

Effective Lignin Utilization Strategy: Major Depolymerization Technologies, Purification Process and Production of Valuable Material

Pallabi Sinha Roy, Gil Garnier, Florent Allais, Kei Saito

▶ **To cite this version:**

Pallabi Sinha Roy, Gil Garnier, Florent Allais, Kei Saito. Effective Lignin Utilization Strategy: Major Depolymerization Technologies, Purification Process and Production of Valuable Material. Chemistry Letters, 2021, 50 (6), pp.1123-1130. 10.1246/cl.200873 . hal-03842366

HAL Id: hal-03842366

https://agroparistech.hal.science/hal-03842366

Submitted on 7 Nov 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Received: November 30, 2020 | Accepted: January 24, 2021 | Web Released: January 28, 2021 CL-200873

Vol. 50 Commemorative Highlight Review

Effective Lignin Utilization Strategy: Major Depolymerization Technologies, Purification Process and Production of Valuable Material

Pallabi Sinha Roy,[1,2] Gil Garnier,[2,3] Florent Allais,[2,3] and Kei Saito*[1,2,4]

[1]School of Chemistry, Monash University, Clayton 3800, VIC, Australia
[2]BioPRIA, Department of Chemical Engineering, Monash University, Clayton 3800, VIC, Australia
[3]URD Agro-Biotechnologies Industrielles (ABI), CEBB, AgroParisTech, 51100, Pomacle, France
[4]Graduate School of Advanced Integrated Studies in Human Survivability, Kyoto University, Higashi-Ichijo-Kan, 1 Yoshida-nakaadachicho, Sakyo-ku, Kyoto 606-8306, Japan

E-mail: kei.saito@monash.edu



Prof. Kei Saito is currently a Professor at Graduate School of Advanced Integrated Studies in Human Survivability, Kyoto University, Japan. Before joining Kyoto University, he was a tenured Associate Professor (2019–2020), Senior Lecturer (2016–2018), and Lecturer (2007–2015) at School of Chemistry, Monash University, Australia and JST PRESTO researcher (2015–2019), Japan. Before then, a Postdoctoral Fellow at the Centre for Green Chemistry, UMass Lowell, USA (2005–2007) and at the Graduate School of Science and Engineering at Waseda University, Japan (2004–2005). His research interests are in developing new synthesis and production methods for novel sustainable polymeric materials for industrial applications.



Pallabi Sinha Roy graduated from the University of Calcutta with a bachelor's degree in textile engineering. She then completed her master's degree in fiber science and textile engineering from the Institute of Chemical Technology (India). She worked as a process engineer in Jindal Poly Films Limited (India) on spunbond-spunmelt technology (Reicofil 4S) for 3.2 years. She is currently pursuing her doctoral research in the field of biopolymers and green chemistry from Monash University (Australia). Her project mainly focuses on developing high-value chemicals or polymers from renewable resources.



Gil Garnier is Director of the Bioresource Processing Research Institute of Australia (BioPRIA) and Professor in Chemical Engineering, Monash University, Australia (2005–). He is also Director of the ARC transformation Hub- Processing Advanced Lignocellulosics (PALS). Previously, Gil was Team Leader/Senior Research Scientist at Kimberly-Clark (2000–2005) and Paprican Professor in Chemical Engineering, McGill University (1993–2000). His expertise is the application of (bio)polymers and Interfacial Engineering to biodiagnostics and lignocellulosic materials. His research team aims at developing novel paper biodiagnostics and implementing biorefineries based on the concepts of green chemistry and sustainable processes.



Florent Allais got a PhD from the University of Florida (USA) in 2004, then did two postdocs in France (ESPCI, Paris – ICSN-CNRS, Gif-sur-Yvette), before joining the INRAe as a Junior Scientist in Versailles, France (2007). In 2012, he became a Full Professor at AgroParisTech and the director of URD ABI at Pomacle, France. Since 2019, Florent Allais is also Adjunct Professor at Monash University and Courtesy Associate Professor at the University of Florida. His research investigates the combined use of biotechnologies, green chemistry and downstream processing for the development and optimization of sustainable processes and high value-added products from biomass.

 © 2021 The Chemical Society of Japan

Abstract

Considering the drawbacks associated with fossil-based molecules, polymers and materials, lignin has acquired immense popularity owing to its distinct advantages. However, to date it has not been widely commercialized to produce fossil replacements mainly due to its complex structure and purification hassle. Constant research is going on to discover ways to depolymerize lignin to produce various aromatic chemicals. This highlight review summarizes the key investigations carried out in the field of lignin valorization, purification and the valuable products generated from lignin.

Keywords: Lignin | Depolymerization | Valorization

Introduction

Being a promising aromatic biopolymer, lignin has a lot to offer as a major source of different aromatic chemicals, which are currently derived from petrochemical sources. The faster depletion rate of fossil resources unquestionably is a huge factor in the current scenario. Lignocellulosic biomass contains 15–35% of lignin by weight.[1] It is a prime source of aromatic polymer in nature, inexpensive and renewable indeed.[2] Lignin structure typically consists of three monolignols, which are phenylpropanoid units, such as *p*-coumaryl alcohol (H-unit), coniferyl alcohol (G-unit) and sinapyl alcohol (S-unit), linked together by strong C-C and labile C-O-C linkages.[3] In the paper-pulp and cardboard packaging industry, cellulose contents are generally isolated from the biomass and lignin is treated as waste material, which is mostly burnt to produce steam energy required for the pulping process.[4] Recently, due to the increasing research interest of lignin in academia and in industry, the lignin contents are isolated after delignification of the cellulose pulp and collected as technical lignins.[5] The main types of technical lignin generated in bulk from the paper industry are kraft lignin, lignosulfonates, soda lignin and to some extent organosolv lignin.[5,6] These isolated lignins from the paper industry are then taken forward to investigate high-value applications. However, utilization of this potent biopolymer has not been straightforward so far mainly due to the challenges associated with its structure. Indeed, it has a very complex three-dimensional crosslinked structure with the presence of a variety of functional groups,[7] moreover, the structures of lignin tend to vary depending on the plant species and their environment.[3] The depolymerization of lignin to break the structure down to monomeric level is certainly a difficult task and even if the degradation or depolymerization is successfully achieved, it mostly provides a mixture of different compounds whose purification is another cumbersome process. Numerous investigations and studies have been carried out in order to find suitable methods for lignin degradation and depolymerization to utilize this biopolymer in valuable applications. Herein, we discuss the efficacy of some of the selected emerging lignin depolymerization techniques published in the last decade, focusing the associated advantages and challenges. In addition to that, a brief discussion of the significant applications devised by researchers are also emphasized.

Depolymerization Technologies: Merits and Challenges

Looking at the potential of lignin aromatic structure as a precursor for bio-based chemicals and polymers, the scientific research extent on this biopolymer has increased multifold in the last two decades. According to Chunping *et al.*, the number of publications on lignin depolymerization in 1990 was 10–20, while in 2013, the number of publications on this topic showed a substantial increase, which was about 60–70,[8] furthermore, in 2019 the number was above 200 (Source: Scopus). Such a huge interest of the scientific community in this biopolymer clearly shows how impactful it would be if any of the depolymerization processes became commercialized successfully and provide valuable aromatic chemicals from waste material.

Several degradation and depolymerization methods have been explored so far, however, only a few of them have gained special attention due to specific advantages, and a very few of them has reached plant-scale production due to the challenges linked with the depolymerization and separation steps.[8] We have selected some of the promising technologies based on the associated merits, to discuss their inherent potential, reaction chemistry, generated compounds and accompanying challenges to highlight the scopes of these technologies for further development. For example, oxidative depolymerization methods, photocatalytic methods, microwave-assisted thermochemical methods, reductive methods, and enzymatic depolymerization methods have the capability to eventually evolve into a viable process and have been further discussed in this study.

The oxidation method is quite popular in the paper industry for the delignification and bleaching of pulp due to its selectivity that can target specific bonds and often provides low molecular weight phenolic mixtures.[9,10] The production of vanillin also is accomplished by the oxidation of lignin. Vanillin production from sulphite waste water was attempted almost a century ago and the alkaline air oxidation method reported by Kürschner in 1928 successfully improved the yield of vanillin.[11] A Norway-based company called Borregaard has been producing vanillin at a commercial level using lignosulfonates via catalytic oxidation.[5] However, the vanillin produced from lignosulfonates has to undergo a stringent purification process, which substantially reduces the yield of vanillin (∼5%).[12] Maeda *et al*. successfully developed a method where vanillin was produced in the presence of tetrabutylammonium ion with a maximum yield of 21 wt %. The oxidation process mainly proceeds by the electrophilic sites of the oxidants targeting the highly electron-dense areas of lignin[13] and the conversion of secondary alcohol at C_α position to ketone occurs [Figure 1].[14,15] Due to the complex structure of lignin, understanding the exact mechanism is generally difficult and relies upon model compounds to approximately comprehend the reaction chemistry.[16] Several metal oxides, organometallics, peracids, hydrogen peroxide and oxygen have been widely investigated and used for oxidative delignification and degradation of lignin.[8,9] Oxygen, however, is not strong enough to oxidize lignin in its normal state and requires strong basic conditions for the phenolic groups to produce phenolate ions.[9] Wet air oxidation (WAO) is one such technique, where lignin can be depolymerized thermochemically in the presence of oxygen and the chemically active degradation products can be readily converted to useful materials, such as platform chemicals and functional aromatic compounds.[17,18] In a similar study, the catalytic WAO method was employed, where lignin was depolymerized using oxygen in the presence of copper sulphate pentahydrate as a catalyst to produce alde-

© 2021 The Chemical Society of Japan

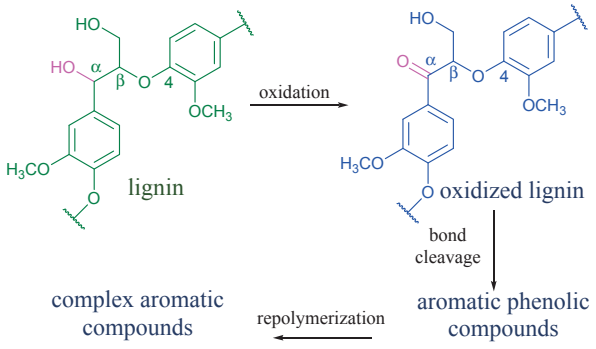


Figure 1. Oxidative depolymerization mechanism of lignin.

hydes.[16] Catalytic degradation methods can help to cleave the bonds under mild conditions and the search for proper catalysts has gained popularity over the years.[19] However, catalytic oxidative techniques break the lignin structures in an uncontrolled manner producing a mixture of several compounds. Recently, Zeng *et al.* developed an oxidative depolymerization method using graphene oxide that can selectively oxidize specific hydroxyl groups and forms a stable enol-ether intermediate. In addition, the radical formation by the phenolic hydroxyl group can attack and further break the intermediate to produce guaiacol.[20] The solubility issue of lignin in organic solvents also holds another specific challenge towards the effective application of the oxidative depolymerization techniques, and ionic liquids have come into the picture of mainstream research for lignin. Ionic liquids are salts with low boiling points (<100 °C) and they possess numerous advantages, such as efficient recycling ability, non-flammability and they can even be designed to dissolve lignin effectively.[10,21] Moreover, it is also believed that ionic liquids can catalyse the modification and fractionation of lignin structure that can, in turn, help in effective depolymerization.[22] One such study demonstrated that oxidized lignin could be depolymerized by using a formate ionic liquid, which can act as a catalyst as well as a solvent and can produce organic solvent-soluble or water-soluble lignin oligomers. These lignin fragments can be a valuable source of polyphenols.[22] Redistribution mechanisms, which have been recently investigated in the field of lignin depolymerization, were found to be effective in breaking down lignin structure to oligomeric lignin under mild conditions and these depolymerized lignin oligomers were then used to produce polyesters.[23,24] However, such a reaction needs basic conditions, which was further optimized by using ionic liquids that can dissolve lignin without a base.[25] Generally, lignin depolymerization with metal catalyst is very popular, however, it usually requires high pressure or temperature. To deal with this challenge, copper complexes with *N*-based ligands were used as catalysts in organic solvents and in ionic liquids to produce lignin oligomers.[26] The main challenge associated with the oxidative method is (1) the radical reactions, which typically recombine lignin fragments to produce even more complex and recalcitrant aromatic structures, and (2) the low yield associated with most of the methods that limits their potential application for lignin depolymerization at the industrial level.[8,27] However, an attempt to resolve this issue has also been made by Hafezisefat *et al*. by using a non-catalytic oxidative method using oxygen and perfluorodecalin as solvent, which has excellent oxygen solubility and can reduce repolymerization by generating radical scavengers and favour the formation of phenolic compounds.[28]

Photocatalysis is another method that has been proven effective for waste-water treatment as it can degrade pollutants efficiently by using a photocatalyst under irradiation.[29] This method was first applied to kraft lignin by Kobayakawa *et al*., where TiO_2 photocatalyst was used under the irradiation of a 500 W high-pressure mercury lamp. However, no useful aromatic compound could be recovered because of the decomposition of the structure.[30] A lignin photodegradation study with TiO_2 under UV ($\lambda > 310$ nm) irradiation was carried out by Tanaka *et al.* using UV, GPC, FTIR and NMR techniques. They found that, during the degradation process, initially aldehydes and carboxylates were produced, which were then decomposed further and resulted in complete degradation of lignin structure.[31] A condition optimization of photocatalysis of lignin using TiO_2 under UV ($\lambda > 290$ nm) irradiation was reported, that can successfully degrade lignin to produce vanillin, syringaldehyde, vanillic acid, catechol and *p*-coumaric acid.[32] However, TiO_2 photocatalyst requires UV light that can result in unwanted side reactions. To deal with such an issue, an effective method of lignin degradation under visible light was developed, where a two-step oxidation and photocatalytic reduction method was employed on several lignin model compounds containing β-*O*-4 linkages and were able to chemo-selectively cleave the C-O bonds to provide phenolic compounds.[33] Recently, a promising photocatalytic method for lignin oxidation was reported. Manganese dioxide (MnO_2) was used as a photocatalyst under blue light ($\lambda \sim 470$ nm) and oxygen flow at room temperature.[15] The oxidized β-*O*-4 bonds were broken easily by employing formate ionic liquid-assisted depolymerization strategy.[15,22] The blue light used here is harmless and MnO_2 photocatalyst can be recycled after a proper reactivation process. Another method reported lately by Li *et al*. using metal-free organo-catalyst perylene diimine can selectively degrade organosolv lignin under visible light at ambient temperature.[34] Despite having promising results of depolymerization on lignin, more intense studies are required to evaluate their effectiveness towards industrial application.

As compared to conventional heating systems, irradiation under microwaves is more energy-efficient, and as reported by Gedye *et al*., certain organic reactions can take place 5 to 1240 times faster, solvents can quickly superheat, and all the polar compounds absorb energy swiftly under microwaves.[35] Furthermore, Yunpu *et al*. discussed several other merits of microwave-activation technology for industrial applications, for instance, they are generally operation-friendly and a very high heating rate or temperature can be achieved quickly.[36] Due to these inherent advantages, technologies that involve microwave-assisted heating have gained popularity. Lignin depolymerization, which is generally a time consuming and challenging process, can be efficiently carried out in a short time span under microwave irradiation. An oxidative depolymerization method of lignin was explored in the presence of hydrogen peroxide and copper sulfate, which could produce hydroxyl radicals under microwaves. This method was able to successfully depolymerize lignin within 7 minutes [Figure 2].[37] In addition, being efficiently soluble in water, copper salts allow the depolymerization

© 2021 The Chemical Society of Japan

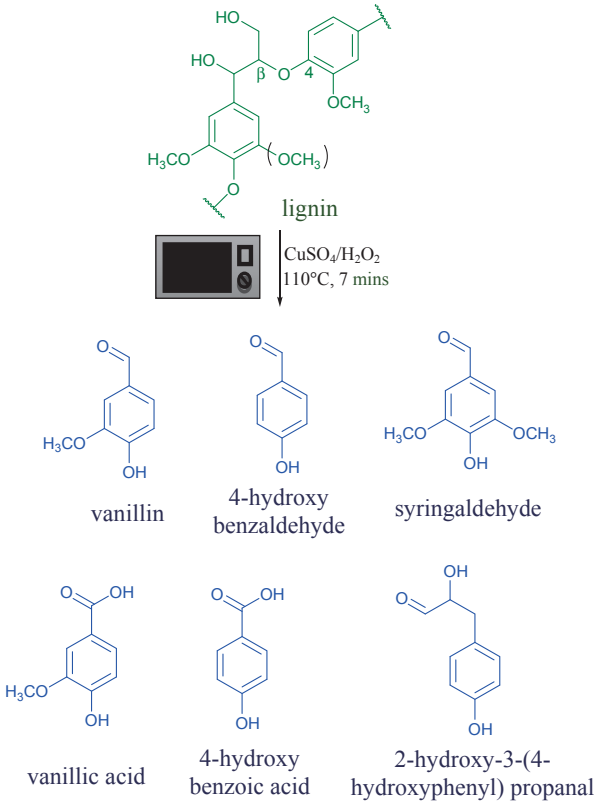


Figure 2. Depolymerization of lignin under microwave irradiation.

to take place in water (as solvent). The main monomers that can be generated using this method are vanillin, vanillic acid and 4-hydroxybenzaldehyde. Another interesting method of microwave-assisted pyrolysis of lignin can produce several valuable compounds, such as phenol, guaiacol, syringol and catechol that can be extracted as phenol-mixtures from the oil using switchable hydrophilicity solvents (SHS). These solvents can switch their properties with appropriate triggers, for example, in the presence or absence of CO_2.[38] In the case of lignin, phenols, which are weak acids, can be extracted by the basicity of these solvents and then again can be recovered from these solvents by switching their properties. However, the heating under microwave irradiation being non-uniform and low diffusion rate in bulk, has restricted its commercial utilization.[39]

Reductive depolymerization is another efficient method to depolymerize lignin which is generally carried out under hydrogen or using a hydrogen-donating compound in the presence of a redox catalyst.[13] This process mainly relies on the attack of the ether bonds of the lignin in presence of hydrogen.[40] The main advantage of this method, in contrast with the oxidative method, is the ability of the redox catalyst to stabilize the reactive sites, hence preventing any further repolymerization,[13] and thus helps to generate phenols and BTX compounds (benzene, toluene, xylene).[41] Huang *et al.* demonstrated a reductive depolymerization method using kraft lignin in ethanol-water with formic acid as a hydrogen donor.[40] Although this method was able to reduce the molecular weight of the lignin from approximately 10000 g/mol to 1270 g/mol, it did not provide monomeric lignin-based compounds. Generally, in the biorefinery, lignin degradation cannot be fully achieved due to the subsequent re-polymerization reaction. This can be avoided to some extent either by removing the lignin fractions immediately or by stabilizing the reactive bonds, such as C=O and C=C by hydrogenation.[42] The latter is known as reductive catalytic fractionation (RCF). In this approach, lignin degradation and stabilization take place before cellulose valorization, thus it can also be termed as lignin-first strategy [Figure 3].[43,44] Bosch *et al*. reported a reductive fractionation of lignocellulosic biomass in the presence of hydrogen with Ru/C catalyst in methanol at elevated temperature. This process generated carbohydrate pulp and lignin oil, which contains phenolic compounds.[45] Further study revealed that by changing the redox catalyst from Ru/C to Pd/C, OH-content could be increased in the lignin oil.[46] This method was applied to softwood lignin, *i.e.* lignin from pine, and a thorough spectroscopic analysis of the RCF lignin oil was carried out in a separate study.[47] Looking at the promising potential of this RCF technology, a scale-up effort has been made from lab to pilot scale, however, there are several aspects to be looked upon before commercialization and further investigation needs to be carried out to evaluate the hurdles associated with this technology and eventually try to eliminate them.[48] Another interesting approach to prevent the formation of the recalcitrant structure is aldehyde-assisted fractionation (AAF).[49] In this method, formaldehyde is used to form protecting groups during extraction process that can block the repolymerization of lignin fractions completely before subjecting to hydrogenolysis.[50] The addition of acetaldehyde and propionaldehyde were also tested and performances were found to be comparable to that of formaldehyde.[51] This method demonstrates an extraction process followed by the subsequent purification and recovery of the stabilized lignin as solid residue.[52] This promising technology was commercialized by Bloom Biorenewables, a company launched in 2019 that is working towards utilization of renewable resources effectively.

The chemical depolymerization methods showed interesting results in many cases, however, catalytic selectivity is a major issue, which means catalytic methods target lignin molecules arbitrarily, not in a selective manner.[8] Usage of the enzyme is an alternative way to have better control over the degradation process. Two types of enzymes are mostly studied in the lignin degradation process – peroxidases and laccases. The phenolic group in lignin gets oxidized by the action of these enzymes and generates free radicals. These radicals are unstable and generally leads to lignin depolymerization.[7] Peroxidases use hydrogen peroxide as electron acceptor, whereas laccases use molecular oxygen.[53] A mediator, which is typically a compound of small size, can be useful while using laccase for lignin degradation, which repetitively gets oxidized by laccase enzyme and gets reduced by the substrate.[54] A recent study carried out using enzymes from white-rot fungi, two peroxidases and laccase enzyme to compare the extent of depolymerization, as well as a different mediator was investigated to assess their performance and importance.[55] This study revealed that the white-rot fungi, which contain both the enzymes increase the complexity of the interaction and laccase enzyme with mediators could be a better substitute to be used in industry. Generally, peroxidase activity can be affected by hydrogen peroxide concentration and a controlled feeding mechanism is required for these enzymes to

© 2021 The Chemical Society of Japan

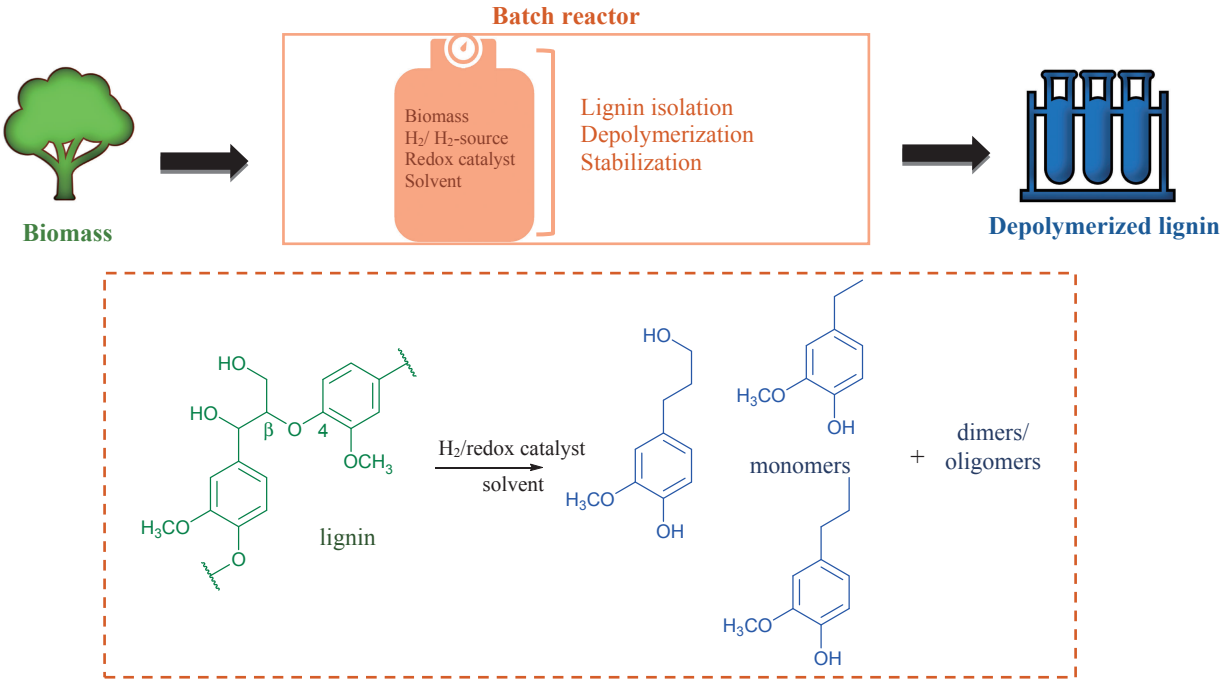


Figure 3. Reductive catalytic fractionation (RCF) of lignin.

work without deactivation.[41] Immobilization of enzymes can also be done to increase the stability of the enzymes in various conditions, as well as to allow their recycling for further reactions.[41]

Lignin-derived Compounds and Their Separation Techniques

Several phenols, aldehydes and phenolic acids can be obtained from the aforementioned lignin depolymerization methods. For example, oxidation of lignin can generate vanillin, syringaldehyde, *p*-hydroxybenzaldehyde, vanillic acid, syringic acid and *p*-hydroxybenzoic acid.[56] Microwave-assisted thermochemical degradation method can provide vanillin, vanillic acid, 4-hydroxybenzaldehyde, syringaldehyde, 4-hydroxybenzoic acid, 2-hydroxy-3-(4-hydroxyphenyl)propanal, phenol, guaiacol, syringol and catechol.[37,38] Moreover, ferulic acid, *p*-coumaric acid, caffeic acid and sinapic acid can be derived from vanillin, *p*-hydroxybenzaldehyde, 3,4-dihydroxybenzaldehyde and syringaldehyde, respectively, through chemical synthesis.[57] Lignin degradation compounds are generally obtained as a mixture whose purification is certainly a hassle. Different separation techniques, such as extraction, crystallization, precipitation, evaporation, and membranes-based techniques are constantly investigated to efficiently separate the degradation compounds.[58] However, the process has to be simple and cost-effective for industrial application and many researchers are aiming to establish an operation-friendly separation method for lignin degradation compounds. Lignin depolymerization techniques commonly generate a mixture of different compounds and only one separation technique is not sufficient and the process has to combine different techniques sequentially to successfully separate the compounds from the mixture.[58] A detailed investigation is essential to establish an effective separation sequence for the processes, which are viable for industrial-scale production.

End-use of Lignin-derived Compounds

Once the aromatic phenolic compounds are obtained from lignin, they can be used to produce various bio-based chemicals, monomers and polymers. One significant application of lignin-based compound is the replacement of toxic bisphenol A (BPA), which is commonly used for the production of polycarbonates, epoxy resins and polyurethanes. Bio-based bisphenols and trisphenols production methods from ferulic acid were demonstrated in one such study[59] and process optimization of the upscaling from lab to kilo lab was also carried out for this potent method.[60] These bio-based bisphenols and trisphenols were then used to successfully produce different polymers,[61] such as polyesters,[62] polyurethanes,[63] isocyanate-free polyurethanes[64] and epoxy resins.[65–67] In another work, α,ω-diene monomers were also synthesized from ferulic acid and were exposed to acyclic diene metathesis (ADMET) polymerization to produce poly(ester-alkenamer)s.[68] These are renewable polymers with high thermal stability and tunable glass transition temperature. Furthermore, the antioxidant properties of the ferulic acid-based bisphenols and trisphenols were evaluated.[69,70] Similarly, sinapic acid was also explored for the synthesis of bio-based syringaresinol[71] that can be used as BPA replacement and can also be used to produce α,ω-diene monomers,[72] polyurethanes[73] and epoxy resins.[74] Another extensive investigation category is the synthesis of bio-based styrene monomers and polystyrenes from ferulic acid, cinnamic acid, *p*-coumaric acid and caffeic acid.[75–77] Synthetic method of polycarbonates[78] and poly(anhydride-ester)s[79] from ferulic acid was also explored for different applications. Liquid crystalline, hyperbranched polymers were

© 2021 The Chemical Society of Japan

synthesized using lignin-based phenolic acids.[80,81] Benzoxazine resins were also prepared using *p*-coumaric acid. Cinnamic acid, which can undergo [2+2] cycloaddition reaction under the irradiation of UV light, is a promising compound for the development of photo-reversible crosslinked polymers.[82,83] Vanillic acid, syringic acid can also be utilized to produce bio-based polyesters,[84,85] polystyrenes[86] and epoxy resins.[87] Vanillin, on the other hand, was explored for the synthesis of a variety of chemicals, for example, amine and curing agents,[88] allyl and acrylate compounds,[89,90] formaldehyde-free phenolic resins,[91] epoxy resins,[92] benzoxazine resins[93] and other dimeric and trimeric compounds.[94,95] There are also increasing demands for these lignin-based compounds in the cosmetic industry for usage in skin-whitening, anti-aging products.[96] The bisphenols and trisphenols synthesized from *p*-hydroxycinnamic acids show antiradical and antioxidant properties that can be used as additives in food packaging to prevent oxidative collapse.[97] Being a natural anti-UV and antiradical compound, sinapic acid was utilized via β-β′ dimerization with improved properties for applications as a cosmetic ingredient and food additive.[98] Ferulic acid derivatives also found application as additives in continuous hot-melt processing of polylactic acid (PLA) that helped in improving the thermal and mechanical properties of PLA blends.[99] Another study reported a sustainable synthesis method of a potential UV filter using lignin-based aldehydes.[100] These aldehydes were also utilized for the production of bio-based UVA filters that can shield our skin from prolonged solar exposure and also blue light filters that can protect our eyes from retinal damage.[101] There are several examples available where lignin-based compounds were utilized to produce effective UV filters and anti-oxidant compounds.[102–104]

Conclusion

Lignin depolymerization is an effective method to generate valuable aromatic chemicals from lignin, which can then be utilized to produce bio-based chemicals and polymers as alternatives to current fossil-based commercial products. However, the challenges associated with the depolymerization and separation technique needs to be taken care of before commercializing any of the processes investigated to date. So far, only vanillin production from lignin and aldehyde-assisted fractionation (AAF) have reached commercial production and some technologies, such as reductive catalytic fractionation (RCF) have found a path to the pilot-scale level. If the hurdles of the lignin depolymerization process are eliminated, and efficient methods are established, there are a lot of application opportunities already available. However, relentless research is going on to discover more novel ways of utilization of lignin-based compounds in various unique areas.

References

1 P. Azadi, O. R. Inderwildi, R. Farnood, D. A. King, *Renewable Sustainable Energy Rev.* **2013**, *21*, 506.
2 J. Zhu, C. Yan, X. Zhang, C. Yang, M. Jiang, X. Zhang, *Prog. Energy Combust. Sci.* **2020**, *76*, 100788.
3 F. G. Calvo-Flores, J. A. Dobado, *ChemSusChem* **2010**, *3*, 1227.
4 G. Gellerstedt, G. Henriksson, in *Monomers, polymers and composites from renewable resources*, Elsevier, **2008**, pp. 201–224.
5 S. Gillet, M. Aguedo, L. Petitjean, A. R. C. Morais, A. M. da Costa Lopes, R. M. Łukasik, P. T. Anastas, *Green Chem.* **2017**, *19*, 4200.
6 C. Fellows, T. Brown, W. Doherty, *Green Chemistry for Environmental Remediation:* **2012**, 561–610.
7 C. Chio, M. Sain, W. Qin, *Renewable Sustainable Energy Rev.* **2019**, *107*, 232.
8 C. Xu, R. A. D. Arancon, J. Labidi, R. Luque, *Chem. Soc. Rev.* **2014**, *43*, 7485.
9 R. Ma, Y. Xu, X. Zhang, *ChemSusChem* **2015**, *8*, 24.
10 J. Dai, A. F. Patti, K. Saito, *Tetrahedron Lett.* **2016**, *57*, 4945.
11 K. Kürschner, *J. Prakt. Chem.* **1928**, *118*, 238.
12 M. Maeda, T. Hosoya, K. Yoshioka, H. Miyafuji, H. Ohno, T. Yamada, *J. Wood Sci.* **2018**, *64*, 810.
13 W. Schutyser, T. Renders, S. Van den Bosch, S.-F. Koelewijn, G. T. Beckham, B. F. Sels, *Chem. Soc. Rev.* **2018**, *47*, 852.
14 A. Rahimi, A. Ulbrich, J. J. Coon, S. S. Stahl, *Nature* **2014**, *515*, 249.
15 J. Dai, A. F. Patti, G. N. Styles, S. Nanayakkara, L. Spiccia, F. Arena, C. Italiano, K. Saito, *Green Chem.* **2019**, *21*, 2005.
16 K. R. Alunga, Y.-Y. Ye, S.-R. Li, D. Wang, Y.-Q. Liu, *Catal. Sci. Technol.* **2015**, *5*, 3746.
17 S. Irmak, J. Kang, M. Wilkins, *Bioresour. Technol. Rep.* **2020**, *9*, 100377.
18 S. Ansaloni, N. Russo, R. Pirone, *Waste Biomass Valoriz.* **2018**, *9*, 2165.
19 X.-F. Zhou, *Environ. Prog. Sustain. Energy* **2015**, *34*, 1120.
20 J. Zeng, Z. Tong, H. Bao, N. Chen, F. Wang, Y. Wang, D. Xiao, *Fuel* **2020**, *267*, 117100.
21 J. Dai, A. F. Patti, K. Saito, in *Encyclopedia of Ionic Liquids*, ed. by S. Zhang, Springer Singapore, Singapore, **2020**, pp. 1–12.
22 J. Dai, A. F. Patti, L. Longé, G. Garnier, K. Saito, *ChemCatChem* **2017**, *9*, 2684.
23 S. Nanayakkara, A. F. Patti, K. Saito, *Green Chem.* **2014**, *16*, 1897.
24 S. Nanayakkara, A. F. Patti, K. Saito, *Aust. J. Chem.* **2013**, *66*, 60.
25 S. Nanayakkara, A. F. Patti, K. Saito, *ACS Sustainable Chem. Eng.* **2014**, *2*, 2159.
26 J. Dai, S. Nanayakkara, T. C. Lamb, A. J. Clark, S.-X. Guo, J. Zhang, A. F. Patti, K. Saito, *New J. Chem.* **2016**, *40*, 3511.
27 J. Zakzeski, P. C. A. Bruijnincx, A. L. Jongerius, B. M. Weckhuysen, *Chem. Rev.* **2010**, *110*, 3552.
28 P. Hafezisefat, J. K. Lindstrom, R. C. Brown, L. Qi, *Green Chem.* **2020**, *22*, 6567.
29 R. Pawar, C. S. Lee, *Heterogeneous Nanocomposite-Photocatalysis for Water Purification*. Editor, William Andrew, **2015**.
30 K. Kobayakawa, Y. Sato, S. Nakamura, A. Fujishima, *Bull. Chem. Soc. Jpn.* **1989**, *62*, 3433.
31 K. Tanaka, R. C. R. Calanag, T. Hisanaga, *J. Mol. Catal. A: Chem.* **1999**, *138*, 287.
32 M. Ksibi, S. B. Amor, S. Cherif, E. Elaloui, A. Houas, M. Elaloui, *J. Photochem. Photobiol., A* **2003**, *154*, 211.

© 2021 The Chemical Society of Japan

33 J. D. Nguyen, B. S. Matsuura, C. R. J. Stephenson, *J. Am. Chem. Soc.* **2014**, *136*, 1218.
34 S. Li, Z. Hao, K. Wang, M. Tong, Y. Yang, H. Jiang, Y. Xiao, F. Zhang, *Chem. Commun.* **2020**, *56*, 11243.
35 R. N. Gedye, F. E. Smith, K. C. Westaway, *Can. J. Chem.* **1988**, *66*, 17.
36 W. Yunpu, D. Leilei, F. Liangliang, S. Shaoqi, L. Yuhuan, R. Roger, *J. Anal. Appl. Pyrolysis* **2016**, *119*, 104.
37 J. Dai, G. N. Styles, A. F. Patti, K. Saito, *ACS Omega* **2018**, *3*, 10433.
38 D. Fu, S. Farag, J. Chaouki, P. G. Jessop, *Bioresour. Technol.* **2014**, *154*, 101.
39 R. Rana, S. Nanda, V. Meda, A. K. Dalai, J. A. Kozinski, *J. Biochem. Eng. Bioprocess. Technol.* **2018**, *1*.
40 S. Huang, N. Mahmood, M. Tymchyshyn, Z. Yuan, C. C. Xu, *Bioresour. Technol.* **2014**, *171*, 95.
41 C. A. Gasser, G. Hommes, A. Schäffer, P. F.-X. Corvini, *Appl. Microbiol. Biotechnol.* **2012**, *95*, 1115.
42 W. Schutyser, T. Renders, G. Van den Bossche, S. Van den Bosch, S.-F. Koelewijn, T. Ennaert, B. F. Sels, *Nanotechnol. Catal.* **2017**, 537.
43 T. Renders, S. Van den Bosch, S.-F. Koelewijn, W. Schutyser, B. F. Sels, *Energy Environ. Sci.* **2017**, *10*, 1551.
44 T. Renders, G. Van den Bossche, T. Vangeel, K. Van Aelst, B. Sels, *Curr. Opin. Biotechnol.* **2019**, *56*, 193.
45 S. Van den Bosch, W. Schutyser, R. Vanholme, T. Driessen, S.-F. Koelewijn, T. Renders, B. De Meester, W. J. J. Huijgen, W. Dehaen, C. M. Courtin, B. Lagrain, W. Boerjan, B. F. Sels, *Energy Environ. Sci.* **2015**, *8*, 1748.
46 S. Van den Bosch, W. Schutyser, S.-F. Koelewijn, T. Renders, C. Courtin, B. F. Sels, *Chem. Commun.* **2015**, *51*, 13158.
47 K. Van Aelst, E. Van Sinay, T. Vangeel, E. Cooreman, G. Van den Bossche, T. Renders, J. Van Aelst, S. Van den Bosch, B. Sels, *Chem. Sci.* **2020**, *11*, 11498.
48 E. Cooreman, T. Vangeel, K. Van Aelst, J. Van Aelst, J. Lauwaert, J. W. Thybaut, S. Van den Bosch, B. F. Sels, *Ind. Eng. Chem. Res.* **2020**, *59*, 17035.
49 R. Vendamme, J. B. de Bueren, J. Gracia-Vitoria, F. Isnard, M. M. Mulunda, P. Ortiz, M. Wadekar, K. Vanbroekhoven, C. Wegmann, R. Buser, F. Héroguel, J. S. Luterbacher, W. Eevers, *Biomacromolecules* **2020**, *21*, 4135.
50 L. Shuai, M. T. Amiri, Y. M. Questell-Santiago, F. Héroguel, Y. Li, H. Kim, R. Meilan, C. Chapple, J. Ralph, J. S. Luterbacher, *Science* **2016**, *354*, 329.
51 W. Lan, M. T. Amiri, C. M. Hunston, J. S. Luterbacher, *Angew. Chem.* **2018**, *130*, 1370.
52 M. T. Amiri, G. R. Dick, Y. M. Questell-Santiago, J. S. Luterbacher, *Nat. Protoc.* **2019**, *14*, 921.
53 L. Longe, G. Garnier, K. Saito, in *Production of Biofuels and Chemicals from Lignin*, Springer, **2016**, pp. 147–179.
54 L. P. Christopher, B. Yao, Y. Ji, *Front. Energy Res.* **2014**, *2*, 12.
55 L. F. Longe, J. Couvreur, M. L. Grandchamp, G. Garnier, F. Allais, K. Saito, *ACS Sustainable Chem. Eng.* **2018**, *6*, 10097.
56 S. Laurichesse, L. Avérous, *Prog. Polym. Sci.* **2014**, *39*, 1266.
57 C. Peyrot, A. A. M. Peru, L. M. M. Mouterde, F. Allais, *ACS Sustainable Chem. Eng.* **2019**, *7*, 9422.
58 M. I. F. Mota, P. C. R. Pinto, J. M. Loureiro, A. E. Rodrigues, *Separ. Purif. Rev.* **2016**, *45*, 227.
59 F. Pion, A. F. Reano, P.-H. Ducrot, F. Allais, *RSC Adv.* **2013**, *3*, 8988.
60 A. R. S. Teixeira, G. Willig, J. Couvreur, A. L. Flourat, A. A. M. Peru, P. Ferchaud, H. Ducatel, F. Allais, *React. Chem. Eng.* **2017**, *2*, 406.
61 F. Pion, A. F. Reano, M. Z. Oulame, I. Barbara, A. L. Flourat, P.-H. Ducrot, F. Allais, in *Green Polymer Chemistry: Biobased Materials and Biocatalysis*, ACS Publications, **2015**, pp. 41–68.
62 F. Pion, P.-H. Ducrot, F. Allais, *Macromol. Chem. Phys.* **2014**, *215*, 431.
63 M. Z. Oulame, F. Pion, S. Allauddin, K. V. S. N. Raju, P.-H. Ducrot, F. Allais, *Eur. Polym. J.* **2015**, *63*, 186.
64 R. Ménard, S. Caillol, F. Allais, *ACS Sustainable Chem. Eng.* **2017**, *5*, 1446.
65 R. Ménard, S. Caillol, F. Allais, *Ind. Crops Prod.* **2017**, *95*, 83.
66 A. Maiorana, A. F. Reano, R. Centore, M. Grimaldi, P. Balaguer, F. Allais, R. A. Gross, *Green Chem.* **2016**, *18*, 4961.
67 L. Hollande, I. Do Marcolino, P. Balaguer, S. Domenek, R. A. Gross, F. Allais, *Front Chem.* **2019**, *7*, 159.
68 I. Barbara, A. L. Flourat, F. Allais, *Eur. Polym. J.* **2015**, *62*, 236.
69 A. F. Reano, S. Domenek, M. Pernes, J. Beaugrand, F. Allais, *ACS Sustainable Chem. Eng.* **2016**, *4*, 6562.
70 A. F. Reano, F. Pion, S. Domenek, P.-H. Ducrot, F. Allais, *Green Chem.* **2016**, *18*, 3334.
71 A. S. Jaufurally, A. R. S. Teixeira, L. Hollande, F. Allais, P.-H. Ducrot, *ChemistrySelect* **2016**, *1*, 5165.
72 L. Hollande, A. S. Jaufurally, P.-H. Ducrot, F. Allais, *RSC Adv.* **2016**, *6*, 44297.
73 M. Janvier, P.-H. Ducrot, F. Allais, *ACS Sustainable Chem. Eng.* **2017**, *5*, 8648.
74 M. Janvier, L. Hollande, A. S. Jaufurally, M. Pernes, R. Ménard, M. Grimaldi, J. Beaugrand, P. Balaguer, P.-H. Ducrot, F. Allais, *ChemSusChem* **2017**, *10*, 738.
75 S. Cadot, N. Rameau, S. Mangematin, C. Pinel, L. Djakovitch, *Green Chem.* **2014**, *16*, 3089.
76 H. T. H. Nguyen, M. H. Reis, P. Qi, S. A. Miller, *Green Chem.* **2015**, *17*, 4512.
77 H. Takeshima, K. Satoh, M. Kamigaito, *Macromolecules* **2017**, *50*, 4206.
78 A. Noel, Y. P. Borguet, J. E. Raymond, K. L. Wooley, *Macromolecules* **2014**, *47*, 2974.
79 M. A. Ouimet, J. Griffin, A. L. Carbone-Howell, W.-H. Wu, N. D. Stebbins, R. Di, K. E. Uhrich, *Biomacromolecules* **2013**, *14*, 854.
80 S. Wang, D. Kaneko, K. Kan, X. Jin, T. Kaneko, *Pure Appl. Chem.* **2012**, *84*, 2559.
81 S. Wang, S. Tateyama, D. Kaneko, S. Ohki, T. Kaneko, *Polym. Degrad. Stab.* **2011**, *96*, 2048.
82 T. Hughes, G. P. Simon, K. Saito, *Mater. Horiz.* **2019**, *6*, 1762.
83 G. Kaur, P. Johnston, K. Saito, *Polym. Chem.* **2014**, *5*, 2171.
84 H. Sun, S. Kanehashi, K. Tsuchiya, K. Ogino, *Chem. Lett.* **2016**, *45*, 439.

© 2021 The Chemical Society of Japan

85 L. Mialon, R. Vanderhenst, A. G. Pemba, S. A. Miller, *Macromol. Rapid Commun.* **2011**, *32*, 1386.
86 L. Longe, G. Garnier, K. Saito, *J. Polymer Sci.* **2020**, *58*, 540.
87 C. Aouf, J. Lecomte, P. Villeneuve, E. Dubreucq, H. Fulcrand, *Green Chem.* **2012**, *14*, 2328.
88 Z. Wang, Y. Li, T. Zhu, L. Xiong, F. Liu, H. Qi, *Polym. Degrad. Stab.* **2019**, *167*, 67.
89 M. Fache, E. Darroman, V. Besse, R. Auvergne, S. Caillol, B. Boutevin, *Green Chem.* **2014**, *16*, 1987.
90 J. F. Stanzione, III, J. M. Sadler, J. J. La Scala, R. P. Wool, *ChemSusChem* **2012**, *5*, 1291.
91 G. Foyer, B.-H. Chanfi, B. Boutevin, S. Caillol, G. David, *Eur. Polym. J.* **2016**, *74*, 296.
92 H. Jiang, L. Sun, Y. Zhang, Q. Liu, C. Ru, W. Zhang, C. Zhao, *Polym. Degrad. Stab.* **2019**, *160*, 45.
93 N. K. Sini, J. Bijwe, I. K. Varma, *J. Polym. Sci., Part A: Polym. Chem.* **2014**, *52*, 7.
94 A. Van, K. Chiou, H. Ishida, *Polymer* **2014**, *55*, 1443.
95 S. Zhao, X. Huang, A. J. Whelton, M. M. Abu-Omar, *ACS Sustainable Chem. Eng.* **2018**, *6*, 7600.
96 A. L. Flourat, J. Combes, C. Bailly-Maitre-Grand, K. Magnien, A. Haudrechy, J.-H. Renault, F. Allais, *ChemSusChem* **2020**, *14*, 118.
97 A. F. Reano, J. Chérubin, A. M. M. Peru, Q. Wang, T. Clément, S. Domenek, F. Allais, *ACS Sustainable Chem. Eng.* **2015**, *3*, 3486.
98 M. M. Mention, A. L. Flourat, C. Peyrot, F. Allais, *Green Chem.* **2020**, *22*, 2077.
99 S. Kasmi, A. Gallos, J. Beaugrand, G. Paës, F. Allais, *Eur. Polym. J.* **2019**, *110*, 293.
100 B. Rioux, C. Peyrot, M. M. Mention, F. Brunissen, F. Allais, *Antioxidants* **2020**, *9*, 331.
101 C. Peyrot, M. M. Mention, F. Brunissen, P. Balaguer, F. Allais, *Molecules* **2020**, *25*, 2178.
102 M. D. Horbury, E. L. Holt, L. M. M. Mouterde, P. Balaguer, J. Cebrián, L. Blasco, F. Allais, V. G. Stavros, *Nat. Commun.* **2019**, *10*, 1.
103 C. Peyrot, M. M. Mention, F. Brunissen, F. Allais, *Antioxidants* **2020**, *9*, 782.
104 L. M. M. Mouterde, A. A. M. Peru, M. M. Mention, F. Brunissen, F. Allais, *J. Agric. Food Chem.* **2020**, *68*, 6998.

© 2021 The Chemical Society of Japan