications, including higher value end uses. Chemistries that can be applied to lignin are, among others, methylolation (hydroxymethylation), demethylation, amination, and phenolation (Gonçalves and Benar 2001; Zhang *et al.* 2013). Sulfomethylation is the means by which methyl sulfonate groups are attached to lignin using a variety of pH and temperature levels and/or reactants (Konduri and Fatehi 2015; Chen *et al.* 2019). Depending on the conditions, the solubility of the sulfomethylated lignins in water is controlled. For example, such lignins have been applied to cement admixtures as a dispersant by Huang *et al.* (2018). A mixture of formaldehyde and sodium sulfite was used to generate sodium hydroxymethylsulfonate, the reactive reagent for the sulfomethylation.

Amination uses the Mannich reaction, which is a relatively simple and straight-forward reaction among the possible lignin modification reactions. The amination of lignin can be achieved under acidic, neutral, or alkaline conditions (Matsushita and Yasuda 2003; Du *et al.* 2014; Wang *et al.* 2016; Wang *et al.* 2018; Jiao *et al.* 2019). Depending on the actual conditions, the reaction can either occur between the deprotonated phenolic lignin and the used N,N-dialkylated amine alcohol or between the phenolic lignin and the iminium ion. Aminated lignins are developed for use as emulsifiers or surfactants (Figueiredo *et al.* 2018).

There is a relative abundance of phenolic and aliphatic hydroxyl groups within the various technical lignins. Substitution reactions using these groups is another major method used to modify technical lignins to obtain lignin polyol derivatives. Esterification is a facile and simple reaction that allows the formation of lignin macromolecular forms of lignin-based polyesters (Duval and Lawoko 2014). Esterification can be carried out by ring-opening reactions, condensation, or dehydration polymerization chemistries. In addition, epichlorohydrin or alkylene oxides have been co-polymerized with lignin. Lignin alkylation (Liu and Li 2006) is another type of modification that uses reactants, such as diazoalkanes and alkylsulfates, in the presence of sodium hydroxide. The phenolation of lignin is among the most widely examined reactions used to replace phenol with technical lignin (Tan 1996; Effendi *et al.* 2008). Phenolation is used to increase the reactivity of lignin for a variety of applications. Lignin is reacted with phenol under acidic conditions, resulting in the condensation of phenol with lignin side chains. The increase in phenolic hydroxyl groups as well as the readily available reactive sites lead to an improvement of the reactivity of the molecules (Jiang *et al.* 2018). Lignosulfonates and kraft lignin are commonly investigated lignin starting materials to which phenolation is applied. Efforts to remove methyl groups from the methoxyl substituents in the aromatic rings of lignin to create demethylated lignins have also appeared in the literature (Duval and Lawoko 2014; Laurichesse and Avérous 2014).

Lignin Applications

Lignin-derived thermoplastics

Thermoplastics are polymers that can be liquefied *via* melting and then reversibly cooled for multiple cycles without notable effects on their inherent properties. Thermoplastic material is composed of polymer chains that are associated *via* noncovalent intermolecular forces. Thus, these materials offer low melt viscosities, excellent processing ability, good thermal stability (at processing temperatures and sometimes at operating temperatures), and robust mechanical properties (Mendis *et al.* 2015; Upton and Kasko 2016).

Lignin-based thermoplastic materials have shown improved processing abilities and recyclability compared to lignin-based thermosetting polymer networks (Wang *et al.* 2016). As such, they have gained increased interest as sustainable, cost-effective, and biodegradable alternatives for petroleum-based thermoplastics. However, lignin has a high glass-transition temperature (T_g) and undergoes radical-induced self-condensation at high temperatures (Pouteau *et al.* 2004; Sadeghifar *et al.* 2012; Sadeghifar and Argyropoulos 2015), which limits its thermal processing ability and eventually hinders the development of high-performance thermoplastic materials. To address these issues, plasticizers or compatible polymers with low T_g values have been added to lignin *via* blending or chemical modification.

Presently, lignin or its derivatives are blended or mixed with different thermoplastic polymers to prepare lignin-based thermoplastic materials. The most commonly used thermoplastic polymers are polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polyacrylonitrile (PAN), polymethylmethacrylate (PMMA), polyvinyl alcohol (PVA), ethylene-vinyl acetate copolymer (EVA), polyester, starch, and protein (de Chirico *et al.* 2003; Pouteau *et al.* 2003, 2004; Liu and Li 2006; Mu *et al.* 2009; Hu *et al.* 2011; Mansouri *et al.* 2011; Barzegari *et al.* 2012; Huo *et al.* 2012; da Silva *et al.* 2013; Thakur *et al.* 2014; Domínguez-Robles *et al.* 2018). Most thermoplastics are prepared using melt-mixing and solution-mixing techniques at temperatures of approximately 170 °C to 210 °C. To produce thermoplastics with melt-mixing, the standard methods used are extrusion, compression, injection, and blow-molding. In contrast, melt-mixing uses casting molding techniques. However, lignin/polyolefin thermoplastic composites are brittle materials with relatively high T_g values with the polar groups in lignin, which limit their compatibility within the nonpolar polyolefin matrix. Plasticizers used in melt-mixing are usually applied during blending with the goal of increasing the interactions on the interfaces of the blended polymers, decreasing micro-phase separation within the composite, and improving the performance of such composite materials (Su *et al.* 2013). Bouajila *et al.* (2006) reported that hydrogen bond forming molecules are suitable plasticizers for dry lignin and that aromatic molecules with a structure similar to monolignols (*e.g.*, vanillin) are more appropriate for hydrated lignin (Gandini *et al.* 2002). In addition, the mechanical properties of lignin-based thermoplastics can be improved using polymer blending techniques (Wang *et al.* 2016). Few polymers are miscible with lignin through hydrogen bonding and acid-base interactions. Miscibility effects depend on the lignin content, as phase separation occurs at high lignin contents (Nahmany and Melman 2004; Effendi *et al.* 2008). Lignin/polyester composite systems, in contrast to other materials, display improved compatibility and overall performance due to the formation of hydrogen bonds between the carbonyl groups of the polyester matrix and the hydroxyl groups of the lignin (Canetti and Bertini 2007, 2009). Lignin can also be incorporated into thermoplastics and composites as a filler. The presence of its aromatic

moieties improves the antioxidant, flame retardant, and (some) mechanical properties of the ensuing materials; further, water resistance and thermal stabililty are improved (de Chirico *et al.* 2003; Pouteau *et al.* 2003; Košíková *et al.* 2007; Ago *et al.* 2012; Barzegari *et al.* 2012). However, some of the observed improvements (*i.e.*, enhanced thermal stability) depend on the improved miscibility of lignin with various polymers. The compatibility of lignin-thermoplastic blends could be easily improved by selecting a suitable structure of the polymer matrix in conjunction with the mixing technique. Further, the compatibility of lignin-based thermoplastics depends on the hydrogen-bonding interactions between the hydroxyls of lignin and thermoplastic polymers. It varies with the abundance of the different aromatic and aliphatic hydroxyl groups in lignin. Better compatibility can be obtained through modification of the macromolecules to create new active chemical sites *via* methods such as alkylation (Liu and Li 2006), hydroxyalkylation (Mu *et al.* 2009; Hu *et al.* 2011; Mansouri *et al.* 2011; da Silva *et al.* 2013), amination (Huo *et al.* 2012), and nitration (Huang and Zhang 2002). Furthermore, the compatibility can be improved by selective masking of the reactive hydroxyl groups in lignin by different chemical modification methods, such as esterification (Gandini *et al.* 2002; Nahmany and Melman 2004), phenolation (Tan 1996; Effendi *et al.* 2008), etherification (da Silva *et al.* 2009; Ahvazi *et al.* 2011; Sadeghifar *et al.* 2012), urethane formation (da Silva *et al.* 2009; Hatakeyama *et al.* 2013), polymer grafting (Kim and Kadla 2010; Wang *et al.* 2011), and copolymerization (Gao *et al.* 2012; Cinelli *et al.* 2013; Laurichesse and Avérous 2014). Recently, specific molecular weight fractions of kraft lignin have been shown to offer beneficial melt, thermal stability (Sadeghifar and Argyropoulos 2016), and antioxidant characteristics (Sadeghifar and Argyropoulos 2015) for blends with polyethylene, which has opened novel utilization possibilities.

Lignin-derived thermosets

Thermosets are three-dimensional cross-linked polymeric materials formed *via* a polyfunctional polymerization (curing) process of reactive resins. Usually, before curing, the components are of lower viscosity than thermoplastics, which makes such systems ideal for the creation of fiber-reinforced composites. Due to its highly branched structure and its large number of functional groups, lignin appears to be a suitable bio-based component for resin formulations of thermosets and thermoset composite materials. In particular, for phenol-formaldehyde (PF), polyurethane (PU), and epoxy (EP) resin systems, lignin may act as a reinforcement and/or a possible replacement of petroleum-based resources. The preparation of lignin-based thermosets follows two general approaches. In one method, lignin is chemically modified to enhance its reactivity. Such lignin materials can be utilized to partially substitute conventional resin components or act as a reactive components, such as toughening or curing agents, in resin systems. Among other methods, chemical modification is typically accomplished by esterification (de Oliveira and Glasser 1994; Hirose *et al.* 2002; Matsushita *et al.* 2011; Chung *et al.* 2013), phenolation (Nimz 1969; Gierer and Pettersson 1977; Kratzl and Oburger 1980; Tan 1996; Lin *et al.* 2001; Effendi *et al.* 2008), and oxypropylation (Nadji *et al.* 2005; Cateto *et al.* 2009; Sadeghifar *et al.* 2012). In another approach, petroleum-derived components are partially substituted with crude lignin. However, due to the polarity of the lignin units and the resulting self-interactions, the degree of substitution is limited. High substitution rates with crude lignin result in the compounded bioplastic exhibiting poor mechanical properties (Laurichesse and Avérous 2014; Kun and Pukánszky 2017). Both approaches are partial solutions, as the conventional petroleum-based components are not entirely substituted. Detailed

bioresources.com

reviews have been conducted on the topic of lignin-derived thermosets and are highly recommended for further reading (Feldman 2002; Lora and Glasser 2002; Matsushita and Yasuda 2003; Raquez *et al.* 2010; Sen *et al.* 2015; Ma *et al.* 2016; Wang *et al.* 2016; Kun and Pukánszky 2017).

Phenolic resins

Phenolic resins (PF-resins) are well known for their dynamic stability and water resistant, chemical resistant, and electrical insulating characteristics. Typical applications for PF-resins are coatings, adhesives, and molded products. These resins are produced either in acidic or basic media (Olivares *et al.* 1988; Gardziella *et al.* 2000; Sen *et al.* 2015). The synthesis of PF-resins occurs *via* the reaction of formaldehyde with the ortho- and para- positions of phenol. The result is a three-dimensional, cross-linked network (Duval and Lawoko 2014). For a reaction with formaldehyde to occur, at least one of the ortho-groups of the lignin-monomers must be unsubstituted (Sen *et al.* 2015).

Due to the similar chemical structures of polyphenolic lignin and phenol, the use of lignin to prepare phenolic resins has been extensively examined, and the topic has been subjected to numerous literature reviews (Wang *et al.* 1992; Belgacem and Gandini 2008; Lora 2008; Doherty *et al.* 2011; Duval and Lawoko 2014). The need for low-cost adhesives of reliable supply and durability is a driving factor for the substitution of phenolic components with different lignin types. Primary application targets for these lignin-based phenolic resins are composites, adhesives, insulation, lamination, wood bonding, molded parts, and plywood-adhesives (Barrett 2018). The degree of substitution in phenolic resin systems by crude lignin is limited, as the deterioration of the properties is proportional to the amount of lignin substituted. As a result, recent research has mainly focused on purified, functionalized, and fractionated lignins with higher reactivity for application in phenolic resin systems (Kun and Pukánszky 2017). Even with modified lignin, the substitution rate of classic phenols in the industrial-scale production of lignin-based PF-resins is limited. However, UPM recently announced a 100% lignin-based phenolic resin (Wisa BioBond) that is produced on a commercial scale (Barrett 2018).

Epoxy resins

Epoxy resins account for 70% of the global production of thermosets (Ma *et al.* 2016). Approximately 90% of epoxy precursors use bisphenol A and epichlorohydrin. However, bisphenol A is an environmentally hazardous molecule, as it can cause cancer, infertility, and impotence, and it has been reported to be hazardous to young children and infants (Asada *et al.* 2015). The use of bisphenol A in materials that come into contact with food has been banned in several countries, and the use of non-toxic, renewable alternative resources is under serious consideration (US FDA 2010; Flint *et al.* 2012). The production of epoxy precursors based on renewable resources, such as lignin, has been reported and accordingly reviewed (Duval and Lawoko 2014; Thakur *et al.* 2014; Sen *et al.* 2015; Ma *et al.* 2016; Sun *et al.* 2018). Modified lignins can be used as both the epoxy component and the curing agent for the synthesis of epoxy resins. However, due to its high molecular weight, crude lignin is not suitable as an epoxy component alone. The resulting epoxy resins from crude lignin are usually characterized by low curing reactivity and unstable properties due to the complex structure and the low mobility of the macromolecules.

Further, the compatibility of crude lignin with curing agents is rather low (Hofmann and Glasser 1993, 1994). However, lignin derivatives of a relatively low molecular weight and enhanced reactivity are currently a prominent feedstock for epoxy resins (Ma *et al.*

bioresources.com

2016). The epoxidation of lignin is performed by reacting its hydroxyl groups with epichlorohydrin, which is followed by epoxide ring closure in alkaline media. The created lignin epoxides are then mixed with curing agents, which causes cross-linking of the resin components. Curing agents contain reactive hydrogen atoms in the form of an amine, anhydride, carboxyl, or hydroxyl groups. Notably, unmodified lignins can also be adequate curing agents without chemical modification, as they contain carboxyl and hydroxyl groups (Kun and Pukánszky 2017).

Polyurethanes and foams

Polyurethanes (PU) are synthesized *via* the reaction of di- or poly-isocyanates and polyols that possess terminal hydroxyl groups (Engels *et al.* 2013). As lignin contains many phenolic and aliphatic hydroxyl functionalities, it can be used to replace the polyol component of polyurethanes (Zhang *et al.* 2015). Lignin-based PUs are more biodegradable than petroleum-based PUs (Cateto *et al.* 2014; Hu *et al.* 2014). Both the aliphatic and phenolic hydroxyl groups of lignin react with an aliphatic isocyanate to form polyurethanes with low T_g (Gandini *et al.* 2002; Bonini *et al.* 2005). However, high molecular weight polyurethane can be produced by controlling the feedstock (kraft, alcoholysis, lignosulfonate, or solvolysis lignin), polyols (PEG or PPG), polymeric methyl-diisocyante, reaction time, and temperature (Thring *et al.* 1997; Hu 2002; Duong *et al.* 2014). However, lignin content was found to be the dominant determinant of material properties over other factors, such as the molecular weight of the polyols, whereas the ratio of isocyanate to hydroxyl groups influenced the tensile properties to some extent and improved the thermal stability (Thring *et al.* 1997; Vanderlaan and Thring 1998; Pohjanlehto *et al.* 2014). Lignin-based rigid and flexible bio-foams have been prepared with better thermal conductivity than traditional fossil-feedstock-based polyurethanes due to their larger cell size and lower density.

Lignin is often functionalized to generate new active sites and to improve its chemical structure, which increases its solubility in organic solvents and improves its processing ability and reactivity. A particularly straightforward functionalization approach was reported by Chung and Washburn (2012). The authors demethylated the lignin with Lewis acid catalysts and generated 28% more hydroxyl groups, which produced polyurethanes with significantly improved cross-link densities (Chung and Washburn 2012). Esterification is another simple method that has been used to produce esterified lignin. These esterified lignins can generate lignin-oleic acid-based polyols that form polyurethanes with relatively low T_gs when reacted with polyisocyanates (Laurichesse *et al.* 2014). Further, the hydroxyl groups of lignin have been functionalized to develop rigid polyurethane foams with comparable insulating and physical properties to those derived from petroleum-based products (Nadji *et al.* 2005). The water solubility and durability of polyurethane products can be improved using the Mannich reaction, which introduces an amine group in the lignin structure using formaldehyde and a primary or secondary amine or ammonia (Liu *et al.* 2013). The development of lignin-based phosphate melamine polyurethanes has also been reported, as they showed improved compression strength, thermal stability, char residue formation, and self-extinguishment (*i.e.*, flame retardancy) (Zhu *et al.* 2014).

Overall, lignin-based polyurethanes have tremendous potential as commodity materials because they display promising (and many times better) physical properties than their petroleum-based counterparts. However, the properties of lignin-based materials can vary due to the batch to batch variability of technical lignins. This is an important drawback

that necessitates the development of processes that offer consistent lignin products. Lignin fractionation is such a process that may provide lignin fractions with tunable and coherent specifications and properties to the end users before entering the market (Argyropoulos 2014; Cui *et al.* 2014).

Hydrogels

Hydrogels are typically polymeric materials that can absorb water, which results in distinct swelling due to the onset of osmotic pressure within them (Passauer 2012). Acrylic acid has been used as a substantial component of commercial hydrogels. Many research efforts have been carried out on the use of biomaterials to create hydrogels. Lignin has been considered a potential source for hydrogel formation, which is mainly due to its documented biodegradability (Thakur *et al.* 2014; Collins *et al.* 2019; Meng *et al.* 2019). The topic of lignin-based hydrogels has been reviewed by several authors who investigated specific applications, such as water purification (Thakur *et al.* 2017), tissue engineering (Figueiredo *et al.* 2018; Witzler *et al.* 2018), biomedicine (Witzler *et al.* 2018), and biosensors or electrodes (Meng *et al.* 2019). Water purification aims to remove pollutants and ions from water, and lignin-based hydrogels are a promising resource in this area (Thakur *et al.* 2017). Lignosulfonate-based graphene hydrogels are composed of a highly porous structure and high specific surface area that has been reported to be able to capture Pb^{2+} with good endurance and reusability (82% adsorption efficiency after 10 cycles) (Li *et al.* 2016). Cellulose-lignin composite hydrogels and bentonite/sodium lignosulfonate/ acrylamide/maleic anhydride hydrogels were also used to adsorb Pb^{2+}. Lignosulfonate-grafted-acyclic acid-based hydrogels have also been examined for the adsorption of dyes in water (Thakur *et al.* 2017). Though excellent chelating performance was observed, the presence of bubbles within the hydrogel, due to entraining air during stirring, was problematic for its transparency. Lignin sulfonate-based mesoporous materials were found to address this problem with improved chelating efficiencies. Overall, Thakur *et al.* (2017) conclude that because lignins have shown promises in this area, technologies to produce quality lignin feedstocks are needed to promote interest in lignin-based hydrogels for the removal of pollutants from water (Thakur *et al.* 2017).

Another proposed use of lignin-based hydrogels was demonstrated by Figueiredo *et al.* (2018), who examined the use of lignin-based hydrogels for tissue engineering and found that operating temperature was a determinant of their functionality. Temperature-induced gelation transitions (thermo-gelation) is a material behavior that occurs at temperatures lower than that of the human body and higher than room temperature. Atom transfer radical polymerization (ATRP) techniques, in which lignin is used as a core, have been developed to make a temperature-sensitive lignin-based hydrogel (Figueiredo *et al.* 2018). Furthermore, Xu *et al.* (2018) created lignin-based hydrogels using three-dimensional printing techniques for various biomedical applications. The authors claimed that lignin has a high potential for use in applications such as cell adhesion using direct ink writing techniques (Xu *et al.* 2018). Notably, several lignin derivatives, including agarose-lignin hydrogels with epichlorohydrin as the cross-linker, have been developed in steam-cell-based tissue engineering (Witzler *et al.* 2018). Overall, Witzler *et al.* (2018) state that value-added lignin applications are currently of increased interest due to the fact that lignin-based hydrogels show considerable promise for the controlled or sustained release of pharmaceuticals (Witzler *et al.* 2018).

Meng *et al.* (2019) classified the various areas of lignin-based hydrogels into four applications: absorption, controlled release, stimuli-responsive, and biosensors and electrodes. The preparation of lignin-based hydrogels towards biosensor application was conducted by copolymerization of organosolv lignin, lignosulphonates, and kraft lignin with poly(propylene oxide), blended with multiwall carbon nanotubes (Meng *et al.* 2019).

To enable the hydrogel to display conductivity, the lignin was modified with cations using ethyltrimethyl ammonium chloride. Graphene and lignosulfonate composites have also been introduced as metal-free supercapacitors (Li *et al.* 2017). Lignosulfonates have been reported to increase conductivity considerations in such hydrogels when compared to pure graphene hydrogels. Single-wall carbon nanotubes were also combined with lignosulfonates to display pressure-sensitive characteristics (Peng *et al.* 2018). The cited authors emphasize that lignin offers good possibilities for the creation of novel hydrogels, but the synthesis routes need to be improved in terms of simplicity, eco-friendliness, and efficiency.

Rubbers

Rubber is a vulcanized heterogeneous material, the property characteristics of which rely heavily on its reinforcement and binding components. Carbon black is the typical reinforcing agent used in rubbers, but lignin could potentially replace it. Such a replacement assumes that the added lignin will be of acceptable uniformity to offer economical and consistent reinforcement characteristics within stringent specifications (Kakroodi and Sain 2016).

The literature contains abundant accounts and reviews that demonstrate the beneficial effects of lignin on the mechanical and other properties of rubbers (Košíková *et al.* 2007; Bova *et al.* 2016; Datta *et al.* 2017) with possible commercial ramifications (Bova *et al.* 2016). For example, Košíková *et al.* (2007) conclude that the role of lignin in rubbers is both that of a strengthening and reinforcing agent and a thermal stabilizer (Košíková and Gregorová 2005; Košíková *et al.* 2007). Other efforts have also accounted for the resistance of lignin-containing vulcanized natural rubber against thermo-oxidative degradation effects (Barana *et al.* 2016). The work of Wang *et al.* (2018) with industrial alkali lignin reported that, when blended with carbon black, a lignin-rubber elastomer was produced with processing energy savings and notable benefits in the mechanical properties of the elastomer.

The miscibility of the lignin with various polymeric components within the rubber is of great importance in this area because such miscibility and compatibility considerations have a profound effect on the interaction between the various polymeric components, which is eventually reflected in the mechanical properties of the blend (Wang *et al.* 2018). Tran *et al.* (2016) attempted to enhance the miscibility of lignin in rubber composites and showed that improvements could be realized by using a fractionated melt-stable lignin (Tran *et al.* 2016). In addition, Yu *et al.* (2016) attempted to enhance the miscibility of lignin in rubber compounds with a fine dispersion of lignin by utilizing latex-compounding methods. Efforts to fundamentally understand and validate these considerations led Setua *et al.* (2000) to compare the properties imparted on rubber composites by crude and modified lignin preparations. They concluded that the modified lignin preparations offered better thermal stability and oil/fuel resistance than phenolic resins or carbon black additives (Setua *et al.* 2000). Other studies have also shown that methylated lignins offer good miscibility with natural rubber (Barana *et al.* 2018).

MARKET ANALYSES

According to the Statistical Review of World Energy (BP Global 2018), the actual global oil reserves in 2017 consisted of 1,700 billion barrels, which would be sufficient to for 50.2 y of global production at the 2017 level of consumption. However, the demand for oil in the global market is growing. For example, between 2016 to 2017, the growth rate was determined to be 1.8% per day, whereas a decade prior, the rate was 1.2% per day. China and the US were the largest contributors to this growth (BP Global 2018).

As resources based on fossil fuels are declining, global society has focused on alternative sources of energy and chemicals. Biomass is the most abundant renewable alternative to petroleum-based feedstock (L'udmila *et al.* 2015). Approximately 150 billion tons to 180 billion tons of biomass are produced annually. Approximately 75% of biomass is polysaccharides (cellulose and hemicellulose) and 20% is lignin. The global annual increase of lignin is estimated at 20 billion tons per y, and the total lignin availability in the biosphere is estimated at 300 billion tons (Blažej and Košík 1993; Gregorová *et al.* 2006; Rossilo-Calle *et al.* 2007; L'udmila *et al.* 2015; Bruijnincx *et al.* 2016).

Lignin Markets

Though approximately 95% of global lignin production is combusted to produce energy, only the remaining 5% is marketed for substantial applications (Tribot *et al.* 2019).

A market report published by Grand View Research (2020) valued the global lignin market at approximately US$ 954.5 million in 2019. The report included a recent market analysis for the period of 2016 to 2018 and a forecast of the market for 2020 to 2027. The lignin market is expected to reach around US$ 1.12 billion by 2027. The Compounded Annual Rate of Growth (CARG) (in terms of revenue) is projected to be 2% between 2020 and 2027. Macromolecules and aromatics are major applications in the lignin market. Macromolecules application accounted for approximately 58% market share in 2019. Water-soluble sulfonates accounted for the largest market segment in macromolecules for 2019 and are estimated to maintain market dominance until 2027 (Grand View Research 2020). Approximately 85% of the existing lignin markets are dominated by water-soluble sulfonates, although sulfite pulping has virtually been replaced by kraft delignification in most countries. This preference of sulfite over kraft lignin is due to the nature of each process, whereby one process involves structural modification (*via* installation of sulfonate groups on lignin) and the other is based on structural degradation (*via* hydrolysis of alkyl aryl ether bonds). A CARG of 1.4% is anticipated for the demand for water-soluble sulfonates from 2020 to 2027. The market share of kraft lignin was over 7% in 2019 (Grand View Research 2020).

The broad application range for products with lignin includes paints and coatings, building and construction, agrochemicals, and many others. Bioplastics made from lignin were not explicitly mentioned in the report (Grand View Research 2020). The growth of the global lignin market is attributable to the strong demand from these applications. The global lignin market is classified based on application segments. The application segments include concrete additives, dyestuffs, animal feed, and others. Over 45% of the global lignin market was used for concrete additives in 2019. According to the report, the North America region was dominant in the global lignin market, followed by Europe. However, Europe is expected to grow rapidly. Europe was followed by the Asia Pacific and Latin American regions, respectively. The fastest growing market during the forecast period is estimated to be the Asia Pacific market (Grand View Research 2020).

bioresources.com

Bioplastics Market

The bioplastics industry requires feedstocks based on renewable resources, such as polysaccharides and lignin from biomass. According to the European Bioplastics Report (European Bioplastics 2019), bioplastics represent less than 1% of the current 335 million tons of plastic produced annually. The report predicted an increase in global production capacities from around 2.11 million tons to 2.62 million tons for 2023. Polylactic acid (PLA) and polyhydroxyalkanoates (PHA) were the main predicted drivers of this growth. Whereas the production capacities of PHAs were estimated to quadruple within the next 5 y, the production capacities of PLA were predicted to grow 60% by 2023. Bio-based polypropylene (PP) production on a commercial scale is expected to enter the market in 2023 (European Bioplastics 2019). Figure 1 shows the shares of the total global production capacities of 2.11 million tons in 2018 by material type (European Bioplastics 2019).
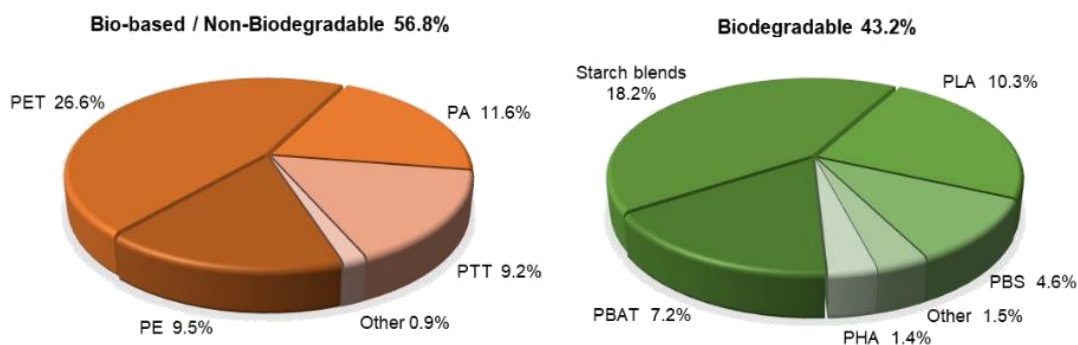

Fig. 1. Global production capacities of bioplastics in 2018 by material type; this figure was created with permission based on data from European Bioplastics (2019)
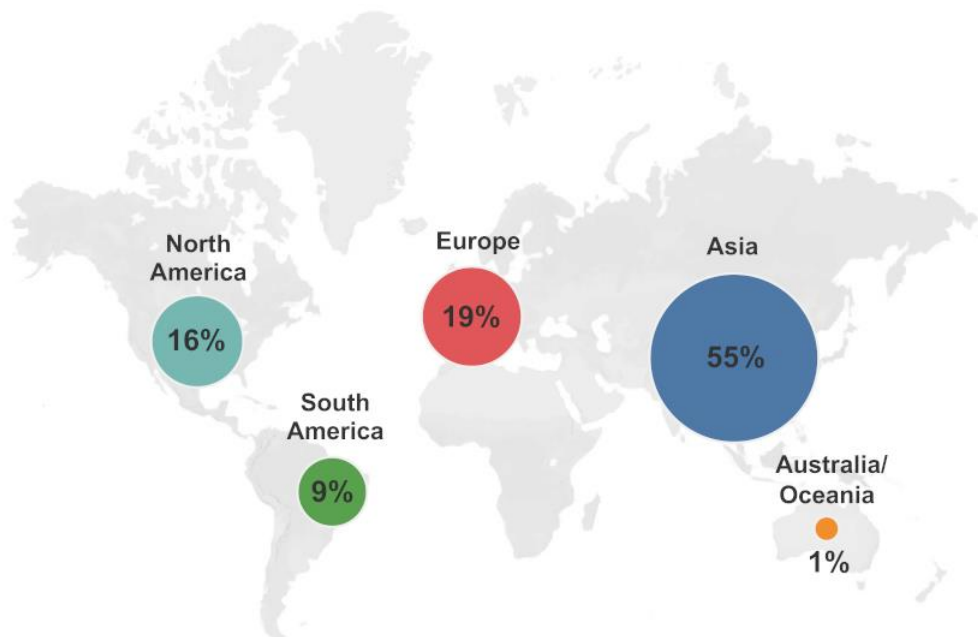
Fig. 2. The global production capacity of bioplastics in 2018 by region; this figure was created with permission based on data from European Bioplastics (2019)

The report describes Asia (with 55%) as the largest contributor to the production capacities of bioplastics, followed by Europe and the U.S., respectively. Figure 2 shows the distribution of the global production capacities of bioplastics by region.

The IBISWorld Industry Report (2018) for bioplastics manufacturing in the U.S reported data about the products and services segmentation of bioplastics in the U.S. The central segment for bioplastics (34.1%) is starch-based bioplastics, whereas bioplastics from lignin were merged in the category of synthetic/others. Figure 3 shows the market shares of the different products and service segments in U.S. bioplastics production (IBISWorld 2018). The report illustrates the scarcity of lignin in current industry-scale applications because most bioplastics are made from polysaccharides. However, the market offers some lignin-based plastic composite materials (*e.g.*, ARBOFORM® and ARBOBLEND®). These composites consist of natural fibers and a thermoplastic made from lignin (Naegele *et al.* 2016). Though Asia is the most substantial contributor to the bioplastics market in general, Europe is the largest contributor to the lignin-based production of bioplastics and composites, followed by the U.S. (Barrett 2018).
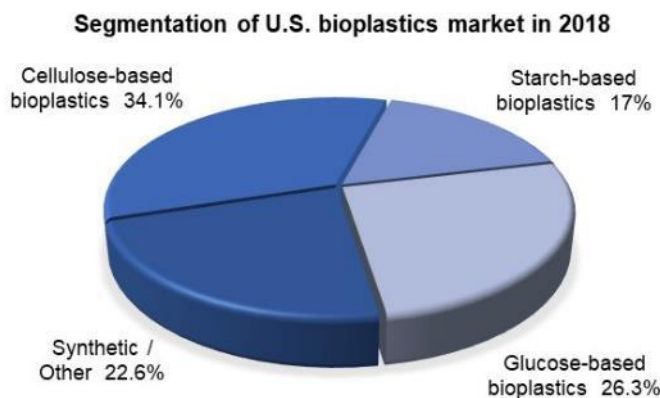
Fig. 3. The product and service segmentation of the U.S. bioplastics market in 2018; this figure was created with permission based on data from European Bioplastics (2019)

TECHNICAL TREND ANALYSES

Based on the analysis of the bioplastics commercial market sizes and segmentation examined above, the amount of actual lignin-based bioplastics that have penetrated the market is low. This exposes the contradiction between the abundance of technologies for lignin-based materials and their little practical use. Further, this reveals the existence of a serious gap between lignin research and development and the actual market. In the following sections, more informed data analysis is offered to reduce the gap between lignin research and the actual market by providing further insights to connect researchers, project managers, and stakeholders.

To address this gap, patent searches and a patent trend analysis methodology developed for this review were employed. Patents, which are globally the most popular means of intellectual property protection, may offer distinct advantages if used as a "technology indicator" (Mogee 1991). Because patents are the bridge that connects industrial applications to academic research, the analysis of patent data can be helpful for both academia and industry. Previous studies performed patent data analyses to determine technological trajectories in different domains, which included the low emission vehicle

bioresources.com

(LEV), radio frequency identification, and semiconductor industries (Almeida 1996; Oltra and Saint-Jean 2009; Trappey *et al.* 2011). Similar patent data analyses are applied in the ensuing text aimed to offer further insights.

Methodology

Patent search engine

Previous studies performed their patent data analyses based on the data provided by the European Patent Office (EPO), which offers a comprehensive collection of documents and the correlated search engine results in esp@cenet (ESPACENET) (Oltra and Saint-Jean 2009). The ESPACENET database contains patents applied for and granted all over the world (more than 70 countries and regions). It is a popular database for relevant technical analyses used in previous studies (Archibugi and Pianta 1992; Maurseth and Verspagen 2002). Though ESPACENET contains more than 110 million patent publications, another patent source with a broader range of patent data (European Patent Office 2019) was used, namely the Google Patent database. Google Patents, developed by Google Inc., includes the patents and patent applications from 17 different patent offices, including the United States Patent and Trademark Office (USPTO), China's National Intellectual Property Administration (CNIPA), Japan's Patent Office (JPO), Korean Intellectual Property Office (KIPO), World Intellectual Property Office (WIPO), Deutsches Patent- und Markenamt (PDMA), Canadian Intellectual Property Office (CIPO), EPO, and others (Google Patents 2019). To avoid replication, the patent data analysis was completed using both the ESPACENET and Google Patent databases/search engines separately. The detailed analysis method is shown in Fig. 4. The first step was a search to determine the number of patents related to specific search term(s), which was correlated to certain key-phrases.

Data collection, refinement, and analysis

As the present review article focused on the utilization of lignin-based materials, the key-phrases included "lignin" and specific material types. In Table 1, the key-phrases were divided into three groups, which corresponded to the feedstock of the production, the different applications of the produced materials, and the different categories of the produced polymer materials.

Table 1. Key-phrases Used for the Patent Data Analysis

Group 1	Group 2: Types of Polymer Materials	Group 3: Specific Polymer Materials
Lignin	Thermoplastic	Polyethylene
	Thermoset	Polyamide
	Rubber	Polyethylene terephthalate
	Foaming Material	Polypropylene
	Hydrogel / Aerogel	Polyethylene furanoate
		Polylactic acid
		Polybutylene adipate terephthalate
		Polybutylene succinate
		Terephthalate

Based on these key-phrases, the patent data was then further refined *via* the following three stages, which had an increasing order of dependency:
- Stage 1: Patents whose content covered the key-phrase in Group 1 and the required key-phrase in Group 2 / Group 3

bioresources.com

- Stage 2: Patents in Stage 1 whose title covered the key-phrase in Group 1 or the required key-phrase in Group 2 / Group 3
- Stage 3: Patents in Stage 2 whose title covered the key-phrase in Group 1 and the required key-phrase in Group 2 / Group 3

Such refining of the patent data was instrumental in ensuring that the discovered patents had a strong correlation to the topics of lignin-based materials. Institutions may not always provide relevant titles to their patents for a variety of reasons. Such citations may partly invalidate some of the data derived from Stage 2 and Stage 3 of the patent search. However, such disparities, if they occurred, were anticipated to be of minor consequence. However, this limitation was included to ensure clarity. Further, some deficiencies may have existed in the presented method. For example, because the data in Stage 3 had a stronger dependence on the desired topic, it may have omitted some patents that use abbreviations of the key-phrases in Groups 2 and 3. Therefore, an additional analysis method was performed on the data extracted from Stage 2. The analysis method used the grant ratio (Eq. 1) and the spatial and temporal distributions of the refined patent data, the details of which are clarified in the ensuing discussion:

$$Grant\ ratio = \frac{Amount\ of\ granted\ patents\ searched\ by\ the\ key\ phrases}{Amount\ of\ total\ patents\ searched\ by\ the\ key\ phrases} \times 100\% \quad (1)$$

Based on the process flow chart shown in Fig. 4, the patent data were initially collected from ESPACENET and the Google Patent search engines. The input parameters were the key-phrases in Groups 1, 2, and 3 (Table 1). Then, Stage 1 refinement was applied, and the data were downloaded and saved. For example, for a search of "lignin-based polyethylene," the input was "(lignin) AND (polyethylene)," which yielded all of the patents whose contents cover "lignin" and "polyethylene." Both Google Patent and ESPACENET provided downloadable CSV-files that allowed the detailed data for Stage 1 for a given topic to be collected. After obtaining the Stage 1 data, further analyses were conducted by proceeding to Stages 2 and 3 to arrive at spatial and temporal distributions and the grant ratios. All analyses were carried out by using the Python 3.6 programming language (Python Software Foundation, Version 3.6, Beaverton, OR, USA).
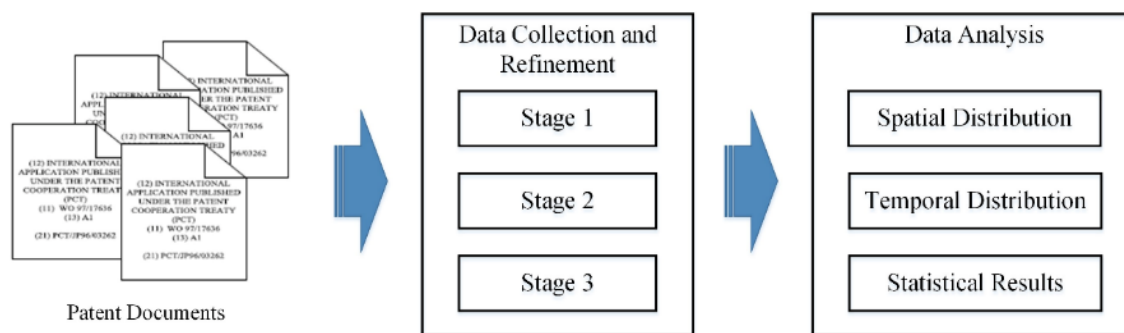
Fig. 4. Patent data analysis methodology

The spatial distributions categorized the patents by their countries of origin or the non-government organizations that published them (*e.g.*, EPO and WIPO). The countries with the most patents are provided, discussed, and analyzed in the following text. The temporal distribution trends were examined for two different periods (a short one and a longer one). The short period showed the patent activity for the recent past (20 y),

bioresources.com

highlighting recent technical trends. The longer period was used to display the patent activity from the beginning of the last century to offer a view of historical developments for a given research topic. Finally, the grant ratio provided insights into the possible commercialization of the relevant applications.

RESULTS AND DISCUSSION

Data Refinement

Table 2 provides the data refinement for Group 2 using the key-phrases shown in Table 1. The values in column Stage 1 directly reflect the relative size of the databases.

The size of the ESPACENET database is considerably smaller than the Google Patents database. Further, for some specific types of lignin-based materials, some notable differences were apparent. For example, in the Google Patents database, the number of patents for lignin-based foaming materials was 16571 (Stage 1). This was a much larger number than that for other types of lignin-based materials. However, in the ESPACENET database, the total number of lignin-based foaming materials patents was only 289 (Stage 1), which was lower than the number for lignin-based rubber (615 for Stage 1). Due to the relatively small size of the ESPACENET database, the grant ratio calculated from this database may not have been representative (*e.g.*, lignin-based thermosets). Because of these discrepancies, further analyses used the results obtained from the Google Patents database.

Table 2. Group 2 Patent Data Refinement Results From Google Patent and ESPACENET

	Stage 1	Stage 2	Stage 3	Grant Ratio in Stage 2 (%)
Google Patents				
Thermoplastics	624	181	25	33.1
Thermosets	4651	275	8	29.1
Rubber	695	268	58	15.7
Foaming Materials	16571	1285	45	16.2
Aerogel / Hydrogel	1076	299	26	18.7
ESPACENET				
Thermoplastics	231	80	21	32.5
Thermosets	18	9	2	77.8
Rubber	615	234	56	10.3
Foaming Materials	289	180	30	13.3
Aerogel / Hydrogel	66	45	13	2.2

To understand the degree of technical maturity of different types of lignin-based materials, the grant ratio was calculated. This is the number of patents granted in Stage 2 divided by the number of overall patents obtained in Stage 2 ($\times 100\%$) for a specific type of lignin-based material. Higher grant ratios indicate industry-preferred areas, in which technologies are likely more mature.

Data analysis

The grant ratios for different types of lignin-based materials based on the Stage 2 refined patent data are provided in Table 2. The patents for lignin-based thermoplastics and

lignin-based thermosets had higher grant ratios (33.2% and 29.1%, respectively) than other types of lignin-based materials. These two market segments are likely more mature than other types of lignin-based materials.

Tables 3 and 4 show the spatial distribution for lignin-based material patents. The top 5 countries with the highest patent activity in a given area are shown first, and the rest are combined and displayed as "Others." China, the United States, and Japan are at the top of the list and responsible for 64% to 83% of the total number of patents for all the different types of lignin-based materials examined.

Through comparing the number of patents (Stage 2 refinement) between China and the United States, it was evident that China had considerably higher activity in lignin-based foaming materials and lignin-based aerogels/hydrogels. In contrast, the United States had higher patent activity in the area of lignin-based thermoplastics, thermosets, and rubbers, which are more traditional materials than foaming material and aerogel/hydrogel applications.

Table 3. Group 2 Patent Data Spatial Distribution Results as Obtained From Google Patent

	China	United States	Japan	WIPO	Korea	Others
Thermoplastics	35	91	13	13	5	24
Thermosets	47	107	40	30	5	46
Rubber	82	117	12	12	4	41
Foaming Materials	653	272	118	73	36	133
Aerogel / Hydrogel	168	66	5	34	16	10
Total	985	653	188	162	66	254

Table 4. Group 2 Patent Data Spatial Distribution Results From ESPACENET

	China	United States	British	Japan	Canada	Others
Thermoplastics	29	17	5	5	2	22
Thermosets	0	6	1	0	1	1
Rubber	131	38	24	8	14	19
Foaming Materials	122	16	8	11	3	20
Aerogel / Hydrogel	34	1	0	0	0	10
Total	316	78	38	24	20	72

The developing trends for different lignin-based materials are also plotted as a function of two time domains to show recent and long-term trends. Figure 5 displays patent activities in the past 20 y (Fig. 5a.) and the past 90 y (Fig. 5b).

There has been notable recent activity in lignin-based foaming materials, aerogels, and hydrogels (Fig. 5a). These trends have accelerated in recent years, and lignin-based aerogels and hydrogels have been in a leading position since 2012. The patent activities for lignin-based thermoplastics, thermosets, and rubbers have stabilized during the past 20 y.

In summary, lignin-based foaming materials and lignin-based aerogels and hydrogels have been subject to increased recent patent activity, which likely indicates commercial interest and possible opportunities.
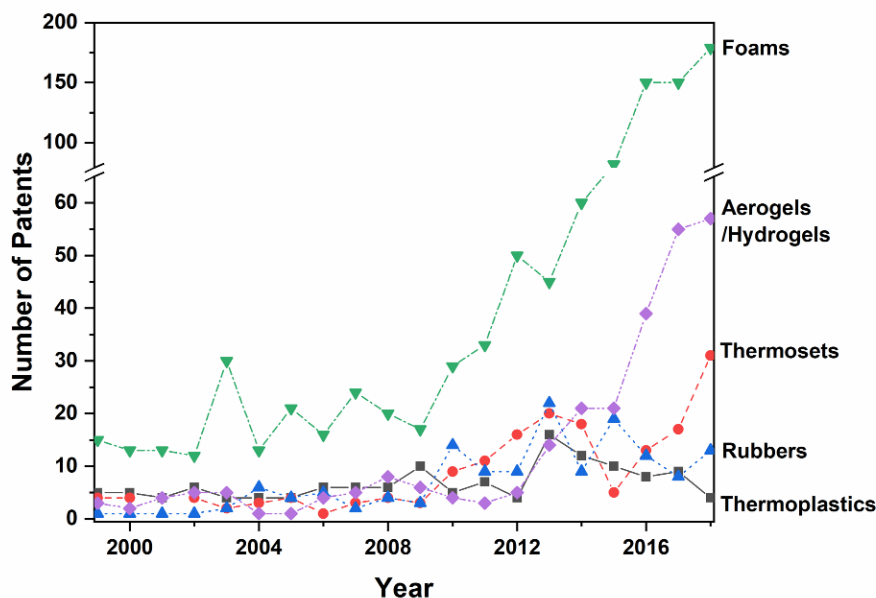
Fig. 5a. Group 2 Google Patent data distribution during the past 20 years
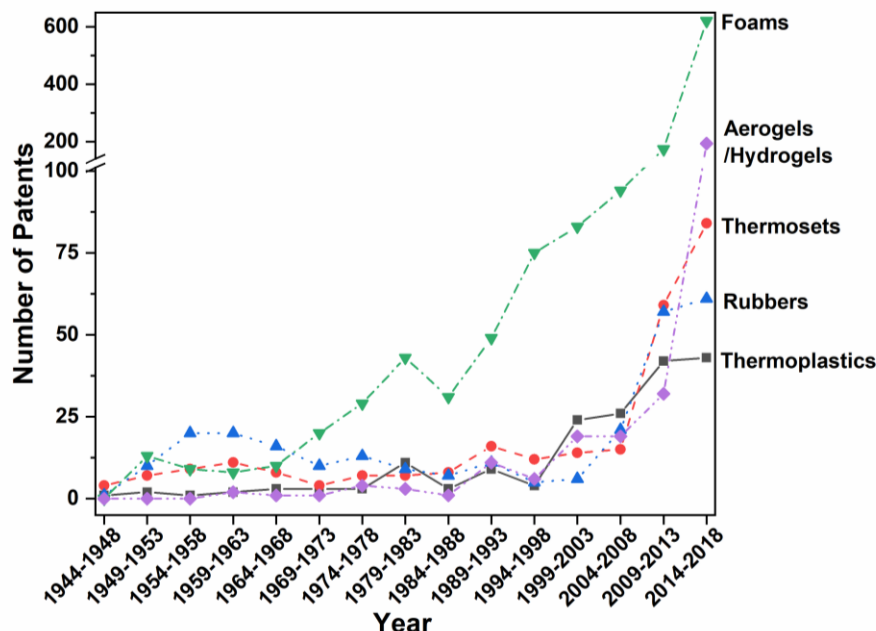

Fig. 5b. Group 2 Google Patent data distribution during the past 90 years

The long-term patent activity trends (Fig. 5b) for the different types of lignin-based materials showed a steadily increasing interest, which can be interpreted as an indicator of the prospective development of lignin-based materials. Interestingly, the number of patents for lignin-based rubber materials exceeded that of other types of materials from the 1950s to the 1970s, but the activity decreased in the 21st century. Overall, the trends discovered and displayed in Fig. 5 can provide a valuable guideline for decision makers (industry, funding agencies, and academics) to determine the direction and importance of projects related to different types of lignin-based materials.

bioresources.com

An analysis of the patent activities for lignin-based blends and composites with various types of synthetic polymers follows. Similar approaches to those applied to Stage 2 were also used on the data accumulated in the patent data analysis of Group 3, which aimed at specific types of materials. In Table 5, the data refinement results based on key-phrases in Groups 1 and 3 are shown. The number of patents for lignin-based polyethylene (PE) (65781 in Stage 1) and polypropylene (PP) (53432 in Stage 1) far exceeded the number of patents for other types of polymers, which followed the same trend due to the high market penetration ratios of PP and PE (Witter 2015). The grant ratios of different lignin-based polymers are also listed in Table 2.

However, some grant ratio data may have been unrepresentative due to small data sizes; thus, it was not included. For example, the number of patents in Stage 2 for polylactic acid, polybutylene adipate terephthalate, and polybutylene succinate was less than 50, whereas the largest number was higher than 1000 (1081 for polyethylene). Therefore, further analysis may be necessary to fully comprehend and validate the technological maturity of these lignin-based polymers. Table 6 shows the spatial distribution for the patent activity of lignin-based polymers. Like the results of Table 4, the top 5 countries with the highest patent activity are provided, and the number under "Others" is the sum of the patents from the remaining countries.

Table 5. Group 3 Patent Data Refinement Results From Google Patent

	Stage 1	Stage 2	Stage 3	Grant Ratio in Stage 2 (%)
Polyethylene	65781	1081	19	18.22
Polyamide	15245	253	5	24.90
Polyethylene terephthalate	7216	90	6	23.33
Polypropylene	53432	906	9	19.65
Polyethylene furanoate	6199	141	0	30.50
Polylactic acid	2676	45	0	11.11
Polybutylene adipate terephthalate	997	18	0	0
Polybutylene succinate	1332	21	0	14.29
Terephthalate	8134	128	8	21.09

Table 6. Group 3 Patent Data Spatial Distribution Results From Google Patent

	China	United States	WIPO	Japan	EPO	Others
Polyethylene	476	238	75	66	33	193
Polyamide	53	81	25	3	14	41
Polyethylene terephthalate	25	34	8	7	2	14
Polypropylene	306	271	54	57	45	173
Polyethylene furanoate	19	63	15	7	4	33
Polylactic acid	21	11	2	6	2	3
Polybutylene adipate terephthalate	6	10	0	1	0	1
Polybutylene succinate	9	4	1	4	0	3
Terephthalate	43	40	9	8	7	21
Total	958	752	189	159	107	482

The sizable activities of China and the United States were apparent, as these countries had the most patent activity for all of the lignin-based polymers. They were followed by WIPO, Japan, and EPO. Interestingly, China showed higher activity in lignin-based polyethylene, polypropylene, polylactic acid, polybutylene succinate, and terephthalate, which have higher annual production (Witter 2015) and higher absolute numbers of patents than other types of lignin-based polymers. The United States was dominant in patent activity for the remaining types of lignin-based polymers, which may indicate differences in lignin-based polymer development between China and the United States.

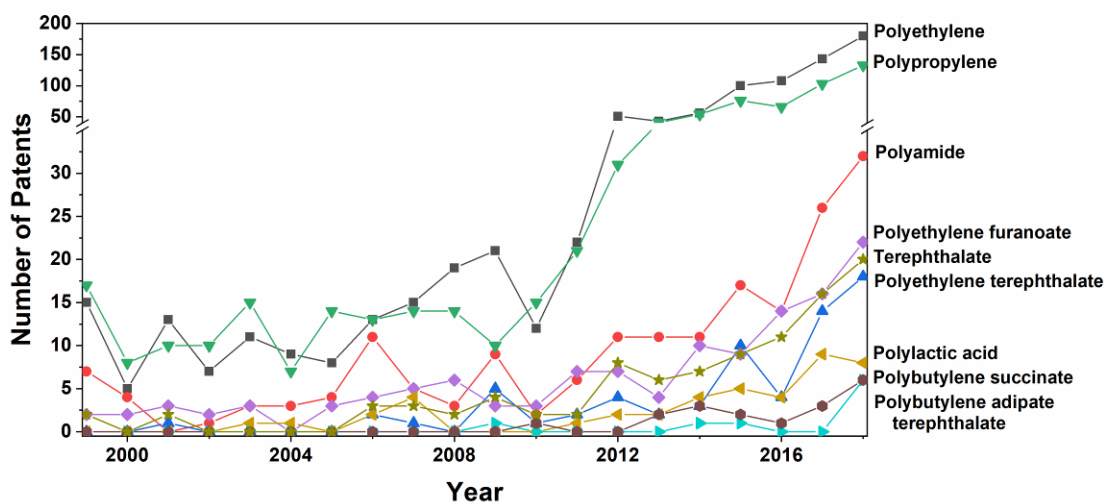Figure 6 displays the development trends for lignin-based polymers in short-term (Fig. 6a) and long-term (Fig. 6b).

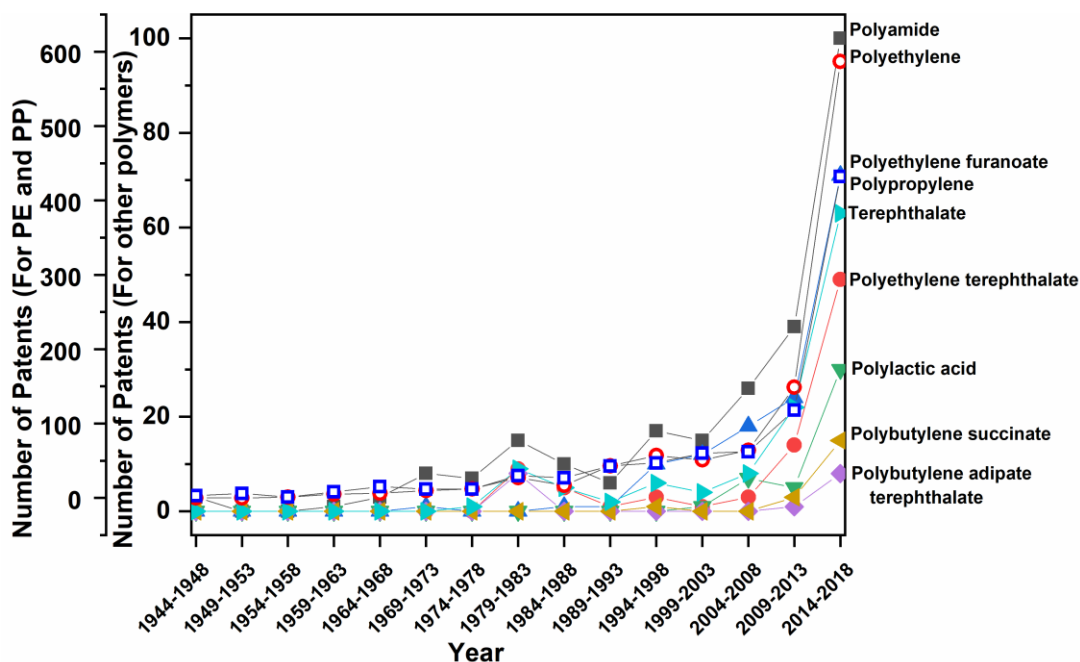**Fig. 6a.** Group 3 Google Patent data distribution in the past 20 years

Fig. 6b. Group 3 Google Patent data distribution in the past 90 years

Recent activity for lignin-based polyethylene, polypropylene, and polyamides was evident in Fig. 6a, especially after 2010. For lignin-based polyethylene furanoate, terephthalate, and terephthalate, a relatively slow incremental increase in patents was observed for recent years (Fig. 6a). Development of the remaining types of lignin-based polymers stabilized and has been of relatively low interest.

Overall, over the next few years, the commercial interest and potential opportunities for lignin-based polymers may focus on lignin-based polyethylene, polypropylene, and polyamide blends.

With regard to the long-term patent activity trends (Fig. 6b), a steadily increasing consistent interest was apparent for all lignin-based polymers. The observed pattern of patents in the 21st century likely indicates a continuing trend and an optimistic future.

CONCLUSIONS

1. Lignin is among the most promising biomass components currently under development. Due to its natural abundance, global availability, chemical versatility, and its aromaticity, lignin is an attractive renewable substitute for fossil-based chemicals.

2. Notable research and development advances and the increasing focus on sustainable resources are beginning to make lignin recovery for non-fuel purposes attractive (and sometimes mandatory) for pulp producers.

3. The global markets for lignin are expected to grow to a market volume of US$ 1.12 billion in 2027, with North America in the lead of production and consumption, followed by Europe. The Asia Pacific region is the fastest growing contributor to the global lignin markets. The global production of bioplastics represents less than 1% of total global plastics production, which currently amounts to approximately 335 million tons. China, with 55% of the global production, is the largest contributor to the bioplastics market, followed by Europe and North America.

4. The current major resource for most bioplastics is polysaccharides, and the largest proportion of globally produced lignin is used for other applications, such as additives for concrete.

5. The present effort showed strong developmental tendencies aimed at using lignin as a resource for bioplastics and an accompanying increase in the bioplastics market. Lignin will likely be an important resource for the future production of bioplastics.

6. This review showed the existence of a gap between lignin research and development and the actual market.

7. The patent searches and patent trend analyses showed that China, the United States, and Japan are responsible for over half of the patents related to lignin-based polymers. China showed considerably higher patent activity in some novel materials (lignin-based foaming materials and aerogels/hydrogels). In contrast, the United States was found to be focused on more traditional materials (lignin-based thermoplastics, thermosets, and rubbers).

8. With regard to the temporal distribution findings, an incremental upward trend was apparent for all types of lignin-based polymers. In contrast, lignin-based rubbers showed an extended period of interest from the 1950s to the 1970s.

9. The analyses presented in this review may offer a guideline for interested stakeholders to determine technical development trends for lignin-based polymeric materials.

ACKNOWLEDGEMENTS

FUNDING

REFERENCES CITED

Ago, M., Okajima, K., Jakes, J. E., Park, S., and Rojas, O. J. (2012). "Lignin-based electrospun nanofibers reinforced with cellulose nanocrystals," *Biomacromolecules* 13(3), 918-926. DOI: 10.1021/bm201828g

Ahvazi, B., Wojciechowicz, O., Ton-That, T.-M., and Hawari, J. (2011). "Preparation of lignopolyols from wheat straw soda lignin," *Journal of Agricultural and Food Chemistry* 59(19), 10505-10516. DOI: 10.1021/jf202452m

Almeida, P. (1996). "Knowledge sourcing by foreign multinationals: Patent citation analysis in the U.S. semiconductor industry," *Strategic Management Journal* 17(S2), 155-165. DOI: 10.1002/smj.4250171113

Archibugi, D., and Pianta, M. (1992). "Specialization and size of technological activities in industrial countries: The analysis of patent data," *Research Policy* 21(1), 79-93. DOI: 10.1016/0048-7333(92)90028-3

Argyropoulos, D. S. (2014). "The emerging bio-refinery industry needs to refine lignin prior to use," *Journal of Biotechnology and Biomaterials* S6, e001. DOI: 10.4172/2155-952X.S6-e001

Argyropoulos, D. S., and Bolker, H. I. (1987a). "The gel degradation theory, Part I; An experimental verification with a model trifunctional network," *Macromolecules* 20, 2915-2922. DOI: 10.1021/ma00177a046

Argyropoulos, D. S., and Bolker, H. I. (1987b). "The gel degradation theory, Part II; An experimental verification with model networks formed by the random crosslinking of monodisperse primary chains," *Die Makromolekulare Chemie* 189, 607-618. DOI: 10.1002/macp.1988.021890314

Argyropoulos, D. S., and Bolker, H. I. (1987c). "The gel degradation theory, Part III; An experimental kinetic verification," *Journal of Wood Chemistry and Technology* 7(4), 499-512. DOI: 10.1080/02773818708085282

Asada, C., Basnet, S., Otsuka, M., Sasaki, C., and Nakamura, Y. (2015). "Epoxy resin synthesis using low molecular weight lignin separated from various lignocellulosic materials," *International Journal of Biological Macromolecules* 74, 413-419. DOI: 10.1016/j.ijbiomac.2014.12.039

Barana, D., Ali, S. D., Salanti, A., Orlandi, M., Castellani, L., Hanel, T., and Zoia, L. (2016). "Influence of lignin features on thermal stability and mechanical properties of natural rubber compounds," *ACS Sustainable Chemistry & Engineering* 4(10), 5258-5267. DOI: 10.1021/acssuschemeng.6b00774

Barana, D., Orlandi, M., Zoia, L., Castellani, L., Hanel, T., Bolck, C., and Gosselink, R. (2018). "Lignin based functional additives for natural rubber," *ACS Sustainable Chemistry & Engineering* 6(9), 11843-11852. DOI: 10.1021/acssuschemeng.8b02145

Barrett, A. (2018). "The European commission papers: The lignin briefing," *Bioplastics News*, (https://bioplasticsnews.com/2018/08/10/european-commission-lignin/), Accessed 25 Feb 2019.

Barzegari, M. R., Alemdar, A., Zhang, Y., and Rodrigue, D. (2012). "Mechanical and rheological behavior of highly filled polystyrene with lignin," *Polymer Composites* 33(3), 353-361. DOI: 10.1002/pc.22154

Belgacem, M. N., and Gandini, A. (2008). *Monomers, Polymers and Composites from Renewable Resources*, Elsevier, Amsterdam, The Netherlands.

Blažej, A., and Košík, M. (1993). *Phytomass: A Raw Material for Chemistry and Biotechnology*, Ellis Horwood Ltd., Chichester, England.

Bonini, C., D'Auria, M., Emanuele, L., Ferri, R., Pucciariello, R., and Sabia, A. R. (2005). "Polyurethanes and polyesters from lignin," *Journal of Applied Polymer Science* 98(3), 1451-1456. DOI: 10.1002/app.22277

Bouajila, J., Dole, P., Joly, C., and Limare, A. (2006). "Some laws of a lignin plasticization," *Journal of Applied Polymer Science* 102(2), 1445-1451. DOI: 10.1002/app.24299

Bova, T., Tran, C. D., Balakshin, M. Y., Chen, J., Capanema, E. A., and Naskar, A. K. (2016). "An approach towards tailoring interfacial structures and properties of multiphase renewable thermoplasics from lignin–nitrile rubber," *Green Chemistry* 18(20), 5423-5437. DOI: 10.1039/C6GC01067A

BP Global (2018). "Statistical review of world energy," (https://www.bp.com/en/global/corporate/energy-economics/statistical-review-of-world-energy.html), Accessed 8 Apr 2019.

Bruijnincx, P., Weckhuysen, B., Gruter, G.-J., and Engelen-Smeets, E. (2016). *Lignin Valorisation: The Importance of a Full Value Chain Approach*, Utrecht University, Utrecht, The Netherlands.

Canetti, M., and Bertini, F. (2007). "Supermolecular structure and thermal properties of poly(ethylene terephthalate)/lignin composites," *Composites Science and Technology* 67(15-16), 3151-3157. DOI: 10.1016/j.compscitech.2007.04.013

Canetti, M., and Bertini, F. (2009). "Influence of the lignin on thermal degradation and melting behaviour of poly(ethylene terephthalate) based composites," *e-Polymers* 9(1), Article number 049. DOI: 10.1515/epoly.2009.9.1.596

Cateto, C. A., Barreiro, M. F., Ottati, C., Lopretti, M., Rodrigues, A. E., and Belgacem, M. N. (2014). "Lignin-based rigid polyurethane foams with improved biodegradation," *Journal of Cellular Plastics* 50(1), 81-95. DOI: 10.1177/0021955X13504774

Cateto, C. A., Barreiro, M. F., Rodrigues, A. E., and Belgacem, M. N. (2009). "Optimization study of lignin oxypropylation in view of the preparation of polyurethane rigid foams," *Industrial & Engineering Chemistry Research* 48(5), 2583-2589. DOI: 10.1021/ie801251r

Chen, K., Qian, Y., Wu, S., Qiu, X., Yang, D., and Lei, L. (2019). "Neutral fabrication of UV-blocking and antioxidation lignin-stabilized high internal phase emulsion encapsulates for high efficient antibacterium of natural curcumin," *Food & Function* 10(6), 3543-3555. DOI: 10.1039/C9FO00320G

Cheng, F., and Brewer, C. E. (2017). "Producing jet fuel from biomass lignin: Potential pathways to alkyl-benzenes and cycloalkanes," *Renewable and Sustainable Energy Reviews* 72, 673-722. DOI: 10.1016/j.rser.2017.01.030

Chuck, C. J., Parker, H. J., Jenkins, R. W., and Donnelly, J. (2013). "Renewable biofuel additives from the ozonolysis of lignin," *Bioresource Technology* 143, 549-554. DOI: 10.1016/j.biortech.2013.06.048

Chung, H., and Washburn, N. R. (2012). "Improved lignin polyurethane properties with lewis acid treatment," *ACS Applied Materials & Interfaces* 4(6), 2840-2846. DOI: 10.1021/am300425x

Chung, Y.-L., Olsson, J. V., Li, R. J., Frank, C. W., Waymouth, R. M., Billington, S. L., and Sattely, E. S. (2013). "A renewable lignin–lactide copolymer and application in biobased composites," *ACS Sustainable Chemistry & Engineering* 1(10), 1231-1238. DOI: 10.1021/sc4000835

Cinelli, P., Anguillesi, I., and Lazzeri, A. (2013). "Green synthesis of flexible polyurethane foams from liquefied lignin," *European Polymer Journal* 49(6), 1174-1184. DOI: 10.1016/j.eurpolymj.2013.04.005

Collins, M. N., Nechifor, M., Tanasă, F., Zănoagă, M., McLoughlin, A., Stróżyk, M. A., Culebras, M., and Teacă, C.-A. (2019). "Valorization of lignin in polymer and composite systems for advanced engineering applications – A review," *International Journal of Biological Macromolecules* 131, 828-849. DOI: 10.1016/j.ijbiomac.2019.03.069

Cui, C., Sun, R., and Argyropoulos, D. S. (2014). "Fractional precipitation of softwood kraft lignin: Isolation of narrow fractions common to a variety of lignins," *ACS Sustainable Chemistry & Engineering* 2(4), 959-968. DOI: 10.1021/sc400545d

da Silva, C. G., Grelier, S., Pichavant, F., Frollini, E., and Castellan, A. (2013). "Adding value to lignins isolated from sugarcane bagasse and *Miscanthus*," *Industrial Crops and Products* 42, 87-95. DOI: 10.1016/j.indcrop.2012.04.040

da Silva, E. A. B., Zabkova, M., Araújo, J. D., Cateto, C. A., Barreiro, M. F., Belgacem, M. N., and Rodrigues, A. E. (2009). "An integrated process to produce vanillin and lignin-based polyurethanes from kraft lignin," *Chemical Engineering Research and Design* 87(9), 1276-1292. DOI: 10.1016/j.cherd.2009.05.008

Datta, J., Parcheta, P., and Surówka, J. (2017). "Softwood-lignin/natural rubber composites containing novel plasticizing agent: Preparation and characterization," *Industrial Crops and Products* 95, 675-685. DOI: 10.1016/j.indcrop.2016.11.036

de Chirico, A., Armanini, M., Chini, P., Cioccolo, G., Provasoli, F., and Audisio, G. (2003). "Flame retardants for polypropylene based on lignin," *Polymer Degradation and Stability* 79(1), 139-145. DOI: 10.1016/S0141-3910(02)00266-5

de Oliveira, W., and Glasser, W. G. (1994). "Multiphase materials with lignin. 11. Starlike copolymers with caprolactone," *Macromolecules* 27(1), 5-11. DOI: 10.1021/ma00079a002

bioresources.com

Doherty, W. O. S., Mousavioun, P., and Fellows, C. M. (2011). "Value-adding to cellulosic ethanol: Lignin polymers," *Industrial Crops and Products* 33(2), 259-276. DOI: 10.1016/j.indcrop.2010.10.022

Domínguez-Robles, J., Peresin, M. S., Tamminen, T., Rodríguez, A., Larrañeta, E., and Jääskeläinen, A.-S. (2018). "Lignin-based hydrogels with "super-swelling" capacities for dye removal," *International Journal of Biological Macromolecules* 115, 1249-1259. DOI: 10.1016/j.ijbiomac.2018.04.044

Du, X., Li, J., and Lindström, M. E. (2014). "Modification of industrial softwood kraft lignin using Mannich reaction with and without phenolation pretreatment," *Industrial Crops and Products* 52, 729-735. DOI: 10.1016/j.indcrop.2013.11.035

Duong, L. D., Nam, G.-Y., Oh, J.-S., Park, I.-K., Luong, N. D., Yoon, H.-K., Lee, S.-H., Lee, Y., Yun, J.-H., and Lee, C.-G., *et al.* (2014). "High molecular-weight thermoplastic polymerization of kraft lignin macromers with diisocyanate," *BioResources* 9(2), 2359-2371. DOI: 10.15376/biores.9.2.2359-2371

Duval, A., and Lawoko, M. (2014). "A review on lignin-based polymeric, micro- and nano-structured materials," *Reactive and Functional Polymers* 85, 78-96. DOI: 10.1016/j.reactfunctpolym.2014.09.017

Effendi, A., Gerhauser, H., and Bridgwater, A. V. (2008). "Production of renewable phenolic resins by thermochemical conversion of biomass: A review," *Renewable and Sustainable Energy Reviews* 12(8), 2092-2116. DOI: 10.1016/j.rser.2007.04.008

Engels, H.-W., Pirkl, H.-G., Albers, R., Albach, R. W., Krause, J., Hoffmann, A., Casselmann, H., and Dormish, J. (2013). "Polyurethanes: Versatile materials and sustainable problem solvers for today's challenges," *Angewandte Chemie International Edition* 52(36), 9422-9441. DOI: 10.1002/anie.201302766

European Bioplastics (2019). "Bioplastic market report 2019," European Bioplastics e.V., (https://www.european-bioplastics.org/market), Accessed 8 Apr 2020.

European Patent Office (2019). "Espacenet: Patent database with over 100 million documents," (https://www.epo.org/searching-for-patents/technical/espacenet.html#tab-1), Accessed 22 May 2019.

Food and Drug Administration (FDA) (2010). *Update on Bisphenol A for Use in Food Contact Applications*, US FDA, Silver Spring, MD, USA.

Feldman, D. (2002). "Lignin and its polyblends—A review," in: *Chemical Modification, Properties, and Usage of Lignin*, T. Q. Hu (ed.), Springer, Boston, MA, USA, pp. 81-99.

Figueiredo, P., Lintinen, K., Hirvonen, J. T., Kostiainen, M. A., and Santos, H. A. (2018). "Properties and chemical modifications of lignin: Towards lignin-based nanomaterials for biomedical applications," *Progress in Materials Science* 93, 233-269. DOI: 10.1016/j.pmatsci.2017.12.001

Flint, S., Markle, T., Thompson, S., and Wallace, E. (2012). "Bisphenol A exposure, effects, and policy: A wildlife perspective," *Journal of Environmental Management* 104, 19-34. DOI: 10.1016/j.jenvman.2012.03.021

Gandini, A., Belgacem, M. N., Guo, Z.-X., and Montanari, S. (2002). "Lignins as macro-monomers for polyesters and polyurethanes," in: *Chemical Modification, Properties, and Usage of Lignin*, T. Q. Hu (ed.), Springer, Boston, MA, USA, pp. 57-80.

Gao, G., Dallmeyer, J. I., and Kadla, J. F. (2012). "Synthesis of lignin nanofibers with ionic-responsive shells: Water-expandable lignin-based nanofibrous mats," *Biomacromolecules* 13(11), 3602-3610. DOI: 10.1021/bm301039f

Gardziella, A., Pilato, L. A., and Knop, A. (2000). "Phenolic resins: Chemistry, reactions, mechanism," in: *Phenolic Resins*, Springer, Berlin, Germany, pp. 24-82.

Gierer, J., and Pettersson, I. (1977). "Studies on the condensation of lignins in alkaline media. Part II. The formation of stilbene and arylcoumaran structures through neighbouring group participation reactions," *Canadian Journal of Chemistry* 55(4), 593-599. DOI: 10.1139/v77-084

Gigli, M., and Crestini, C. (2020). "Fractionation of industrial lignins: Opportunities and challenges," *Green Chem.* 22, 4722-4746. DOI: 10.1039/d0gc01606c

Gonçalves, A. R., and Benar, P. (2001). "Hydroxymethylation and oxidation of organosolv lignins and utilization of the products," *Bioresource Technology* 79(2), 103-111. DOI: 10.1016/S0960-8524(01)00056-6

Google Patents (2019). "Coverage - Google help," (https://support.google.com/faqs/answer/7049585), Accessed 22 May 2019.

Grand View Research (2020). "Lignin market size, growth 2016-2027 | Global industry analysis report," (https://www.grandviewresearch.com/industry-analysis/lignin-market), Accessed 9 March 2020.

Gregorová, A., Košíková, B., and Moravčík, R. (2006). "Stabilization effect of lignin in natural rubber," *Polymer Degradation and Stability* 91(2), 229-233. DOI: 10.1016/j.polymdegradstab.2005.05.009

Hatakeyama, H., Hirogaki, A., Matsumua, H., and Hatakeyama, T. (2013). "Glass transition temperature of polyurethane foams derived from lignin by controlled reaction rate," *Journal of Thermal Analysis and Calorimetry* 114(3), 1075-1082. DOI: 10.1007/s10973-013-3132-1

Hirose, S., Hatakeyama, T., Izuta, Y., and Hatakeyama, H. (2002). "TG-FTIR studies on lignin-based polycaprolactones," *Journal of Thermal Analysis and Calorimetry* 70(3), 853-860. DOI: 10.1023/A:1022212421525

Ho, H. C., Goswami, M., Chen, J., Keum, J. K., and Naskar, A. K. (2018). "Amending the structure of renewable carbon from biorefinery waste-streams for energy storage applications," *Scientific Reports* 8(1), Article number 8355. DOI: 10.1038/s41598-018-25880-0

Hofmann, K., and Glasser, W. (1994). "Engineering plastics from lignin, 23. Network formation of lignin-based epoxy resins," *Macromolecular Chemistry and Physics* 195(1), 65-80. DOI: 10.1002/macp.1994.021950106

Hofmann, K., and Glasser, W. G. (1993). "Engineering plastics from lignin. 22. Cure of lignin-based epoxy resins," *The Journal of Adhesion* 40(2-4), 229-241. DOI: 10.1080/00218469308031286

Hu, L., Pan, H., Zhou, Y., and Zhang, M. (2011). "Methods to improve lignin's reactivity as a phenol substitute and as replacement for other phenolic compounds: A brief review," *BioResources* 6(3), 3515-3525.

Hu, S., Luo, X., and Li, Y. (2014). "Polyols and polyurethanes from the liquefaction of lignocellulosic biomass," *ChemSusChem* 7(1), 66-72. DOI: 10.1002/cssc.201300760

Hu, T. Q. (2002). *Chemical Modification, Properties, and Usage of Lignin*, T. Q. Hu (ed.), Springer, Boston, MA, USA.

Huang, C., Ma, J., Zhang, W., Huang, G., and Yong, Q. (2018). "Preparation of lignosulfonates from biorefinery lignins by sulfomethylation and their application as a water reducer for concrete," *Polymers* 10(8), Article number 841. DOI: 10.3390/polym10080841

Huang, J., and Zhang, L. (2002). "Effects of NCO/OH molar ratio on structure and properties of graft-interpenetrating polymer networks from polyurethane and nitrolignin," *Polymer* 43(8), 2287-2294. DOI: 10.1016/S0032-3861(02)00028-9

Huo, S.-P., Nie, M.-C., Kong, Z.-W., Wu, G.-M., and Chen, J. (2012). "Crosslinking kinetics of the formation of lignin-aminated polyol-based polyurethane foam," *Journal of Applied Polymer Science* 125(1), 152-157. DOI: 10.1002/app.35401

IBISWorld (2018). "IBISWorld industry report global plastic product & packaging manufacturing," (https://clients1.ibisworld.com/reports/gl/industry/default.aspx?entid=770), Accessed 8 Apr 2019.

Jiang, X., Liu, J., Du, X., Hu, Z., Chang, H. M., and Jameel, H. (2018). "Phenolation to improve lignin reactivity toward thermosets application," *ACS Sustainable Chemistry & Engineering* 6(4), 5504-5512. DOI:10.1021/acssuschemeng.8b00369

Jiao, G.-J., Peng, P., Sun, S.-L., Geng, Z.-C., and She, D. (2019). "Amination of biorefinery technical lignin by Mannich reaction for preparing highly efficient nitrogen fertilizer," *International Journal of Biological Macromolecules* 127, 544-554. DOI: 10.1016/j.ijbiomac.2019.01.076

Jungmeier, G., Van Ree, R., De Jong, E., Stichnothe, H., De Bari, I., Jørgensen, H., Wellisch, M., Bell, G., Spaeth, J., Torr, K., and Kimura, S. (2015). "The "Biorefinery Fact Sheet" and its application to wood based biorefining - Case studies of IEA Bioenergy Task 42 "Biorefining,"" in: *The 6th Nordic Wood Biorefinery Conference* (NWBC) *2015*, Helsinki, Finland, pp. 62-68.

Kakroodi, A. R., and Sain, M. (2016). "Lignin-reinforced rubber composites," in: *Lignin in Polymer Composites*, Elsevier, Waltham, MA, USA, pp. 195-206.

Kim, Y. S., and Kadla, J. F. (2010). "Preparation of a thermoresponsive lignin-based biomaterial through atom transfer radical polymerization," *Biomacromolecules* 11(4), 981-988. DOI: 10.1021/bm901455p

Konduri, M. K. R., and Fatehi, P. (2015). "Production of water-soluble hardwood kraft lignin *via* sulfomethylation using formaldehyde and sodium sulfite," *ACS Sustainable Chemistry & Engineering* 3(6), 1172-1182. DOI: 10.1021/acssuschemeng.5b00098

Košíková, B., and Gregorová, A. (2005). "Sulfur-free lignin as reinforcing component of styrene–butadiene rubber," *Journal of Applied Polymer Science* 97(3), 924-929. DOI: 10.1002/app.21448

Košíková, B., Gregorová, A., Osvald, A., and Krajčovičová, J. (2007). "Role of lignin filler in stabilization of natural rubber–based composites," *Journal of Applied Polymer Science* 103(2), 1226-1231. DOI: 10.1002/app.24530

Kratzl, K., and Oburger, M. (1980). "Condensation reactions of lignin model compounds with phenol under acid catalysis, 2 [beechwood, spruce wood]," *Holzforschung* 34(1), 11-16. DOI: 10.1515/hfsg.1980.34.6.191

Kun, D., and Pukánszky, B. (2017). "Polymer/lignin blends: Interactions, properties, applications," *European Polymer Journal* 93, 618-641. DOI: 10.1016/j.eurpolymj.2017.04.035

Laurichesse, S., and Avérous, L. (2014). "Chemical modification of lignins: Towards biobased polymers," *Progress in Polymer Science* 39(7), 1266-1290. DOI: 10.1016/j.progpolymsci.2013.11.004

Laurichesse, S., Huillet, C., and Avérous, L. (2014). "Original polyols based on organosolv lignin and fatty acids: New bio-based building blocks for segmented

bioresources.*com*

polyurethane synthesis," *Green Chemistry* 16(8), 3958-3970. DOI: 10.1039/C4GC00596A

Li, F., Wang, X., and Sun, R. (2017). "A metal-free and flexible supercapacitor based on redox-active lignosulfonate functionalized graphene hydrogels," *Journal of Materials Chemistry A* 5(39), 20643-20650. DOI: 10.1039/C7TA03789A

Li, F., Wang, X., Yuan, T., and Sun, R. (2016). "A lignosulfonate-modified graphene hydrogel with ultrahigh adsorption capacity for Pb(II) removal," *Journal of Materials Chemistry A* 4(30), 11888-11896. DOI: 10.1039/C6TA03779H

Lin, L., Nakagame, S., Yao, Y., Yoshioka, M., Shiraishi, M. N., and Shiraishi, N. (2001). "Liquefaction mechanism of β-O-4 lignin model compound in the presence of phenol under acid catalysis. Part 2. Reaction behaviour and pathways," *Holzforschung* 55(6), 625-630. DOI: 10.1515/HF.2001.102

Liu, J., Liu, H.-F., Deng, L., Liao, B., and Guo, Q.-X. (2013). "Improving aging resistance and mechanical properties of waterborne polyurethanes modified by lignin amines," *Journal of Applied Polymer Science* 130(3), 1736-1742. DOI: 10.1002/app.39267

Liu, Y., and Li, K. (2006). "Preparation and characterization of demethylated lignin-polyethylenimine adhesives," *The Journal of Adhesion* 82(6), 593-605. DOI: 10.1080/00218460600766632

Lora, J. (2008). "Industrial commercial lignins: Sources, properties and applications," in: *Monomers, Polymers and Composites from Renewable Resources*, M. N. Belgacem, and A. Gandini (eds.), Elsevier, Amsterdam, The Netherlands, pp. 225-241.

Lora, J. H., and Glasser, W. G. (2002). "Recent industrial applications of lignin: A sustainable alternative to non-renewable materials," *Journal of Polymers and the Environment* 10(1-2), 39-48. DOI: 10.1023/A:1021070006895

L'udmila, H., Michal, J., Andrea, Š., and Aleš, H. (2015). "Lignin, potential products and their market value," *Wood Research* 60(6), 973-986.

Ma, S., Li, T., Liu, X., and Zhu, J. (2016). "Research progress on bio-based thermosetting resins," *Polymer International* 65(2), 164-173. DOI: 10.1002/pi.5027

Mansouri, N.-E. E., Yuan, Q., and Huang, F. (2011). "Study of chemical modification of alkaline lignin by the glyoxalation reaction," *BioResources* 6(4), 4523-4536.

Matsushita, Y., Inomata, T., Takagi, Y., Hasegawa, T., and Fukushima, K. (2011). "Conversion of sulfuric acid lignin generated during bioethanol production from lignocellulosic materials into polyesters with ε-caprolactone," *Journal of Wood Science* 57(3), 214-218. DOI: 10.1007/s10086-010-1158-6

Matsushita, Y., and Yasuda, S. (2003). "Reactivity of a condensed–type lignin model compound in the Mannich reaction and preparation of cationic surfactant from sulfuric acid lignin," *Journal of Wood Science* 49(2), 166-171. DOI: 10.1007/s100860300026

Maurseth, P. B., and Verspagen, B. (2002). "Knowledge spillovers in Europe: A patent citations analysis," *The Scandinavian Journal of Economics* 104(4), 531-545. DOI: 10.1111/1467-9442.00300

Mendis, G. P., Hua, I., Youngblood, J. P., and Howarter, J. A. (2015). "Enhanced dispersion of lignin in epoxy composites through hydration and Mannich functionalization," *Journal of Applied Polymer Science* 132, Article ID 41263. DOI: 10.1002/app.41263

Meng, Y., Lu, J., Cheng, Y., Li, Q., and Wang, H. (2019). "Lignin-based hydrogels: A review of preparation, properties, and application," *International Journal of Biological Macromolecules* 135, 1006-1019. DOI: 10.1016/j.ijbiomac.2019.05.198

Mogee, M. E. (1991). "Using patent data for technology analysis and planning," *Research-Technology Management* 34(4), 43-49. DOI: 10.1080/08956308.1991.11670755

Mu, Y. B., Wang, C.-P., Zhao, L.-W., and Chu, F.-X. (2009). "Study on composite adhesive of hydroxymethylated lignosulfonate/phenol-formaldehyde resin with low free formaldehyde," *Chemistry and Industry of Forest Products* 29(3), 38-42.

Nadji, H., Bruzzèse, C., Belgacem, M. N., Benaboura, A., and Gandini, A. (2005). "Oxypropylation of lignins and preparation of rigid polyurethane foams from the ensuing polyols," *Macromolecular Materials and Engineering* 290(10), 1009-1016. DOI: 10.1002/mame.200500200

Naegele, H., Pfitzer, J., Ziegler, L., Inone-Kauffmann, E. R., and Eisenreich, N. (2016). "Applications of lignin materials and their composites (lignin applications in various industrial sectors, future trends of lignin and their composites)," in: *Lignin in Polymer Composites*, William Andrew Publishing, New York, NY, USA, pp. 233-244.

Nahmany, M., and Melman, A. (2004). "Chemoselectivity in reactions of esterification," *Organic & Biomolecular Chemistry* 2(11), 1563-1572. DOI: 10.1039/B403161J

Nimz, H. (1969). "Condensation reactions of lignin: Reaction of lignin model compounds with resorcinol and hydrochloric acid," *Holzforschung* 23(3), 84-88. DOI: 10.1515/hfsg.1969.23.3.84

Ogunkoya, D., Li, S., Rojas, O. J., and Fang, T. (2015). "Performance, combustion, and emissions in a diesel engine operated with fuel-in-water emulsions based on lignin," *Applied Energy* 154, 851-861. DOI: 10.1016/j.apenergy.2015.05.036

Olivares, M., Guzmán, J. A., Natho, A., and Saavedra, A. (1988). "Kraft lignin utilization in adhesives," *Wood Science and Technology* 22(2), 157-165. DOI: 10.1007/BF00355851

Oltra, V., and Saint-Jean, M. (2009). "Variety of technological trajectories in low emission vehicles (LEVs): A patent data analysis," *Journal of Cleaner Production* 17(2), 201-213. DOI: 10.1016/j.jclepro.2008.04.023

Pan, H., Sun, G., and Zhao, T. (2013). "Synthesis and characterization of aminated lignin," *International Journal of Biological Macromolecules* 59, 221-226. DOI: 10.1016/j.ijbiomac.2013.04.049

Passauer, L. (2012). "Highly swellable lignin hydrogels: Novel materials with interesting properties," in: *Functional Materials from Renewable Sources*, F. Liebner, and T. Rosenau (eds.), American Chemical Society, Washington D.C., USA, pp. 211-228.

Passoni, V., Scarica, C., Levi, M., Turri, S., and Griffini, G. (2016). "Fractionation of industrial softwood kraft lignin: Solvent selection as a tool for tailored material properties," *ACS Sustainable Chemistry & Engineering* 4(4), 2232-2242. DOI: 10.1021/acssuschemeng.5b01722

Peng, Z., Zou, Y., Xu, S., Zhong, W., and Yang, W. (2018). "High-performance biomass-based flexible solid-state supercapacitor constructed of pressure-sensitive lignin-based and cellulose hydrogels," *ACS Applied Materials & Interfaces* 10(26), 22190-22200. DOI: 10.1021/acsami.8b05171

Perlack, R. D., Wright, L. L., Turhollow, A. F., Graham, R. L., Stokes, B. J., and Erbach, D. C. (2005). *Biomass as Feedstock for a Bioenergy and Bioproducts Industry: The*

bioresources.com

Technical Feasibility of a Billion-ton Annual Supply, Oak Ridge National Laboratory, Oak Ridge, TN, USA.

Pohjanlehto, H., Setälä, H. M., Kiely, D. E., and McDonald, A. G. (2014). "Lignin-xylaric acid-polyurethane-based polymer network systems: Preparation and characterization," *Journal of Applied Polymer Science* 131(1), Article ID 39714. DOI: 10.1002/app.39714

Pouteau, C., Baumberger, S., Cathala, B., and Dole, P. (2004). "Lignin-polymer blends: Evaluation of compatibility by image analysis," *Comptes Rendus Biologies* 327(9-10), 935-943. DOI: 10.1016/j.crvi.2004.08.008

Pouteau, C., Dole, P., Cathala, B., Averous, L., and Boquillon, N. (2003). "Antioxidant properties of lignin in polypropylene," *Polymer Degradation and Stability* 81(1), 9-18. DOI: 10.1016/S0141-3910(03)00057-0

Raquez, J.-M., Deléglise, M., Lacrampe, M.-F., and Krawczak, P. (2010). "Thermosetting (bio)materials derived from renewable resources: A critical review," *Progress in Polymer Science* 35(4), 487-509. DOI: 10.1016/j.progpolymsci.2010.01.001

Rossilo-Calle, F., de Groot, P., Hemstock, S. L., and Woods, J. (2007). *The Biomass Assessment Handbook*, Earthscan, London, England.

Sadeghifar, H., and Argyropoulos, D. S. (2015). "Correlations of the antioxidant properties of softwood kraft lignin fractions with the thermal stability of its blends with polyethylene," *ACS Sustainable Chemistry & Engineering* 3(2), 349-356. DOI: 10.1021/sc500756n

Sadeghifar, H., and Argyropoulos, D. S. (2016). "Macroscopic behavior of kraft lignin fractions: Melt stability considerations for lignin–polyethylene blends," *ACS Sustainable Chemistry & Engineering* 4(10), 5160-5166. DOI: 10.1021/acssuschemeng.6b00636

Sadeghifar, H., Cui, C., and Argyropoulos, D. S. (2012). "Toward thermoplastic lignin polymers. Part 1. Selective masking of phenolic hydroxyl groups in kraft lignins *via* methylation and oxypropylation chemistries," *Industrial & Engineering Chemistry Research* 51(51), 16713-16720. DOI: 10.1021/ie301848j

Schutyser, W., Renders, T., Van den Bosch, S., Koelewijn, S.-F., Beckham, G. T., and Sels, B. F. (2018). "Chemicals from lignin: An interplay of lignocellulose fractionation, depolymerisation, and upgrading," *Chemical Society Reviews* 47(3), 852-908. DOI: 10.1039/C7CS00566K

Sen, S., Patil, S., and Argyropoulos, D. S. (2015). "Thermal properties of lignin in copolymers, blends, and composites: A review," *Green Chemistry* 17(11), 4862-4887. DOI: 10.1039/C5GC01066G

Setua, D. K., Shukla, M. K., Nigam, V., Singh, H., and Mathur, G. N. (2000). "Lignin reinforced rubber composites," *Polymer Composites* 21(6), 988-995. DOI: 10.1002/pc.10252

Su, L., Xing, Z., Wang, D., Xu, G., Ren, S., and Fang, G. (2013). "Mechanical properties research and structural characterization of alkali lignin / poly(vinyl alcohol) reaction films," *BioResources* 8(3), 3532-3543. DOI: 10.15376/biores.8.3.3532-3543

Sun, Z., Fridrich, B., de Santi, A., Elangovan, S., and Barta, K. (2018). "Bright side of lignin depolymerization: Toward new platform chemicals," *Chemical Reviews* 118(2), 614-678. DOI: 10.1021/acs.chemrev.7b00588

Tan, T. T. M. (1996). "Cardanol–lignin-based polyurethanes," *Polymer International* 41(1), 13-16. DOI: 10.1002/(SICI)1097-0126(199609)41:1<13::AID-PI557>3.0.CO;2-8

Thakur, S., Govender, P. P., Mamo, M. A., Tamulevicius, S., Mishra, Y. K., and Thakur, V. K. (2017). "Progress in lignin hydrogels and nanocomposites for water purification: Future perspectives," *Vacuum* 146, 342-355. DOI: 10.1016/j.vacuum.2017.08.011

Thakur, V. K., Thakur, M. K., Raghavan, P., and Kessler, M. R. (2014). "Progress in green polymer composites from lignin for multifunctional applications: A review," *ACS Sustainable Chemistry & Engineering* 2(5), 1072-1092. DOI: 10.1021/sc500087z

Thring, R. W., Vanderlaan, M. N., and Griffin, S. L. (1997). "Polyurethanes from Alcell® lignin," *Biomass and Bioenergy* 13(3), 125-132. DOI: 10.1016/S0961-9534(97)00030-5

Tran, C. D., Chen, J., Keum, J. K., and Naskar, A. K. (2016). "A new class of renewable thermoplastics with extraordinary performance from nanostructured lignin-elastomers," *Advanced Functional Materials* 26(16), 2677-2685. DOI: 10.1002/adfm.201504990

Trappey, C. V., Wu, H.-Y., Taghaboni-Dutta, F., and Trappey, A. J. C. (2011). "Using patent data for technology forecasting: China RFID patent analysis," *Advanced Engineering Informatics* 25(1), 53-64. DOI: 10.1016/j.aei.2010.05.007

Tribot, A., Amer, G., Abdou Alio, M., de Baynast, H., Delattre, C., Pons, A., Mathias, J.-D., Callois, J.-M., Vial, C., and Michaud, P., *et al.* (2019). "Wood-lignin: Supply, extraction processes and use as bio-based material," *European Polymer Journal* 112, 228-240. DOI: 10.1016/j.eurpolymj.2019.01.007

Tuck, C. O., Pérez, E., Horváth, I. T., Sheldon, R. A., and Poliakoff, M. (2012). "Valorization of biomass: Deriving more value from waste," *Science* 337(6095), 695-699. DOI: 10.1126/science.1218930

Upton, B. M., and Kasko, A. M. (2016). "Strategies for the conversion of lignin to high-value polymeric materials: Review and perspective," *Chemical Reviews* 116(4), 2275-2306. DOI: 10.1021/acs.chemrev.5b00345

Vanderlaan, M. N., and Thring, R. W. (1998). "Polyurethanes from Alcell® lignin fractions obtained by sequential solvent extraction," *Biomass and Bioenergy* 14(5-6), 525-531. DOI: 10.1016/S0961-9534(97)10058-7

Wang, C., Kelley, S. S., and Venditti, R. A. (2016). "Lignin-based thermoplastic materials," *ChemSusChem* 9(8), 770-783. DOI: 10.1002/cssc.201501531

Wang, H., Liu, W., Huang, J., Yang, D., and Qiu, X. (2018). "Bioinspired engineering towards tailoring advanced lignin/rubber elastomers," *Polymers* 10(9), Article number 1033. DOI: 10.3390/polym10091033

Wang, H., Ruan, H., Pei, H., Wang, H., Chen, X., Tucker, M. P., Cort, J. R., and Yang, B. (2015). "Biomass-derived lignin to jet fuel range hydrocarbons *via* aqueous phase hydrodeoxygenation," *Green Chemistry* 17(12), 5131-5135. DOI: 10.1039/C5GC01534K

Wang, J., Manley, R. S. J., and Feldman, D. (1992). "Synthetic polymer-lignin copolymers and blends," *Progress in Polymer Science* 17(4), 611-646. DOI: 10.1016/0079-6700(92)90003-H

Wang, J., Yao, K., Korich, A. L., Li, S., Ma, S., Ploehn, H. J., Iovine, P. M., Wang, C., Chu, F., and Tang, C. (2011). "Combining renewable gum rosin and lignin: Towards

bioresources.com

hydrophobic polymer composites by controlled polymerization," *Journal of Polymer Science Part A: Polymer Chemistry* 49(17), 3728-3738. DOI: 10.1002/pola.24809

Witter, D. (2015*). IBIS World Industry Report 32521: Plastic & Resin Manufacturing in the US*, IBIS World, Melbourne, Australia.

Witzler, M., Alzagameem, A., Bergs, M., Khaldi-Hansen, B. E., Klein, S. E., Hielscher, D., Kamm, B., Kreyenschmidt, J., Tobiasch, E., and Schulze, M. (2018). "Lignin-derived biomaterials for drug release and tissue engineering," *Molecules* 23(8), Article number 1885. DOI: 10.3390/molecules23081885

Xu, W., Wang, X., Sandler, N., Willför, S., and Xu, C. (2018). "Three-dimensional printing of wood-derived biopolymers: A review focused on biomedical applications," *ACS Sustainable Chemistry & Engineering* 6(5), 5663-5680. DOI: 10.1021/acssuschemeng.7b03924

Yu, P., He, H., Jia, Y., Tian, S., Chen, J., Jia, D., and Luo, Y. (2016). "A comprehensive study on lignin as a green alternative of silica in natural rubber composites," *Polymer Testing* 54, 176-185. DOI: 10.1016/j.polymertesting.2016.07.014

Zhang, Q., Zhang, G., Xu, J., Gao, C., and Wu, Y. (2015). "Recent advances on lignin-derived polyurethane polymers," *Reviews on Advanced Materials Science* 40(2), 146-154.

Zhang, W., Ma, Y., Wang, C., Li, S., Zhang, M., and Chu, F. (2013). "Preparation and properties of lignin–phenol–formaldehyde resins based on different biorefinery residues of agricultural biomass," *Industrial Crops and Products* 43, 326-333. DOI: 10.1016/j.indcrop.2012.07.037

Zhu, H., Peng, Z., Chen, Y., Li, G., Wang, L., Tang, Y., Pang, R., Khan, Z. U. H., and Wan, P. (2014). "Preparation and characterization of flame retardant polyurethane foams containing phosphorus–nitrogen-functionalized lignin," *RSC Advances* 4(98), 55271-55279. DOI: 10.1039/C4RA08429B