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Cellulose first fractionation strategy in lignin valorization: A mini review

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ABSTRACT

Lignin, a naturally abundant aromatic polymer of natural origin, offers numerous desired intrinsic properties belonging to rich functional groups. However, the lignin properties vary influenced by the source of biomass (hardwood, softwood, and herbaceous) with different monomer unit proportions, delignification methods, and isolation techniques. To extract lignin, two routes have been introduced i.e. cellulose first fractionation and lignin first fractionation. The focus of this review is revisiting the strategy of cellulose first fractionation in which lignin is mainly present as a side product of the delignification process via the sulfur-bearing process and the non-sulfur-bearing process. After that process, the isolation process was employed in black liquor as a by-product of the process. By this route, technical lignin is produced with the potential to convert into biomaterial feedstocks. The main property concern of this lignin is its condensed structure which requires further modification for specific purposes. Physical and chemical modification can be introduced to increase the reactivity of lignin to widen the application.

Keyword: Biorefinery, Condensation, Fractionation, Lignin Modification, Technical Lignin

1. Introduction

The size of the world market for lignin was projected to be USD 1.04 billion in 2022, and between 2023 and 2030, it is projected to expand at a compound yearly growth rate (CAGR) of 4.9%. In the upcoming years, it is projected that the increasing trend of employing lignin will accelerate market expansion [1]. Lignin is the main source of bio-aromatic compounds on earth and has a variety of possible commercial applications [2] due to the richness of its functional groups and complexity [3, 4]. It can serve as a substrate for the synthesis of chemicals, biofuels, and composite materials, particularly aromatic and phenolic compounds [5]. In 2022, lignosulfonates became the market's largest product segment. Throughout the forecast period, it is anticipated that this market segment will continue to dominate at a CAGR of 4.4% [1].

It is still regarded as a secondary chance to obtain some more value of lignin, though, and is not given top priority such as cellulose in the processing of lignocellulosic biomass. Many attempts Continue to valorize lignin effectively to reach profitability of biomass in the biorefinery concept. Harnessing lignin as renewable chemical feedstock is still challenging in the view of complementary valorization. The condensed structure of lignin brings new challenges in disassembly into chemicals. Thus, prevention of structural lignin degradation that provides efficient and selective lignin into aromatics conversion becomes interesting in new biorefinery platforms.

There are two strategies to produce lignin "cellulose first fractionation and lignin first fractionation [6]. Interestingly, fractionation methods that preserve the structural integrity of the carbohydrates while preventing lignin condensation are based on active stabilizing processes [6, 7]. In the first method, the main concern is how to obtain rich cellulose with lignin as a by-product contained in black liquor. Practically in the pulp and paper industry, the main source of this lignin type (further call as technical lignin) has used this route, in which lignin was used to generate power and heat via combustion [8]. Technical lignin can be obtained by the precipitating method by adding some chemical agents in the alkaline black liquor to precipitate lignin such as common mineral acids, or organic acids while considering the pH of the liquor. There are two technical lignin types i.e. non-sulfur lignin and sulfur lignin depending on the delignification technic used (sulfur-bearing process vs non-sulfur-bearing process).

However, in first method faces a challenge in which technical lignin becomes a condensed structure that can lead to difficulty in the reactivity in future processes. Therefore, to produce native-like lignin having non condensed structure is proposed in in second method route, lignin first fractionation. Biomass has been fractionated with the first concern being native-like-lignin or lignin does not by-product from cellulose extraction. Catalytic oxidative depolymerization and catalytic reductive depolymerization are two fractionation techniques that have been carried out to yield aromatics for energy and fine chemistry [9] in the form of a mixture of bifunctional monoaromatics and a mixture of mono phenolics, respectively (Figure 1).

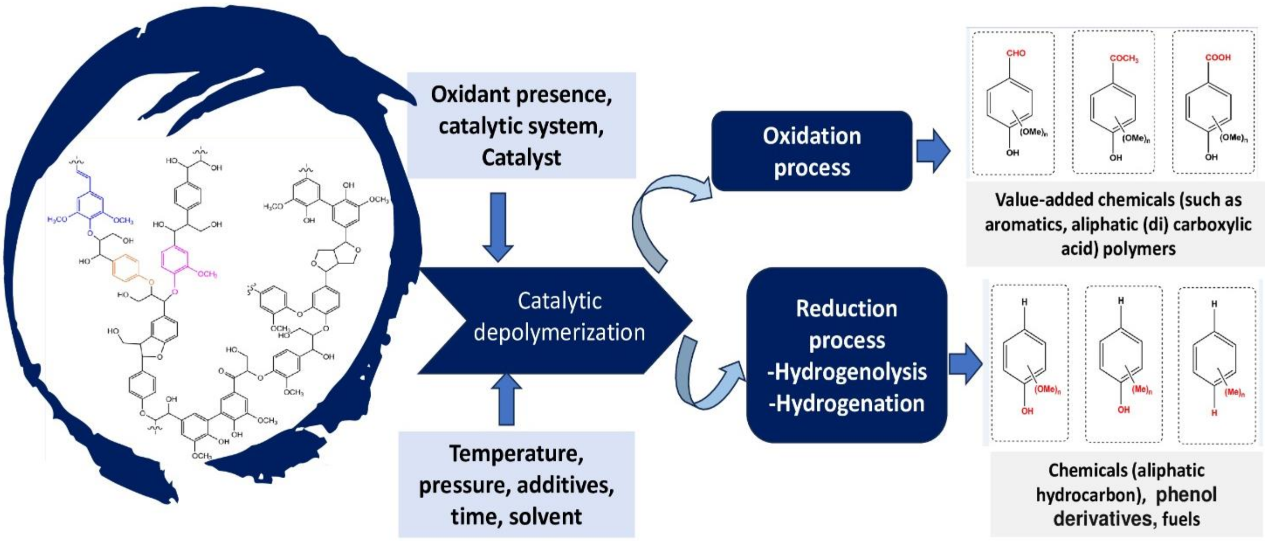

Figure 1. Catalytic depolymerization of lignin via oxidation and reduction to produce aromatics, polymers, and BTX

In this literature review, we revisit the strategy for producing technical lignin with the potential for its valorization including the modification technique of lignin to improve the reactivity functional group of lignin. This perspective can become a guide for future research and development of cellulose first fractionation for prospective lignin-based bioproducts that have not yet been presented in previous literature. Several public databases including Scopus, WOS, PubMed, and Google Scholar were used as a basis for this literature review. Keywords such as biorefinery, lignin first fractionation, cellulose first fractionation, biomass, and lignin application were applied in the screening of literature.

2. Lignin production strategy of cellulose first fractionation

Delignification of lignocellulose biomass is a critical step that affects the purity of lignin and makes it easier to break down lignin-lignin and lignin-carbohydrate complexes that surround cellulose [10]. The origin of biomass, processing techniques, and isolation methods all have a substantial impact on the physicochemical characteristics of lignin, which presents a considerable obstacle to its application [8, 10, 11]. The variability and recalcitrance of the structure resulting from the three-dimensional polymeric structure of aromatic compounds is the primary obstacle to the valorization of lignin. The problem of lignin from this cellulose first fractionation method is a condensed structure that needs severe conditions to handle it.

The route in cellulose's first fractionation to produce lignin involves high temperature and equipment. Some methods such as alkaline delignification such as kraft and sulfite pulping as a sulfur-bearing process, or soda, and organosolv pretreatment, steam explosion pretreatment, etc as a non-sulfur-bearing process are wellknown as effective techniques in lignin-extraction [9, 11]. This technique inevitably leads to condensation [12]. The green delignification method for lignin production has gained interest lately even still on a laboratory scale such as ionic liquid, liquid hot water, and deep eutectic solvent (DES) pretreatment. Figure 2 shows the route of the first cellulose fractionation to produce lignin from biomass in which lignin is mined from black liquor after the delignification process. This lignin has a high cross-linked structure which for breaking down requires high energy that is linear with high production cost. Therefore, valorizing lignin for bioproducts such as polymer material and aromatic will not be optimal [7].

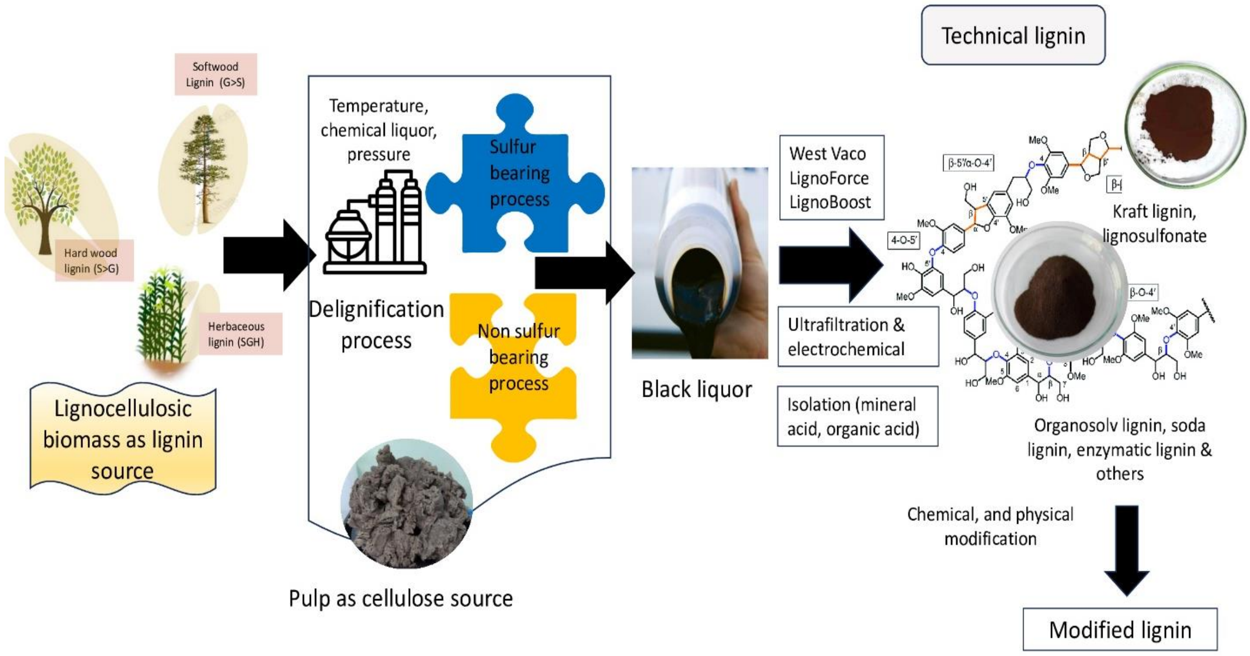

Figure 2. Cellulose first fractionation route of biomass to produce lignin

As can be seen in Figure 2, there are 3 groups of lignocellulosic biomass as lignin sources with variation in lignin unit proportion which are connected by C-C and aryl ether interunit linkages, including hardwood (Guiacyl (G), Syringyl (S), trace of para-hydroxyphenyl (H)), softwood (majority G with low H level), and herbaceous biomass (G, H, S) [13, 14]. Common interunit linkages found in lignin with different quantities include most abundance aryl ether linkage (β-O-4), two C-C linkage (resinol (β-β) and phenylcomaran (β-5)). The other linkage such as biphenyl (5–5), spirodienone (β-1), and the biphenyl ether (4-O-5) were present in fewer amounts [15, 16].

The chemistry and characteristics of lignin are greatly impacted by these differences, particularly. Thus, lignin's functional groups and overall chemical structure have a substantial influence on the result of its processing [9]. High-content ash in herbaceous biomass can interfere with the effective process and lignin characteristics such as purity. To increase the lignin purity, some techniques have been employed such as various washing treatment frequencies during the isolation process [17, 18] or the fractionation step [19]. Other than that, pretreatment before delignification has successfully improved the lignin yield by removing extractives attached to biomass such as in areca leaf sheath (ALS) [20].

Fitria et al. [21] summarize some strategies to manage high ash content in biomass. Washing/leaching treatment by leaching agents such as water, acid, and chelating agents are reported for demineralization of high-mineral content biomass after harvesting. In line with that review, to lower the inorganic component (ash), demineralization usually entails leaching biomass in water or diluted acid [22]. Besides that, pretreatment such as acid infusion, metal-enriched pretreatment, and pH adjustment can be applied to manage the mineral-containing biomass. All mentioned technique helps to reach lignin.

The effective separation of native high molecular-weight lignin is severely limited by the intact matrix of lignocellulosic biomass, which exhibits substantial resistance to physicochemical treatment. Though they differ greatly from the techniques usually employed for larger-scale lignin isolation, many unique isolation techniques are comparable [16]. The acidification process is an effective and cost-effective method for lignin extraction from black liquor [23]. Mainly mineral acids such as hydrochloric acid, sulfuric acid, phosphoric acid, etc were used to precipitate lignin in black liquor. A method of acidifying black liquor to extract lignin is called LignoBoost. Using CO_2 injection to get the pH down to roughly 9 to 10.5 precipitates lignin in this procedure [24]. However, acidification with mineral acid can negative effect on the environment. Also minimizing the alteration of structural integration of lignin motivates to search the green extraction process involving relatively "safe" chemical agents. Negligeable structural modifications in lignin can be obtained by isolation using organic extraction under milder circumstances without the need for any basic or acidic catalysts [16]. Additionally effective at improving lignin extraction, organic acids can also be used as solvents. Two of the most researched organic acids for lignin isolation without significant structural modification are formic and acetic acids [16]. Citric acid and lactic acid are also included as organic acids that can be employed on a large scale with citric acid being the most used [25].

Gaining the high-level purity of lignin is highly important in the isolation strategy, but lignin with a non-condense structure is also taking consideration. Compared to the "native" lignin structure in biomass the lignin, structure turns to modification after fractionation, through condensation reaction (a stable C-C bond formation) in producing "technical" lignin. Figure 3 describes the formation of C-C linkage when harsh treatment is employed in lignin extraction. It is more challenging toward depolymerization [9, 26] and overwhelms their downstream upgrading [16]. Li and colleagues showed that the lignin extracted using Deep eutectic solvent (DES), a green solvent, exhibited exceptional levels of purity and thermostability [7, 27]. DESs, which are made up of compounds with hydrogen bonding networks and choline chloride (ChCl), with considered low-cost, simple production, have no toxic characteristics and have minimum disposal costs [16].

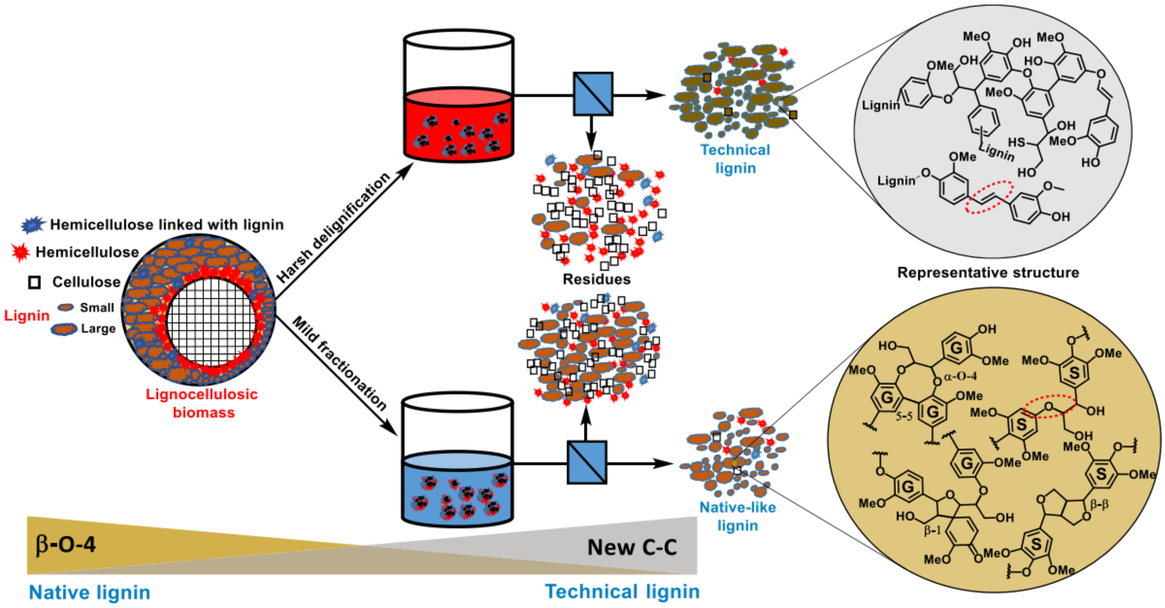

Figure 3. Representative formation of carbon-carbon linkage in technical lignin after harsh delignification of biomass containing native lignin with high β-0-4 [16]. Copyright CC BY 4.0 Deed | Attribution 4.0 International | Creative Commons

3. Mapping of potency to the valorization lignin

It is still very desirable to valorize a significant portion of co-formed lignin in biorefineries or the pulp industry that is intended for cellulose exploitation [9]. Only 2-5% of the lignin produced in the industry is specifically processed for use in the commercial sector; the majority is burned directly to provide heat and electricity [11]. As the largest abundance of aromatic polymer, lignin becomes feedstock for valorizing into various bioproducts except for money [28] which can be utilized in many applications. The extraction step provides lignin in microsize that can be directly processed; however, to widen the application with homogenous properties the size can be modified in nanosize. The advantages of lignin nanoparticles (LNPs) include enhanced structural and size control, high stability, antioxidant activity, high activity, and superior biocompatibility and biodegradability [29]. Nano lignin can be obtained with two strategies i.e. top-down and bottom-up techniques. Chemical, physical, or combination methods of them have been reported by several previous literature [30]. Self-assembly, cross-linking or polymerization, solvent shifting (THF, DMSO, acetone some of such as the self-assembly method), acid precipitation, or solvent exchange [29].

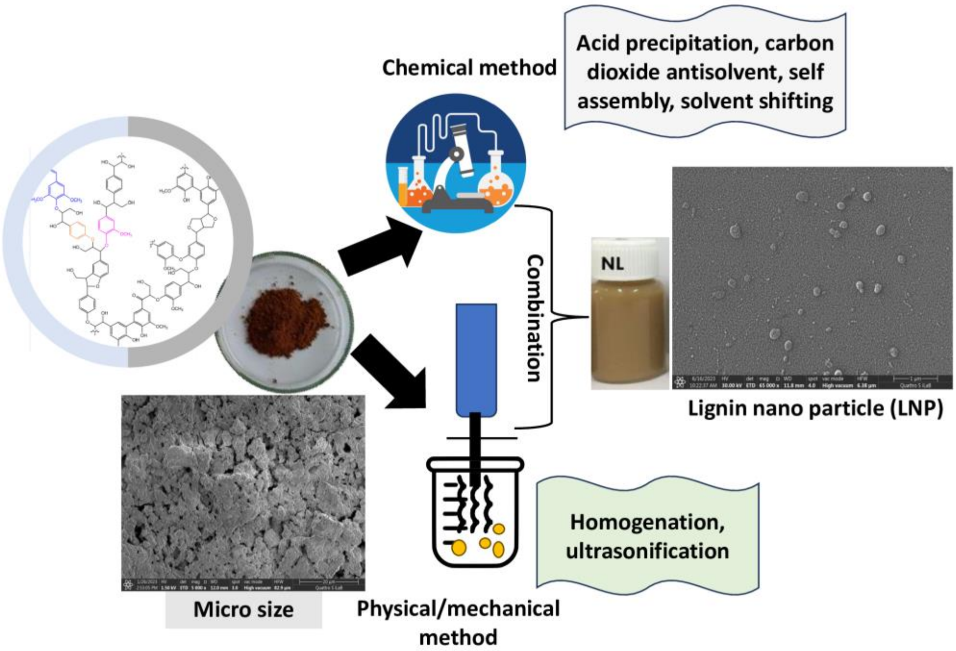

Figure 4. Preparation of lignin nanoparticles via chemical and physical/mechanical methods

In lignin conversion into bioproducts, lignin has been employed in any modification treatment for improving the reactivity of the functional group of lignin as indicated in Figure 2. The functionalization of lignin can be achieved through graft copolymerization, aromatic ring modification, hydroxyl group modification, and methoxy group modification [31]. On the other hand, physical methods are created to improve the surface properties of lignin and the resulting composite materials, such as freeze-drying, sorption, and radiation [32]. Three main routes of chemical modification of lignin are (1) depolymerization/fragmentation to produce chemicals rich in aromatic structure, (2) reaction of hydroxyl groups with chemical agents, (3) formation of new chemically active sites [4, 32]. Most of the attempt to modify lignin was carried out via esterification as a chemical reaction type by using chemical agents such as acyl chlorides, carboxylic anhydrides, carboxylic acids, and lactones [32].

4. Conclusion

Lignin extracted from cellulose first fractionation has shown potential as a source of natural aromatic polymers. In this method, variation in lignin characteristics is influenced by variation in lignocellulosic biomass, method of delignification, isolation technique, etc needs to be considered. Biomass with high ash and extractive content needs to be pretreated such as by leaching/washing treatment or boiling. This technique facilitates to production of high-yield lignin. The acidification method with inorganic acid is a common method to precipitate lignin from black liquor. Considering reducing the negative impact on the lignin properties and the environment, the introduction of green chemical agents is highlighted. The condensed structure of technical liqnin can limit on wide application area. chemical modification of lignin can become the solution to increase the reactivity of the available functional groups of lignin. Besides that, the size reduction of microsize into nano by top-down and bottom-up approach is also the method for improving the lignin properties and to some extent altering the reaction reactivity.

References

[1] G. V. Research. "Lignin Market Size, Share & Trends Analysis Report By Product (Lingo-sulfonates, Kraft Lignin, Organosolv Lignin, Others), By Application, By Region, And Segment Forecasts, 2023 - 2030." grand View Research. https://www.grandviewresearch.com/industry-analysis/lignin-market# (accessed 16 January 2024, 2024).

[2] T. Aro and P. Fatehi, "Production and Application of Lignosulfonates and Sulfonated Lignin," *ChemSusChem*, vol. 10, no. 9, pp. 1861-1877, 2017, doi: https://doi.org/10.1002/cssc.201700082.

[3] J. Xu *et al.*, "Biomass Fractionation and Lignin Fractionation towards Lignin Valorization," *ChemSusChem,* vol. 13, no. 17, pp. 4284-4295, 2020/09/07 2020, doi: https://doi.org/10.1002/cssc.202001491.

[4] E. A. Agustiany *et al.*, "Recent developments in lignin modification and its application in lignin-based green composites: A review," *Polymer Composites,* vol. 43, no. 8, pp. 4848-4865, 2022/08/01 2022, doi: https://doi.org/10.1002/pc.26824.

[5] P. Yadav *et al.*, "Sugarcane bagasse: an important lignocellulosic substrate for production of enzymes and biofuels," *Biomass Conversion and Biorefinery,* 2022/05/28 2022, doi: 10.1007/s13399-022-02791-9.

[6] T. Renders, S. Van den Bosch, S. F. Koelewijn, W. Schutyser, and B. F. Sels, "Lignin-first biomass fractionation: the advent of active stabilisation strategies," *Energy & Environmental Science,* 10.1039/C7EE01298E vol. 10, no. 7, pp. 1551-1557, 2017, doi: 10.1039/C7EE01298E.

[7] S. Ma *et al.*, "Chemical structure change of lignin extracted from bamboo biomass by maleic acid," *International Journal of Biological Macromolecules,* vol. 221, pp. 986-993, 2022/11/30/ 2022, doi: https://doi.org/10.1016/j.ijbiomac.2022.09.002.

[8] J. Liu, X. Li, M. Li, and Y. Zheng, "Chapter Six - Lignin biorefinery: Lignin source, isolation, characterization, and bioconversion," in *Advances in Bioenergy*, vol. 7, Y. Li and Y. Zhou Eds.: Elsevier, 2022, pp. 211-270.

[9] D. Bourbiaux, J. Pu, F. Rataboul, L. Djakovitch, C. Geantet, and D. Laurenti, "Reductive or oxidative catalytic lignin depolymerization: An overview of recent advances," *Catalysis Today,* vol. 373, pp. 24-37, 2021/08/01/ 2021, doi: https://doi.org/10.1016/j.cattod.2021.03.027.

[10] M. H. Tanis, O. Wallberg, M. Galbe, and B. Al-Rudainy, "Lignin Extraction by Using Two-Step Fractionation: A Review," *Molecules,* vol. 29, no. 1, p. 98, 2024. [Online]. Available: https://www.mdpi.com/1420-3049/29/1/98.

[11] M. R. Ridho *et al.*, "Lignin as Green Filler in Polymer Composites: Development Methods, Characteristics, and Potential Applications," *Advances in Materials Science and Engineering,* vol. 2022, p. 1363481, 2022/04/30 2022, doi: 10.1155/2022/1363481.

[12] B. M. Upton and A. M. Kasko, "Strategies for the conversion of lignin to high-value polymeric materials: review and perspective," *Chemical reviews,* vol. 116, no. 4, pp. 2275-2306, 2016.

[13] W. O. S. Doherty, P. Mousavioun, and C. M. Fellows, "Value-adding to cellulosic ethanol: Lignin polymers," *Industrial Crops and Products,* vol. 33, no. 2, pp. 259-276, 2011/03/01/ 2011, doi: https://doi.org/10.1016/j.indcrop.2010.10.022.

[14] S. Sethupathy *et al.*, "Lignin valorization: Status, challenges and opportunities," *Bioresource Technology,* vol. 347, p. 126696, 2022.

[15] L. Yao, H. Yang, X. Meng, and A. J. Ragauskas, "Toward a Fundamental Understanding of the Role of Lignin in the Biorefinery Process," (in English), *Frontiers in Energy Research,* Review vol. 9, 2022-January-03 2022, doi: 10.3389/fenrg.2021.804086.

[16] Z. Wang and P. J. Deuss, "The isolation of lignin with native-like structure," *Biotechnology Advances,* vol. 68, p. 108230, 2023/11/01/ 2023, doi: https://doi.org/10.1016/j.biotechadv.2023.108230.

[17] E. W. Madyaratri, A. H. Iswanto, D. S. Nawawi, S. H. Lee, and W. Fatriasari, "Improvement of Thermal Behavior of Rattan by Lignosulphonate Impregnation Treatment," *Forests,* vol. 13, no. 11, p. 1773, 2022. [Online]. Available: https://www.mdpi.com/1999-4907/13/11/1773.

[18] E. A. Agustiany, K. Suzana, I. Guswenrivo, A. H. Prianto, D. S. Nawawi, and W. Fatriasari, "The effect of the lignin isolation method from oil palm empty fruit bunch black liquor for seed coating material," *Biomass Conversion and Biorefinery,* 2023/09/20 2023, doi: 10.1007/s13399-023-04874-7.

[19] N. N. Solihat *et al.*, "Physical and Chemical Properties of Acacia mangium Lignin Isolated from Pulp Mill Byproduct for Potential Application in Wood Composites," *Polymers,* vol. 14, no. 3, p. 491, 2022. [Online]. Available: https://www.mdpi.com/2073-4360/14/3/491.

[20] M. R. Ridho, D. S. Nawawi, I. Juliana, and W. Fatriasari, "The kraft lignin characteristics of areca leaf sheath isolated by phosphoric acid," *Bioresource Technology Reports,* vol. 23, p. 101569, 2023/09/01/ 2023, doi: https://doi.org/10.1016/j.biteb.2023.101569.

[21] Fitria, J. Liu, and B. Yang, "Roles of mineral matter in biomass processing to biofuels," *Biofuels, Bioproducts and Biorefining,* vol. 17, no. 3, pp. 696-717, 2023/05/01 2023, doi: https://doi.org/10.1002/bbb.2468.

[22] T. Wigley, A. C. K. Yip, and S. Pang, "The use of demineralisation and torrefaction to improve the properties of biomass intended as a feedstock for fast pyrolysis," *Journal of Analytical and Applied Pyrolysis,* vol. 113, pp. 296-306, 2015/05/01/ 2015, doi: https://doi.org/10.1016/j.jaap.2015.02.007.

[23] N. D. Luong *et al.*, "An eco-friendly and efficient route of lignin extraction from black liquor and a lignin-based copolyester synthesis," *Polymer Bulletin*, vol. 68, no. 3, pp. 879-890, 2012/02/01 2012, doi: 10.1007/s00289-011-0658-x.

[24] F. Gomes, R. Eloy de Souza, E. Brito, and R. Lelis, "A review on lignin sources and uses," *Journal of Applied Biotechnology & Bioengineering*, pp. 100-105, 05/22 2020, doi: 10.15406/jabb.2020.07.00222.

[25] P. Singh nee' Nigam, "Production of organic acids from agro-industrial residues," *Biotechnology for Agro-Industrial Residues Utilisation: Utilisation of Agro-Residues*, pp. 37-60, 2009.

[26] R. Souza, F. Gomes, E. Brito, and R. Costa Lelis, "A review on lignin sources and uses," *J Appl Biotechnol Bioeng*, vol. 7, no. 3, pp. 100-105, 2020.

[27] W.-X. Li *et al.*, "Insights into bamboo delignification with acidic deep eutectic solvents pretreatment for enhanced lignin fractionation and valorization," *Industrial Crops and Products*, vol. 170, p. 113692, 2021.

[28] F. H. M. Graichen *et al.*, "Yes, we can make money out of lignin and other bio-based resources," *Industrial Crops and Products*, vol. 106, pp. 74-85, 2017/11/01/ 2017, doi: https://doi.org/10.1016/j.indcrop.2016.10.036.

[29] B. Zhu, Y. Xu, and H. Xu, "Preparation and application of lignin nanoparticles: a review," *Nano Futures*, vol. 6, no. 3, p. 032004, 2022/08/11 2022, doi: 10.1088/2399-1984/ac8400.

[30] M. H. Hussin *et al.*, "A recent advancement on preparation, characterization and application of nanolignin," *International Journal of Biological Macromolecules*, vol. 200, pp. 303-326, 2022/03/01/ 2022, doi: https://doi.org/10.1016/j.ijbiomac.2022.01.007.

[31] M. J. Gan, Y. Q. Niu, X. J. Qu, and C. H. Zhou, "Lignin to value-added chemicals and advanced materials: extraction, degradation, and functionalization," *Green Chemistry*, 10.1039/D2GC00092J vol. 24, no. 20, pp. 7705-7750, 2022, doi: 10.1039/D2GC00092J.

[32] K. Komisarz, T. M. Majka, and K. Pielichowski, "Chemical and Physical Modification of Lignin for Green Polymeric Composite Materials," *Materials*, vol. 16, no. 1, doi: 10.3390/ma16010016.