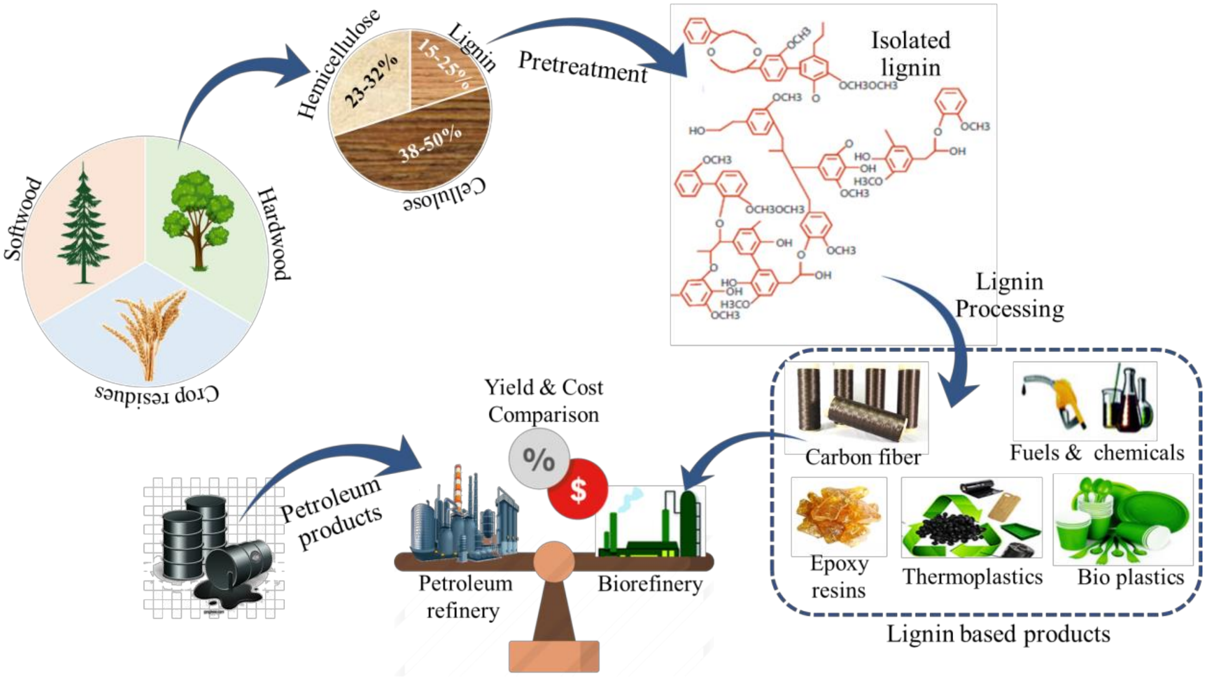
The following publication Khan, R. J., Lau, C. Y., Guan, J., Lam, C. H., Zhao, J., Ji, Y., ... & Leu, S. Y. (2022). Recent advances of lignin valorization techniques toward sustainable aromatics and potential benchmarks to fossil refinery products. Bioresource Technology, 346, 126419 is available at https://doi.org/10.1016/j.biortech.2021.126419.

Graphical Abstract



Highlights

- Functionalities and potential values of petroleum and biorefinery aromatics were compared;
- Important linkages that offer lignin particular characteristics in valorization were overviewed;
- Valuable lignin products derived from various techniques were reviewed and evaluated;
- State-of-the-art fractionation and depolymerization techniques were discussed with criticism;
- Future directions on technology development and economic assessment were summarized.

Recent Advances of Lignin Valorization Techniques Toward Sustainable Aromatics and Potential Benchmarks to Fossil Refinery Products

Rabia Jalil Khan[a†], Chun Yin Lau[a†], Jianyu Guan[a], Chun Ho Lam[b], Jun Zhao[c], Ying Ji[d], Huaimin Wang[a], Jingliang Xu[e], Duu-Jong Lee[f], and Shao-Yuan Leu[a]

[a] Department of Civil and Environmental Engineering, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong;
[b] School of Energy and Environment, City University of Hong Kong, Tat Chee Avenue, Kowloon Tong, Hong Kong, China;
[c] Department of Biology, Hong Kong Baptist University, Kowloon Tong, Hong Kong, China;
[d] Institute of Textiles and Clothing, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong;
[e] School of Chemical Engineering, Zhengzhou University, Zhengzhou, China;
[f] Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan;

[†] Equal contributions as first authors
[*] Correspondence: syleu@polyu.edu.hk

Abstract

Aromatic compounds are important fuels and key chemical precursors for organic synthesis, however the current aromatics market are mainly relying on fossil resources which will eventually contribute to carbon emissions. Lignin has been recognized as a drop-in substitution to conventional aromatics, with its values gradually realized after tremendous research efforts in the recent five years. To facilitate the development of a possible lignin economics, this study overviewed the recent advances of various biorefinery techniques and the remaining challenging for lignin valorization. Starting with recent discovery of unexplored lignin structures, the potential functions of lignin related chemical structures were emphasized. The important breakthrough of lignin-first pretreatment, catalytic lignin depolymerization, and the high value products with possible benchmark with modern aromatics were reviewed with possible future targets. Possible retrofit of conventional petroleum refinery for lignin products were also introduced and hopefully paving a way to progressively migrate the industry towards carbon neutrality.

Keywords: Biorefinery, Pretreatment, Lignin Valorization, Catalytic Depolymerization, Aromatics Market

1. Introduction

Aromatic compounds are important chemical intermediates in industrial organic synthesis. They are the building block chemicals used to manufacture our everyday life items and have long been applied as the precursors of high-performance engineering materials. The global demand of aromatic compounds is continuous rising due to the increasing needs of healthcare, pharmaceuticals, paint, and coating industries. Such high demands for aromatic chemicals have increased the production capacity, which is estimated to grow at the growth rate of 5.67% for the forecast period of 2020 to 2027 (AgileIntel, 2021) **(Figure 1a)**. Aromatic hydrocarbons are the second most important constituent of crude oil with their content ranging widely from 13.3% (Ke et al., 2019) to 34.1% by weight (Dai et al., 2020b). Benzene, toluene, and xylenes (BTX) are the most commercially significant aromatics **(Figure 1b)**. Benzene has been used as a precursor for the production of styrene, phenol, nylon, and aniline production, while toluene is typically blended into unleaded gasoline, but has also been converted into benzene and xylenes. Xylene includes the o-, m-, and p- types based on the positions of methyl groups on the aromatic rings, of which o-Xylene is used to produce phthalic anhydride; m-xylene is converted into isophthalic acid; and p-Xylene is converted into terephthalic acid and dimethyl terephthalate, which are ultimately used to produce polyethylene terephthalate (PET) fibers, resins, and films (Che et al., 2019). These hydrocarbons have numerous industrial applications as chemical intermediates such as in the production of polymers, pharmaceuticals, food additives, biofuel and as solvent.

Biorefineries have been foreshadowed as a possible substitution of oil refineries as well as for valorization of the entire biomass into fuel, energy, and high value-added products. Like crude oil, biomass also can be refined into a wide spectrum of products, but its feasibility has long been challenged due to direct competition with crude oil economy, while the technologies have not yet considered "green" especially when completely utilization of whole biomass cannot be achieved. Efforts are therefore now being put to generate green aromatics from the renewable and abundantly available biomass feedstock to restrict the use of depleting fossil fuels and save the environment. As a consequence, the vision of biomass as a surrogate for petroleum is now a central tenet of national biomass valorization strategies all over the world.

Lignin aromatics is ideally fit for second-generation biorefineries for the extraction of value-added chemicals along with hydrocarbons (Wang & Song, 2018). Lignin is the second most abundant aromatic feedstock in plant-derived biomass. It constitutes about 15-40% as dry mass in terrestrial plants and 40% by energy content (Islam et al., 2020). It is estimated that 150 billion tons of lignin is produced worldwide on an annual basis (Hu et al., 2018). Lignin derived from paper and pulp industry has been considered as a by-product, which contributes to 50 million tons per year, out of which only 2% is converted to lignin-based products and the remaining is either burnt for energy or disposed of in landfills. At present, the market size of lignin and its products is accelerating at a growth rate of 2.28% annually from $599 million in 2014 to $704 million by 2022 (Garlapati et al., 2020). While the greater energy density, high C:H ratio (above 10:1), and exclusive aromatic monomers favors its utilization in biorefinery, the complexity and heterogeneity of lignin makes challenging its valorization and application.

Till now, many review papers have discussed lignin characterization (Meng et al., 2019), structural changes (Sheng et al., 2021), pretreatment methods (Yoo et al., 2020), fractionation (Matsakas et al., 2019), extraction (Wang et al., 2019), thermochemical (Ponnusamy et al., 2019), catalytic hydrothermal (Biswas et al., 2021), biological (Zhang et al., 2020b) responses, lignin valorization potential in biorefineries (Banu et al., 2019), and lignin-based materials (Wang et al., 2019), and its applications (Supanchaiyamat et al., 2019). However, most of the published literature lacks the detailed insights on benchmarking the aromatics produced from lignin and the conventional petrochemicals. In view of this, the current review attempts to summarize the emerging potential of bio-based aromatics as a sustainable substitute to traditional aromatics. Future research directions for sustainable and cost-effective lignin-based biorefineries are also proposed.

2. Material properties of lignin

2.1. Types of lignin from different pretreatment principles

Lignin is a long-chain polymer that is vital to the structural rigidity and turgidity of woody plants. Lignin pretreatment principles have been widely investigated and various reviews have been done on distinguishing the benefits and the lignin properties obtained through different pretreatment principles. Lignin mainly consists of three different monomers, namely syringyl alcohol (S), guaiacyl alcohol (G), and p-coumayl alcohol (H) **(Figure 2)** (Islam et al., 2020). The composition and concentrations of these three monomers varies with wood species and botanic regions. Lignin also consists of a large concentration of aliphatic hydroxyl groups, phenolic groups and carboxylic groups, providing specific functions in chemical synthesis. Lignin extraction from lignocellulosic biomass is challenging as there are also other biopolymers in the plant cell wall like cellulose and hemicellulose, which complicated the physiochemical characteristics of the feedstock. To harvest the needed functional groups, various extraction methods were therefore adopted to obtain lignin chains for further valorization and functionalization **(Table 1)**.

The types and contents of fractionated lignin greatly depend on the biomass feedstock and the pretreatment principles. The commonly adopted pretreatment principles include dilute acid (DA), base (DB), organosolv, deep eutectic solvents (DESs), and ionic liquids (ILs) pretreatment. DA pretreatment involve the use of acid or inorganic acids as catalysts for bond-breaking processes (Duan et al., 2018; Huang et al., 2019). However, DA pretreatment shows higher tendency in the formation of carbocations, aldehydes, and Hibbert ketones (Liu et al., 2020b). These factors are mainly responsible for the high condensation tendency of lignin after extraction, which will lead to repolymerization of lignin chains. One extension of DA pretreatment in biorefinery is the sulfite pretreatment process, of which the lignosulfonate by-products is known to its low inhibition to enzymatic hydrolysis (Huang et al., 2019) and fermentation, making the "whole slurry" fermentation feasible (Rehman et al., 2021). DB pretreatment mainly utilize sodium hydroxide or sodium sulfide for pretreatment, which have been more frequently applied as a mild pretreatment process for the conversion of low recalcitrant biomass (Yan et al., 2020; Zhao et al., 2020). Lignin extracted through this process is more base-soluble and also leads to substitution of functional groups like hydrosulfide (-SH) groups (Chu et al., 2021). In organosolv pretreatment, various types of organic solvents have been introduced with acid or other catalysts for biomass fractionation. The approach tends to increase the solubility of lignin and protect the lignin structure and provide extra stability during pretreatment (Islam et al., 2020). For example, 1,4-butanediol are responsible for attaching the solvent molecules on the lignin molecule, which may further protect the lignin from rapid condensation and facilitate its depolymerization (Dong et al., 2019). DESs (Thomas et al., 2017; Wang & Lee, 2021) and ILs (Sharma et al., 2019; Sorn et al., 2019) pretreatment pertains to solubilize solid biomass at variable temperature and pressure settings. Due to the low volatility, high stability and the combining organic and ionic nature, DESs and ILs may achieve a higher efficiency in biomass dissolution as compared to DA process, but its costs, viscosity, and recyclability still make process design complex and challenging.

The molecular weights of pretreated lignins have aroused significant attentions in the current research as it directly affects the solubility in solvents. The molecular weights of DB pretreated lignin (1,500-3,270 g/mol) are in average much smaller when compared to those obtained by organosolv pretreatment (2,180-8,500 g/mol), which may be due to the high tendency of the base to break the crosslinks among lignin chains (Takada et al., 2018). Organosolv, however, tends to mainly work as a solvent and not to react directly with lignin, therefore not lead to large amount of bond cleavages. More intramolecular bonds in between repeating units can be preserved. The molecular weight of DA and IL lignin varies significantly due to the low solubility nature of condensed lignin in acid. A part of lignin in reaction mixture cannot be extracted and the degree of extraction greatly depends on the acid introduced into the reaction mixture. The steric effects and the anionic powers of the IL will also affect the delignification efficiency from biomass (Singh et al., 2018). Based on the needs of applications, lignin with different physiochemical properties may be considered. For example, nano-lignin with smaller and more homogenous molecular weight and less original lignin-lignin linkages may be suitable for the backbone of solid catalysts (Tse et al., 2019); while organosolv lignin may result in higher monomer yields after depolymerization (Dong et al., 2019).

2.2. Chemical and structural characteristics of lignin

Lignin is biosynthesized through various enzymatic oxidation and dehydrogenation process from phenylalanine and the three basic building blocks. The high variability of phenolic hydroxyl groups introduced the high functionality for promotion of rigidity and turgidity in various parts of woody plantations. Different functional groups are responsible for introducing the functions such as enhanced stiffness, surface-activeness, high thermal stability and anti-oxidative abilities into the lignin chains. These features made lignin a potential material for replacing the conventional synthetic products as summarized follow **(Figure 2a)**:

2.2.1. Stiffness

Lignin is known to enhance the rigidity and stiffness of the woody biomass. It also provides resistance against physical corrosions like bending through the strong adherences with cellulosic fibers. The stiffness of lignin can be accounted for the high abundance of van der Waals' interactions between cellulose and lignin, which increase with the molecular weights and amounts of phenolic groups of the lignin (Youssefian & Rahbar, 2015). The strength and modulus of lignocellulosic biomass can also be further promoted by the presence of hydrogen bonds in between the hydroxyl groups of cellulose and lignin (Jiang et al., 2020).

2.2.2. Surface chemistry

Lignin is a macromolecule which consists of a large phenolic network linked together mainly by different ether bond linkages. This network and the presence of many fat-soluble groups like methoxy groups ($-OCH_3$) can account for the high hydrophobicity of lignin (Li et al., 2018b). The highly hydrophobic nature can be of great potential in the development of green lignocellulosic biomass-derived surfactants if hydrophilic heads are attached on the lignin. Lignosulfonates has gained its attention as surfactant as the sulfite treatment is amongst the most common and major process in pulping industry (Cai et al., 2017). Lignosulfonate consists of hydrophilic sulfonate groups supported by a giant hydrophobic aromatic ring structure, making it proper surfactants and flocculants (Xu et al., 2019). In addition to lignosulfonate, recent studies have also introduced other cationic/anionic groups or polymers on lignin, so it can further reduce the surface tension on the air/water interface and oil/water interface, and hence enhance the removal of organic and hydrophobic wastes from water (Guo et al., 2021). As lignin is also a natural and biodegradable polymer, it will be more environmentally friendly comparing with the conventional ionic surfactants like cetylammonium bromide and soap less detergents. Due to the hydrophobic nature of the large covalent network, lignin based surfactants has been used and incorporated in enhancing the encapsulation and drug control-release strategies (Li et al., 2017b).

The large number of hydroxyl groups in lignin have also made this macromolecule a potential catalyst on the ring-opening and nucleophilic addition of certain molecules, like epoxides can exhibit high amount of dimeric hydrogen bonding. The intermolecular hydrogen bonds can reduce the activation energies of the molecules and weaken the chemical bonds in molecules like epoxides and carbon dioxide (Guo et al., 2019), which increase the tendency for the nucleophile to attack the molecules. The aromatic three-dimensional (3D) interpenetrating polymer network is also vital for being an excellent catalyst support. Lignin with high sulfonate group content has shown to be an excellent candidate for the conversion of monosaccharides like glucose, fructose and xylose to hydroxymethylfurfural (HMF) or furfural (Gan et al., 2019; Li et al., 2020).

2.2.3. Structural heterogeneity

Lignin is a microstructure with various kinds of linkages among the basic molecules, such as β-O-4, α-O-4, β-β, and many other linkages. These different linkages introduce structural heterogeneity to the macromolecules. Studies have shown that structural heterogeneity can enhance the variability of lignin macromolecules formed, which can be utilized in various parts of woody biomass (Polo et al., 2020). However, the heterogeneity also introduces a large variability of crosslinks and intermolecular forces in different lignin chains and hence enhances the difficulty in reproducibility of bond and crosslinks breakages during valorization. The difficulty in formulation and uniformity of lignin valorizations and applications is further increased due to the variation of aliphatic and phenolic hydroxyl groups in the structure. In order to enhance the functionality and reproducibility of lignin-derived materials, recent research has been focusing on the development of c-type lignin. C-type lignin is a type of benzodioxane homopolymer which is made up of only one monomer, *i.e*., caffeyl alcohol **(Figure 2b)**. Caffeyl alcohol is classified into the hydroxycinnamyl alcohol group and the catechol groups are linked together by β-O-4 bonds. C-lignin proved to have a higher thermal and chemical stability than ordinary hetero-polymeric lignin due to the difference in the attachment of hydroxyl groups on benzyl groups instead of the usual methoxy groups (Li et al., 2018a). The post-radical coupling reaction is allowed for the re-aromatization of the intermediates on the benzodioxane ring production, which can in turn protect the reactive hydroxyl groups on the benzyl ring (Berstis et al., 2016). C-lignin chains have high uniformity and homogeneity due to the unique repeating unit in the group. Therefore, it enhances the repeatability and reproducibility of lignin-derived products. These properties have showed that c-lignin can be a potential material for adopting in various applications which may bring better performance than conventional hetero-polymeric lignin chains like photosensitizers and dyes. Studies have also extended further into the production of genetically modified lignin, which can control the S, G, and H ratio of lignin in a woody biomass. The control of various repeating units on lignin can reduce the possibility of condensation reaction during the pretreatment process and hence enhancing the enzymatic digestibility of cellulose and chemical digestibility, delignification and depolymerization of lignocellulosic biomass and lignin chains.

2.2.4. Thermal stability

The extra stability provided among the conjugated aromatic rings and the ether linkages in the 3D covalent network of lignin increase the activation energies for the bond-breaking process. Hence the thermal stability of lignin can be exploited to enhance the structural integrity of synthetic biomaterials. Recent studies have shown that the incorporation of lignin has significantly improved the thermal stability of cellulose nanofibers (Zhang et al., 2019a). Lignin has also been incorporated into vulcanized rubber and showed an increase in the stability of thermosetting plastics under high temperatures (Barana et al., 2016). Adopting various functional groups into lignin chains will affect the ability to withstand high temperatures. Phenolated sulfuric acid lignin, of which the lignin treated with p-toluenesulfonic acid, has showed higher thermal stability than aliphatic sulfonated lignin and sulfuric acid lignin (Taleb et al., 2020). Lignin treated with P_2O_5 introduces the flameproof ability due to the addition of phosphate and phosphonate groups on lignin chains (Prieur et al., 2017; Zhang et al., 2018c).

2.2.5. Antioxidant activity

The high phenolic hydroxyl groups linked together by β-O-4, β-β, α-O-4 allowed lignin to be a potential antioxidant which can serve as a quencher for mild oxidants or scavengers for various reactive oxygen species (ROS) like hydroxyl radical ($OH^{\cdot}$), superoxide radical (O_2^{-}.). Recent research has revealed that shorter lignin chains with higher abundance of phenolic hydroxyl groups showed a higher ability on resisting antioxidant attacks (Gordobil et al., 2018). Lignin also has excellent ultraviolet (UV) radiation absorbing property due to the presence of conjugated systems like carbon-carbon double bonds, aromatic groups and carboxyl groups. Depending on the degree of conjugation, lignin chains can have the ability to absorb various electromagnetic radiations like deep UV radiations or near-visible light radiations. The presence of auxochromes like methoxy ($-OCH_3$) and carbonyl groups ($-C=O$) also enhance the UV absorption and hence reduce the probability of ROS formation. However, the antioxidant ability decreases as the degree of lignin condensation increases (Piccinino et al., 2021). This shows that lignin from certain pretreatment methods like acid-catalyzed pretreated lignin may not be suitable for antioxidant usage. This property allowed the extension of lignin application in healthcare or cosmetic product as UV radiation and absorption agent.

2.3. Lignin derivatives and their characteristics

Recent research has functionalized lignin with various groups of chemicals which introduced new properties to lignin. A large group of research has studied the addition of photosensitizers into lignin chains in order to functionalize the lignin and further extend the potential real-life applications. Lignin has also been treated with acetic anhydride, which leads to the acetylation of aliphatic and phenolic hydroxyl groups in lignin. Although the antioxidant activity of acetylated lignin is greatly lower than non-acetylated lignin, acetylated lignin exhibited significant reactive oxygen generation under light irradiation, especially for superoxide anions (Marchand et al., 2018). The increase in carboxylic groups and benzoquinone groups in lignin after alkaline hydrogen peroxide treatment enhanced the hydrophilicity of the lignin chains and showed compelling achievement as a dispersant for clay and kaolinite when comparing with lignosulfonate (He et al., 2017).

Recent research has been focusing on utilization of lignin-derived materials or functionalized lignin incorporated materials to replace the conventional synthetic materials, which are not biodegradable and can pose environmental hazards. Lignin has been crafted with azo compounds to form into photo-resistant colorant due to its reversible cis-trans isomerization property under electromagnetic radiation (Deng et al., 2015; Meng et al., 2020). Lignin has been incorporated with photosensitizers such as porphyrins. When linking with lignin, porphyrins can reduce its aggregation in high water environments and hence lessen the aggregation quenching effects (Tse et al., 2019). The photoluminescence effects and performance of porphyrins can be significantly improved under aqueous environments with the enhancement of lifetime. This can thus broaden the application of photosensitizers which suffer from aggregation-caused and other quenching effects. The incorporation of porphyrins and some other photosensitizers like BODIPY (Panovic et al., 2017) can extend the fluorescence regions of lignin from UV regions to visible regions and even near-infrared (IR) regions. The photosensitizer-incorporated lignin can extend the application of lignin into bio-imaging and drug sensing applications by using larger excitation wavelength electromagnetic waves to reduce the potential hazards on human cell damages and accumulation of harmful synthetic products in human body. Lignin derivatives can also be attached by certain hydrophobic light-absorbing functional linkers as multi-functional materials. Wang et al. (2021b) incorporated imidazole-derived compounds on the fabrication of a UV protecting, self-healing and skin adhesive products. This extended the application of lignin as gluing agents and showed that lignin-derived structures can serve as a precursor for decorative materials and even bandages.

3. Current progress in valorization of lignin to high value materials

The research roadmap and related product values toward future applications have been demonstrated in **Figure 3**. The most important lignin derived materials reported in the recent five years, including carbon fibers, resins, plastics, adsorbents, and energy storage devices, which have been reviewed in the following section.

3.1. Carbon fibers

Carbon fibers (CFs) have attracted tremendous recent research interests due to their unique physical and chemical properties, while approximately 90% of the commercial CFs are manufactured from non-renewable polyacrylonitrile (PAN) (Patil et al., 2013). Lignin with its excellent physiochemical properties has served as a cost-effective and green precursor for CFs production. Production of lignin-based carbon fiber (LCFs) can be with high carbon efficiency and the carbonization is with no toxic emissions during the manufacturing process (Zhang et al., 2019b). Various technical lignins have been investigated as potential CF precursors, such as Kraft lignin (Otromke et al., 2019), organosolv lignin (Sun et al., 2016), and ionic liquid extracted lignin (Vincent et al., 2018). Sun et al. (2016) reported the synthesis of LCFs with novel microstructures, excellent mechanical properties, fiber diameter (30-80 μm) using chemical modification and/or physical blending. With the properties, Mandeep et al. (2020) stated the huge exploitation potential of LCFs for a wide variety of applications, such as supercapacitors, separation, electrodes, catalysis and dye-synthesized solar cells.

Despite all this progress of LCFs production, LCFs were struggling at lab-scale due to long stabilization time and low mechanical performance as compared to PAN-based CFs. The tensile strength of LCFs was less than 500MPa, and the highest reported value was ~1,200 MPa, much lower than that of PAN-based CFs in the range of 3-7 GPa. The lower mechanical strength was attributed to intrinsic heterogeneity of lignin structure, wide molecular weight distribution and low purity. By altering molecular orientation, structure modification, precursor pretreatment the mechanical performance of LCFs were further enhanced (Li et al., 2017a). The LCFs prepared by further optimizing the molecular weight of lignin had an average tensile strength and modulus of 1.39 GPa and 98 GPa, respectively. The study represented the LCFs with the highest mechanical properties ever obtained from low cost, chemically unmodified lignin (Jin et al., 2018), although the final properties of LCFs are not up to the mark due to its diversity, heterogeneity.

The high manufacture cost has also limited the wide production of LCFs, even though lignin itself is inexpensive. In order to address these challenges, the future trend of lignin chemical modification should focus on increasing molecular weight and polymer linearity by grafting lignin onto different polymers or via polymerization or copolymerization. More works are needed with the main focus on further investigating thermo-stabilization and carbonization of lignin fibers as currently both the mentioned processes are simply based on using PAN fibers as a reference. The other properties of LCFs such as electronic conductivity and thermal resistance should also be studied in order to excavate the other possible applications of LCFs. More efficient pretreatment methods should be adapted in order to extract and purify lignin with less impurities at low costs.

3.2. Plastics and resin

The production bio-based materials, specifically lignin or lignin-derived monomers has drawn an enormous interest among the scientific community. Lignin has been used for the polymer production such as polyurethanes, phenol-formaldehyde resins, polyesters, and phenolic and epoxy resins, typically by the various modifications in its chemical structure or as copolymers, blends, and composites (Rajesh Banu et al., 2019). Organosolv lignin has been successfully used as a 3D printing ink when mixed with nylon, revealing that lignin could improve the printability of the structure by reducing the melt viscosity and thus enhancing its stiffness and tensile strength (Nguyen et al., 2018).

From the structural perspective of lignin and the similarity between polyphenolic lignin and phenol, there has been extensive research on where lignin is used in the preparation of phenolic resins (Chen et al., 2020). The main focus of the recent related researches, in summary, is to synthesize purified, functionalized, and fractionated lignin with higher reactivity for application in phenolic resin systems. However, the substitution rate of classic phenols using lignin-based resins is still limited, partially due to incomplete depolymerization and high diversities of monolignols in the reaction products. A more comprehensive pretreatment and depolymerization process is needed by the integration of various techniques. In addition to polyphenolic resins, epoxy is also of immense importance. The use of lignin in the composition of epoxy resins is a natural fit as such renewable precursors are responsible for the strength and rigidity of the molecular architectures. Therefore, the production of epoxy precursors based on lignin, has been widely reported and reviewed accordingly (Banu et al., 2019). Generally, lignin with low molecular weight, low glass-transition temperatures (Tg), and high polydispersity with high phenolic-hydroxyl group content, would be more preferred for resin production. However, the synthesis of epoxies from lignin is complicated by the varied reactivity resulting from epoxy groups created from the crosslinked structure of lignin. Applying lignin with lower molecular weights for epoxy resins may create critical impacts to the properties of the epoxy resins products (Diaz-Baca & Fatehi, 2021).

To sum up, a large variety of promising methods and approaches have been developed with high scientific interests in lignin based adhesives; but how to obtain lignin-rich phenolic compounds with higher reactivity at low cost and in an environmentally friendly manner still remain challenging. For 3D printing, the lignin-based feedstock needs to be benchmarked against established feedstock to assess feature resolution and shape-forming flexibility. A holistic approach towards the specific goal and application is most recommended. While the science and engineering of lignin 3D printing is valuable new knowledge as itself, it will be in as valuable as it paves the way to commercial utilization of lignin.

3.3. Adsorption materials

Lignin have been known as a suitable precursor in the synthesis of activated carbons (LAC) for the adsorption of dyes, organics, gases, and metals (Lee et al., 2018). Derived from acid hydrotropic lignin, alkali lignin, and lignosulfonate the surface area of LAC achieved more than 2,000 $m^2 \cdot g^{-1}$ by phosphoric acid at moderate temperature (450°C) (Yang et al., 2020). The application of lignin and its derivatives for adsorption covers a wide range of chemicals such as air pollutants, dyes, and metals (Supanchaiyamat et al., 2019). In addition to LACs, lignin-based hydrogels have also been synthesized for water purification (Thakur et al., 2017) and tissue engineering (Figueiredo et al., 2018). Overall, LACs and lignin-based hydrogels are with comparably high surface areas and pore volumes similarly to the commercial activated carbon.

More studies are expected with special emphasize on cross-linking, grafting, copolymerizing, and hybridizing to develop more advanced lignin adsorbents.

Despite of the outstanding properties and performances, lignin derived adsorbents however still face significant challenges toward full-scale commercialization. Even though lignin from pulp industry is a low cost feedstock, activated carbon is also with variable or even marginal market values. There are many other low-cost and sustainable carbon materials to be applied as the precursor of adsorbents. The sources of current activated carbon are generally agricultural waste (*e.g.*, coconut shell biomass), which is also a non-fossil based carbon as lignin. The technique is green and established. Even with carbohydrates, similar practices applied on lignin may also be used on raw biomass. Lignin based adsorbent need to provide extraordinarily outstanding or biomass-specific functions in comparing with other carbon materials, such as selectivity, costs, and recyclability. Its applicability may otherwise be limited in certain applications or industries. More studies would be critical on the sustainability and economic aspects of the lignin based adsorbents in the future.

3.4. Energy storage applications

In order to meet the fast growing demands of the energy storage market, lignin has been utilized as electrochemical electrodes in batteries and supercapacitors, *e.g.*, the expander of lead-acid batteries and organic cathodes in lithium batteries (Luo et al., 2018). Supercapacitors are more favorable than batteries because of their high-power density and long lifespan. Along with the other unique properties of lignin, the high abundance of oxygen-containing functional groups on the surface of processed lignin could offer extra pseudo capacitance in such materials (Yun et al., 2019). The research related to the uses of various types of lignin for energy storage devices development has increased enormously, but it is still very challenging for applying it in commercialized rechargeable batteries and fuel cells. With the expectation of boosting demand of energy storage and usage, more detailed techno-economic analysis of new lignin-derived materials is required to identify the bottlenecks of the process for further study.

4. Technologies

4.1. Lignin depolymerization

4.1.1. Overview on lignin valorization from raw biomass

The feasibility of lignin valorization rests in our ability to depolymerize it into the smaller aromatic unit. This section devotes to summarize the latest strategies of lignin valorization, which is divided into three stages: isolation, depolymerization, and recovery. Throughout the past several decades, researchers from different catalysis communities have attempted to break open the recalcitrant nature of lignin to unlock the second largest renewable carbon source for chemical and fuel production **(Figure 4)**. However, despite much devotion, there are still minor technological gaps exist within each research domain. Overcoming these challenges could strengthen the competitiveness of lignin in the current petroleum-dominated infrastructure. Therefore, we would like to take this opportunity to highlight these challenges identified in the lignin depolymerization research areas.

4.1.2. Lignin depolymerization

The effort to achieve efficient depolymerization of lignin has sustained decades of research in the renewable chemicals and fuel community (Van et al., 2018). Different degradation protocols, such as thermal, chemical, and biological routes, or a combination of those, have been studied extensively (Song et al., 2021). These methods include thermochemical (pyrolysis, gasification, hydrothermal liquefaction, and microwave-assisted), chemical (acid/base- catalysed, IL-, sub-, or supercritical fluid- assisted, oxidative, hydroprocessing, and bioinspired/biomimetic), and biological (bacterial, fungal, or enzymatic) processes (Klinger et al., 2020). Several reviews were recently published to address the advances in lignin conversion and upgrading (Wong et al., 2020). Various depolymerization strategies based on their redox properties and temperature ranges have been summarized in **Figure 4**.

4.1.2.1. Hydrogenolysis

In the hydrogenolysis process, hydrogen or other hydrogen sources have been used to thermally reduce lignin. Through the hydrogenation treatment, depolymerized lignin, phenols and other chemicals with high added value can be obtained, as well as low molecular weight hydrocarbon fuels can also be prepared. The main types of reactions involved in the hydrotreating process of lignin include hydrogenolysis, hydrodeoxygenation, hydrogenation, and integrated hydrogen-processing. Those thermal catalytic processes include a broad consideration of the application of a catalyst at an elevated temperature in a pressurized setting. They often include the design of solvent systems too. For the most part, hydrogenolysis by reductive catalytic depolymerization has received more attention than the oxidative approach because of the preservation of the linkages, such as β-O-4, during the lignin isolation process. An increasing number of research articles have also demonstrated convenient one-pot lignin isolation and depolymerization in a reductive environment (Renders et al., 2017). The strategy has resulted in a newly found "lignin-first" concept, where lignocellulosic biomass undergoes an in-tandem depolymerization-stabilization treatment while having the β-O-4 bonds preserved for further treatment, which can produce higher-value chemicals (Renders et al., 2017).

4.1.2.2. Solvolytic treatment

The use of an organic solvent to solubilize lignin at elevated temperature can also promote lignin depolymerization. Solvent choices can be protic (water or alcohols) or aprotic organics (*e.g.*, dioxane, acetone, tetrahydrofuran, and tetralin) or a combination of both. The degree of substitution of the products can be influenced by the reaction temperature. In general, a lower temperature would favour the alkylated phenols and guaiacols, whereas a higher temperature could favour the less substituted phenols or catechols. One of the advantages of solvolytic treatment is that it would allow researchers to fine-tune the chemical reactivity by adjusting the solvent system strategically. For example, Lewis-based solvents, such as methanol, has shown to preserve the aromaticity of the depolymerized product by suppressing hydrogenation. However, solvent recovery through distillation methods can be energy-intensive and solvent loss during the recovery has shown to be one of the most sensitive operating cost expenditures of large-scale lignin depolymerization (Kouris et al., 2018). Innovative approach could be sought by considering a higher boiling point solvent systems, for instance, IL, to promote the boiling point differences between the solvent and the solutes.

4.1.2.3. Ionic liquid

Many articles have considered the use of IL to enable a comprehensive lignin valorization protocol: extraction, depolymerization, and recovery. Although often criticized for its environmental toxicity, IL exhibits some remarkable chemical activities towards lignin degradation and transformation. IL can offer a high extraction yield and minimal structural alteration in extraction, which makes it more suitable for aromatic feedstock production (Ji & Lv, 2020). Other ILs have demonstrated the conversion of commercial lignin into speciality chemicals, namely homovanillic and vanillic acid, using the combination of [EMIM][Triflate] and triethylammonium methanesulfonate (TMS) with water and H_2O_2 (Dier et al., 2017). However, some of the ILs are known to induce additional chemical changes. For example, alkali and sulphate-based IL could lead to a decrease in β-O-4 bond cleavage while promoting more stable C-C bond formation, which leads to less depolymerization. The uses of ILs require comprehensive considerations. For example, the production of byproduct waste and odour from the amine- or sulphate-based ILs could make the process environmentally unfavourable. If the depolymerization aims to produce aromatic fuel additive of BTEX, any nitrogen-based or sulphur-based IL may require additional purifications to minimize residual hetero-atom contaminant, as they may induce NOx or SOx formation during combustion.

4.1.2.4. Thermal treatment

Thermal treatment of lignin concerns the transformation of solid lignin into liquid or gas products by supplying thermal energy. Depending on the temperature profile and the reaction environment, the degree of lignin fragmentation can be adjusted. Pyrolysis and gasification are the two most common examples in the category. Pyrolysis of biomass is typically performed in an oxygen-free environment, and the temperature can rise from room to 400-600°C in several seconds. The rate of heating, final temperature, and the residences time scan be used to control the resulting product. Compared to chemical-based fragmentation, pyrolysis is a low-cost method to achieve lignin depolymerization efficiently, but the resulting liquid products, such as bio-oil, typically exhibit multiple phase separation issues and may contain highly reactive carbonyl groups that are prone to uncontrolled polymerization. The chemical instability of the product requires additional hydro-stabilization treatment before the bio-oil can be used for further upgrading or stored (Lam et al., 2020). Meanwhile, the lignin based bio-oil has high oxygen content, leading to significant deficiencies in heating value, which has also become a bottleneck problem in the practical application of the technology. It is essential to add a suitable catalyst during the pyrolysis process to control the degree of lignin pyrolysis and product distribution, which will be discussed in Section 4.2.

4.1.2.5. Electrochemical depolymerization

Electrochemical depolymerization of lignin has recently gained increasing attention because of its unique advantages to achieve chemical redox mildly at below water-boiling temperature and atmospheric pressure. Moreover, electrocatalysis offers a direct connection between the renewable electricity harnessed from intermittent sources and chemical transformation, enabling a renewable-energy powered electrified biorefinery. Several recent reviews have discussed the advancement of electrocatalysis to valorize lignin for fuel and chemicals production (Garedew et al., 2021). Electrochemical depolymerization of lignin is typically achieved in a strongly alkaline aqueous environment, which provides conductivity and improves lignin solubility. Electrochemical degradation often occurs in oxidative environments, while electrochemical hydrogenation are usually applied toward upgrading the degraded aromatic units (Garedew et al., 2019; Lam et al., 2020). Cai et al. (2018) demonstrated the production of mono-aromatic specialty chemicals, such as vanillin, syringaldehyde, guaiacol, trans-ferulic acid, syringaldehyde, and acetosyringone, but the overall yield remains low due to a few reasons. First of all, the reaction medium must be conductive, and the electrolyte recovery can be an energy-intensive process (Tu et al., 2021). The reaction rate is dictated by the current flow, and electrochemical reactions operate on a low current flow to avoid side reaction, such as water oxidation. Future works must develop high surface area electrodes to compensate for the low current density and develop specific electrocatalytic surface to improve adsorption. Over-oxidation of the product can be another issue because of the indiscriminative nature of electrocatalysis; the development of a membrane reactor may protect the products from undesired additional redox reaction (Bawareth et al., 2019).

4.2. Catalysts for and from thermochemical processes

The thermochemical methods for the conversion of lignin can be divided into three major ways **(Figure 5)**, *i.e.*, catalytic pyrolysis in an inert atmosphere, catalytic hydrogenolysis in a reducing atmosphere such as hydrogen (Type I), and catalytic oxidation in an oxidizing atmosphere or in the presence of an oxidant (Type II). At the same time, lignin as a carbon source can be used as a raw material for the preparation of carbon-based catalysts (Type III).

4.2.1. Catalytic pyrolysis of lignin

Zeolite is a typical catalyst for the catalytic pyrolysis of lignin. Zeolite has a huge pore volume and specific surface area, which is beneficial to promote the pyrolysis of lignin and reduce the energy consumption of the process. Generally, zeolite with higher acidity and larger pore size shows higher activity, while non-acidic zeolite preferentially resulted in oxygenated aromatics, such as guaiacyl units. In the pyrolysis of lignin, the activity of zeolite catalysts will be reduced or even deactivated due to carbon deposits. Therefore, the used catalysts need to be calcined in an aerobic environment to remove the carbon deposits to restore catalytic activity. Y-zeolite and BETA zeolite catalysts were used for the conversion of phenol intermediates (Kim et al., 2020). Y-type zeolite was the most effective catalyst for monocyclic aromatic hydrocarbons production and BETA zeolite was the most effective catalyst for naphthalene products. Doping other metal elements such as Ni, Zn, Fe, Mo, Ga, etc. in the zeolite can improve the activity, selectivity and carbon deposition resistance of the catalyst. For example, when Fe-modified ZSM-5 zeolite catalyst was used for lignin catalytic pyrolysis, the product selectivity of BTX and the yield of upgraded bio-oil were improved (Zhang et al., 2018b). In addition to the optimization of reaction conditions such as reaction temperature, heating rate, and reaction time, pretreatment can also increase the efficiency of lignin depolymerization and pyrolysis. Microwave-assisted heating technology has also been applied in lignin pyrolysis.

Studies have shown that microwave-assisted technology is an effective way to shorten the reaction time and increase the yield of the target product (Ma et al., 2017).

Metals or metal oxides are also commonly used catalysts in chemical reactions. The surface of metal or metal oxides has a variety of adsorption reaction centers and high activity. Various chemical reactions proceed on the surface of the catalyst at the same time, and hence reduce the selectivity of the product. Cu/C, Pd/C, Pd-Ag catalysts can reduce the temperature required for larch sawdust pyrolysis to produce phenol-rich bio-oil. Different catalysts exhibit different catalytic performance. Among them, the proportion of phenols (GC-area) increased from 25.28% to 35.11% in the presence of Pd/C catalysts (Wang et al., 2018). Ru@N-doped carbon catalysts with homogeneously dispersed Ru nanoparticles and defect-rich carbon supports were synthesized by a two-stage pyrolysis method and used in lignin pyrolysis, resulting in 30.5% yield of aromatic monomers at 300℃ (Li et al., 2019). Metal or metal oxide can also regulate the composition of pyrolysis gas. Nickel oxide derived from nickel plating slag was applied in the pyrolysis of woody biomass for the improved hydrogen production (Guo et al., 2020). Metal doping is an effective method for the preparation of catalysts with enhanced selectivity towards different products. Hendry et al. (2020) used ZrO_2 as a carrier to load Na, Ce, NiCe, MgCe, Fe and FePd for lignin pyrolysis and reported improved production of monomeric phenolics and alkyphenols when the Na/ZrO_2 to lignin ratio is 3:1 at 500℃.

Metal salts have been also used as catalysts for the pyrolysis of lignin. The lignin and the metal salt undergo pyrolysis after being mixed or impregnated, and the metal salt can promote the reaction through complexation with the reactant. Fan et al. (2020) studied the effect of K_2CO_3 for the catalytic pyrolysis of pinewood, peanut shell, rice straw in a fixed-bed reactor. It was found that the addition of K_2CO_3 lead to a decrease in liquid product yield, while the gas yield increased obviously. Ketones and phenols were the main components in the liquid products. Yin et al. (2020) used KCl, KOH and K_2CO_3 in catalytic pyrolysis process and demonstrated the important role of anions deployed in two lignin-related polymers. They found that KOH and K_2CO_3 can reduce the thermal stability of lignin polymers and effectively promote the breaking of C_β-O bonds, but the effect of KCl is very limited.

4.2.2. Catalysts used in hydrogenolysis process

Hydrogenation is a chemical reaction that uses hydrogen atoms to saturate or reduce organic compounds. C=C bonds, C≡C bonds, and C=O bonds become saturated during the hydrogenation process, increasing the content of hydrogen atoms in the product. The hydrogenation can be selectively controlled by applying appropriate catalysts and reaction conditions. Various Ni based catalysts have been developed for lignin hydrogenolysis. Ni/C showed high thermal stability during lignin hydrogenolysis and produce arenes and phenols in high yield (Gao et al., 2016). Ni/MSN-Al prepared by the immobilization of Ni clusters in the channel of mesoporous aluminum silica nanospheres showed much higher activity than the Ni-γ-Al_2O_3 in the hydrogeneolysis of lignin C-O linkages (Si et al., 2019). Platinum group metal-based catalysts were also used in lignin hydrogenolysis. Zhang et al. (2021a) found that the synergy of Pt nanoparticles and basic sites in hydroxyapatite supported Pt catalysts facilitate the production of monomers in high yield in the catalytic hydrogenolysis of alkaline lignin. Hu et al. use isopropanol as hydrogen donor to study the lignin hydrogenolysis with different catalysts include Pd/C, HZSM-5, Pt/TiO_2 and Re/TiO_2 under different reaction conditions such as hydrogen, temperature and pretreatment. They found that PtRe/TiO_2 showed higher activity on the cleavage of C-O bond than the other catalysts (Hu et al., 2019). Finally, hydrodeoxygenation (HDO) process can remove oxygen from phenolic molecules and is an important method of bio-oil upgrading. Mukundan et al. (2021) developed a solvent-free HDO process for the conversion of softwood lignin to aromatics with carbon-ZrO_2 supported Ni/MoS_2 catalyts. The highest deoxygenation of 82.2% was achieved with a 69.1% yield of monomer after optimization. The catalysts Fe_2P, Co_2P, and WP have been applied to the HDO reaction of lignin and lignin derived products. Compared with noble metal catalysts, these metal phosphide catalysts can improve the products selectivity and exhibit good stability.

4.2.3. Catalytic oxidation of lignin

The catalytic oxidation of lignin has milder reaction conditions and shorter reaction time than pyrolysis and hydrogenation. In the lignin oxidation process, oxygen is introduced into the side chain or aromatic ring, which reduces the electron density and increases the steric hindrance between the lignin aromatic rings, making the lignin structural units easier to dissociate. Therefore, catalytic oxidation of lignin is a very promising method for lignin utilization. The lignin catalytic oxidative depolymerization catalysis can be divided into homogeneous catalysis and heterogeneous catalysis reactions, in which transition metals and precious metals catalysts such as Pt and Pd are widely applied. Kumar et al. (2020) prepared a series of catalysts by supporting cobalt on TiO_2, CeO_2 and ZrO_2 for the oxidative depolymerization of prot lignin (a commercial lignin) and alkali lignin. Results showed that high bio-oil yield was obtained when Co/CeO_2 was used as the catalyst, and high selectivity of acetosyringone was achieved with Co/TiO_2 as catalysts. Cabral Almada et al. (2021) loaded Au and Pt particles on TiO_2 for the oxidative depolymerization of Kraft and ethanol organosolv lignins, and showed that Au-TiO_2 can further oxidize the aromatic hydrocarbons produced by the depolymerization of lignin, resulting in a lower yield of the target product, while Pt-TiO_2 can promote the conversion of lignin into high value-added aromatic hydrocarbons.

Walch et al. (2021) used $VO(acac)_2$ and $Cu(OAc)_2$ as homogeneous catalysts for the oxidative depolymerization of Kraft lignin to high-value aromatics with oxygen. A 50% bio-oil yield and increased production of aromatic monomers were achieved by the use of both catalysts, suggesting the favorable combined effect. Cai et al. (2019b) applied polyoxometalate ionic liquid (POM-IL) catalysts in the oxidative cleavage of lignin aromatic unit. The high yield of diethyl maleate was attributed to the combined catalytic effect with acidic and redox active sites from the POM and IL. Das et al. (2017) tested the catalytic performances of $CoCl_2·6H_2O$, $CuSO_4$, $MnN_2O_6·4H_2O$, $CrKO_8S_2·12H_2O$, and $NiCl_2·XH_2O$ in the catalytic oxidative depolymerization of lignin in aqueous 1-ethyl-3-methylimidazolium acetate $[C_2C_1Im][OAc]$ with H_2O_2 and found that $CoCl_2$ was the most active catalyst for the production of aromatic compounds from lignin. Whether heterogeneous or homogeneous catalysis, the conversion rate and yield of the catalyst in the depolymerization of lignin model compounds are much higher than that of real lignin. The real lignin has a complex structure with various functional groups and linkages, which cannot be fully simulated by using model compounds.

4.2.4. Catalysts from lignin

Lignin can be used as a carbon source to prepare carbon based catalysts through surface modification, loading or doping with other elements. The synthesis of lignin derived catalysts starts from the carbonization of lignin through hydrothermal carbonization or thermal pyrolysis. Due to the low surface area and limited functional groups of the hydrothermal char or pyrolysis char from lignin, post modification such as acid or base treatment is necessary. Elements such as N, P, S and metals doping can further enhance the catalytic activity for the target chemical reaction. Li et al. (2020) prepared a LAC-based solid acid by the activation with KOH and H_2SO_4 sulfonation; and used it for the dehydration of fructose to HMF, achieving a high product yield at 5.7%. In addition to non-metal doping catalyst, metal doped lignin-based catalysts are also used for thermal catalysis, electrocatalysis and photocatalysis. Pt-lignin-based carbon fiber electrocatalyst was prepared by electrospinning and thermochemical treatments and used for alcohol electro-oxidation (García-Mateos et al., 2017). Carbon-based Pd catalysts were prepared by loading Pd particles on the chemical activated kraft lignin with H_3PO_4. The catalyst showed high activity in toluene oxidation (Bedia et al., 2010). A magnetic catalyst with lignosulfonate supported Pd and Fe_3O_4 nanoparticles was developed and applied in aqueous Suzuki-Miyaura reaction, showing high activity for CS(sp^2)-C(sp^2) coupling in water (Nasrollahzadeh et al., 2019). However, the current preparation process of lignin-derived catalysts still faces harsh preparation conditions. For example, the preparation process may use a lot of acids, bases, and excessive metal salts, which may cause environmental pollution problems. Thus, in order to tackle this issue, the development of green preparation processes will be an important future trend.

4.3. Lignin-first pretreatment

Lignin-first pretreatment is a pretreatment method that considers the preservation of both lignin and polysaccharide as the first and foremost aspect in whole biomass valorization. This approach can actively reduce possible side and unwanted reactions that arise from the conventional biorefinery processes. The principle of the lignin-first pretreatment aims at fractionating lignin from the biomass while protecting its structure against condensation and repolymerization (Islam et al., 2020). The general lignin-first pretreatment processes are operated by staged, of which lignin is first extracted from woody biomass by various organosolv or acid-catalyzed pretreatment reactions in order to break the lignin-sugar linkages (Islam et al., 2021). The reactive intermediates are then stabilized by certain chemicals which prevent the formation of reactive functional groups that can lead to lignin condensation. The ether bond linkages of lignin and oligomers are then cleaved into monomers and stabilized through hydrogenolysis (Sun et al., 2018b).

Lignin-first technique in lignocellulosic biomass fractionalization has gained much attention and continued to contribute to the lignin biorefinery development and industry. Among the various techniques, the most common approach is Reductive Catalytic Fractionation (RCF) (Sun et al., 2020). This approach involves the introduction of a transition metal catalyst into pretreatment spent liquor under reductive and inert atmosphere with the presence of hydrogen donors. Significant cleavage of β-O-4 bond can be observed with more than 50% mono-phenolic compounds. Stabilization of reactive intermediates formed during the depolymerization process is achieved by the metal catalyst. Solvent is also crucial for the delignification process and the selectivity of monomers (Renders et al., 2018). Polar solvents are excellent in delignification but may hydrolyze the polysaccharides, being reduced during the hydrogenation process or react with the monomers formed and solvents. Therefore, choosing suitable solvent is essential to attain the most optimal lignin yield and bond cleavage efficiency. The choice of solvents should depend on the targeted monomers and the proportions of cellulose, hemicellulose and lignin in a particular type of biomass. Stabilization of reactive intermediates and aldehyde groups can be achieved by the addition of diol as solvents. Ethylene glycol has been broadly used to trap C2 aldehyde, leading to the formation of acetals. Acetal terminated the aldehyde reactions to form benzylic cations, prevented the condensation and repolymerization reaction (Shuai et al., 2016).

A lack of standard protocols in the process and product evaluations have been a great challenge for the performance evaluation that could advance the research field. The exact role of the transition metal catalyst has not been fully understood. Further research of the role and working mechanism of the related catalysts shall improve the reactor design and the related performances behind the reaction.

4.4. Lignin separation

Lignin separation has aroused a lot of attention in recent research. Fractionated lignin in pretreatment spent liquors have been carried out by ultrafiltration and nanofiltration (Islam et al., 2021). Separation of lignin monomers from catalytic depolymerization are usually performed by gas chromatography and liquid chromatography techniques, which utilize inert gas and mixed solvent systems for analytical separations. However, a small volume of reaction mixture can only be inserted for chromatographic separations. Lignin is a hetero-polymer which consists of more than one repeating units with different linkages, resulting in lengthened retention time and high energy consumption for separation. Different methods have been developed in order to ease the separation methods and reduce the energy used during the separation methods. Gomes and Rodrigues (2019) adopted resins and ultrafiltration methods to separate vanillin, vanillic acid, and acetovanillone from the reaction mixture due to the differences in polarity. The authors have also utilized low toxicity solvent extraction methods aiding with crystallization under mild pH conditions (Gomes & Rodrigues, 2020). Anion exchange chromatography was also adopted to separate vanillin from the monolignol mixture with amination and pH workup (Liu et al., 2020a).

The separation methods of monomers derived from lignin depolymerization are scarce to the best of our knowledge. Different catalytic lignin depolymerization reactions usually produce many different products which further increases the difficulties in separating products from reaction mixture. Therefore, more investigations should be done to search for innovative separation methods in order to separate monomers more conveniently and energy efficiently.

5. Challenges

5.1.1. Economic trajectory (Technoeconomic assessment)

Although lignin plays a vital role in sustainable biorefineries and circular bioeconomy, the lack of its economic feasibility has become the real bottleneck in its commercialization. The situation is further aggravated by its heterogeneity and wide molecular mass distribution from different feedstock. One of the challenges is the ineffectiveness of downstream processes used to produce the value-added chemicals from lignin, which lacks the technological feasibility and economic viability. In-depth knowledge on the market demand, economic potential, and maturity of technology is crucial. The economic potential is important concept that can be used as a benchmark to identify whether the process is profitable or not in the long run. To clarify the technical, economic, and energy related factors affecting the economic feasibility of biorefinery technologies, Huang et al. (2020) performed TEA on γ-valerolactone-based process and obtained a minimum ethanol selling price (MESP) of US$3.44/ gasoline gallon equivalent (GGE) from the optimized system (not including lignin). Martinez-Hernandez et al. (2019) performed TEA and greenhouse gas (GHG) analyses on IL pretreated lignocellulosic biomass for lignin derived phenol and cellulosic ethanol, suggesting a MESPof US$2.02/GGE. The market analysis (as MESP) would not only set the choice of product to be manufactured, but will also enables the researcher to predict on the future market trends. In this way, one may clearly identify the research efforts that can lower the barrier of the "cost-determining" step. Similarly, a comprehensive understanding of the maturity of a technology is important in selecting the most promising process that is viable at the current stage of technological development, which will also help highlighting the distance away from commercialization.

Recent advances in lignin depolymerization via many creative methods produces identified products in high yields, at the same time, raises the question: lignin-first biorefinery is reaching the commercial market or not (Sun et al., 2018a). Few techno-economic analysis (TEA) study on lignocellulosic biorefinery has been reported recently, however, only self-generated data was used, and there is a lack of comparison with other lignin depolymerization processes (Yadav et al., 2021). A comprehensive TEA that evaluates recent lignin works is needed to reveal the gap between technology development and real application, which further provide feedback to the researcher of where the improvement is required from an economic perspective. Recently, Khwanjaisakun et al. (2020) demonstrated the TEA of vanillin produced from Kraft lignin (synthesized via the oxidation process) and compared with the vanillin produced from petroleum-based feed. The study simulated three different separation cases, *i.e.*, solvent extraction followed by distillation (Case I), solvent extraction (Case II), and vacuum distillation (Case III) and were then compared to identify the most suitable separation process. The results revealed that the highest vanillin yield of 9.25% was attained using 30 g/l feed concentration of Kraft lignin. Case I appeared to be the most suitable method of separation since it consumes the lowest amount of energy and gives the best economic returns, with a payback period of 6.19 years and internal rate of return (IRR) of 22.63%. Despite the low yield of vanillin, the abundant supply and low cost of Kraft lignin make the valorization technique able to compete with the commercial process.

5.1.2. Mass balance

The overall process mass balance is important in building complete process model for TEA and lifecycle assessment (LCA). In lignin conversion process, most of the mass balance can be separated into two aspects, *i.e.*, (a) mass balance of extraction, depolymerization and separation processes, and (b) mass balance of catalyst synthesis process. For (a), most recent lignin research was focused on depolymerization processes, to some extent, mass balance in lignin extraction and monomer and/or dimer separation were ignored. For example, beech wood lignin was oxidative depolymerized to vanillin and syringaldehyde with high yields, however, the yield of substrates to extracted lignin was not reported, therefore, makes it difficult to understand the economic value (Gu et al., 2012). Moreover, downstream separation and purification processes were frequently ignored in related research, in fact, most of lignin research only reported the monomer and/or dimer yield without further actions in separation and purification (Gu et al., 2012). It is definitely understandable that experimentalist always aims for better performance in depolymerization, but it is also important to include mass balance from the original substrate to final product. For (b), another significant issue is the absence of mass balance for catalyst synthesis. Currently, conventional catalyst like Ru/C was widely used and commercially available, but its cost and environmental impact were unpredictable. Unconventional novel catalysts such as La/SBA-15, Cu-PMO, HZSM-5 and Cu/Mo ZSM-5 have been synthesized, but the monomer yields have not been reported (Gu et al., 2012). From economic perspective, catalyst cost constitutes a considerable amount of operational cost and significantly affect the profitability of the overall process and hence should be included in literatures for future references.

6. Research Needs and Future Direction

The current review has implied that lignin holds huge potential as a sustainable feedstock for the production of aromatic compounds. Based on the results of TEA, however, lignin based aromatics may hardly be competitive without government subsidies especially when the built of industry needs to developed upon the existing refinery products, such as energy and chemicals. In order to expand the industrial production of lignin, the aspects related to reactor scaling up, cost and risk analysis, supply chain, market assessments and regulatory and policy implications, which forms into significant sizes of needed investments. If the price of oil remains low, the constraints would be more acute and not suitable for local recyclers or departments. The industry may need to associate with (not competing with) conventional refinery before large scale utilization. A conceptual diagram of incorporating biorefinery process in a petroleum refinery, its related products, and instrumental retrofits f have been illustrated in **Figure 6**. As hydrogenation catalysis and distillation systems are the most critical elements in petroleum refinery and the key unit operations for lignin depolymerization, solvent recovery, and product separation, the combine system may provide useful carbon benefits if some part of the fossil based feedstock can be replaced by biomass carbon.

One serious barrier in lignin valorization is the lack of rapid and comprehensive approach for lignin structure analysis. Evaluation of lignin depolymerization is currently time-consuming and hence real-time process control is not possible. Most lignin researches therefore do not include the detailed product information, market values, and potential applications. Furthermore, lignin is chemically and structurally inherently different from the currently used petrochemicals, therefore needs advance and innovative technologies for the one-to-one replacement of petrochemical precursors with lignin. This further indicates the need for adjustment and optimization of the existing formulation process, along with lignin. Although there has been tremendous research in the area, there is serious lack in synergy and collaborations. We need to go beyond the “proof-of-concept” stage and to take a deeper dive into the “proof-of-value” stage in order to showcase on a commercial scale that lignin is a superior feedstock for certain chemicals and materials.

7. Conclusions

This review summarizes the findings of recent scientific research and industrial advances in lignin valorization. The biorefinery potential and functionality of lignin-based aromatics to compare with or even substitute petroleum-based aromatics have been highlighted. The ongoing research on lignin structures, reaction routes, functions of important linkages, fractionation and/or depolymerization technologies, and downstream processes have been explored for possible uses of lignin products in various novel applications. The techno-economic analysis and overall economic challenges has been evaluated in order to strengthen the shift of lignin aromatics into the current petroleum-dominated infrastructure.

Acknowledgments

The authors thank the Hong Kong General Research Fund (PolyU 152123/17E and 15212317) and Innovation and Technology Fund (GHP/042/18GD) for the financial supports on this study.

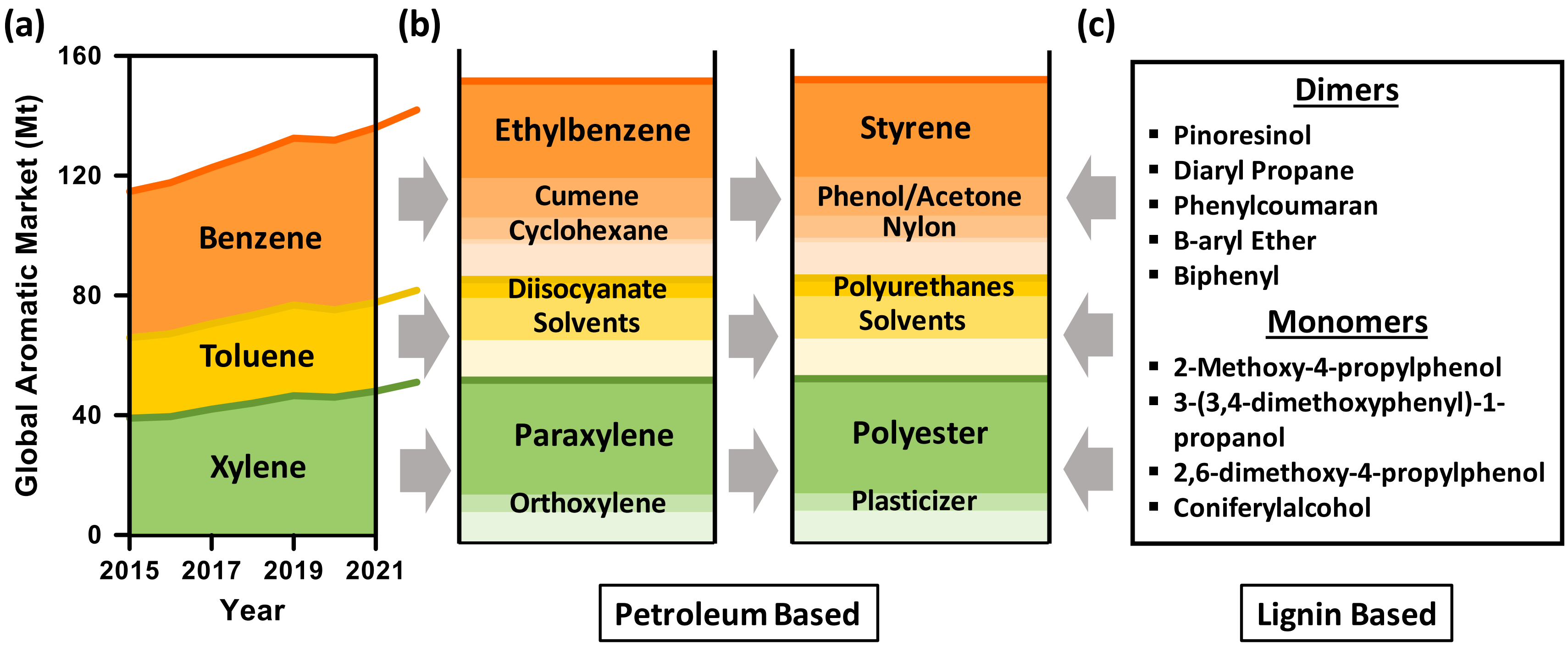


Figure 1. (a) Statistical (2015-2018) and predicted (2019-2021) quantities of global aromatic compounds consumptions; (b) fractions of benzene, toluene, and xylene used in various applications in a petroleum refinery; and (c) key lignin monomers and dimers from a biorefinery.

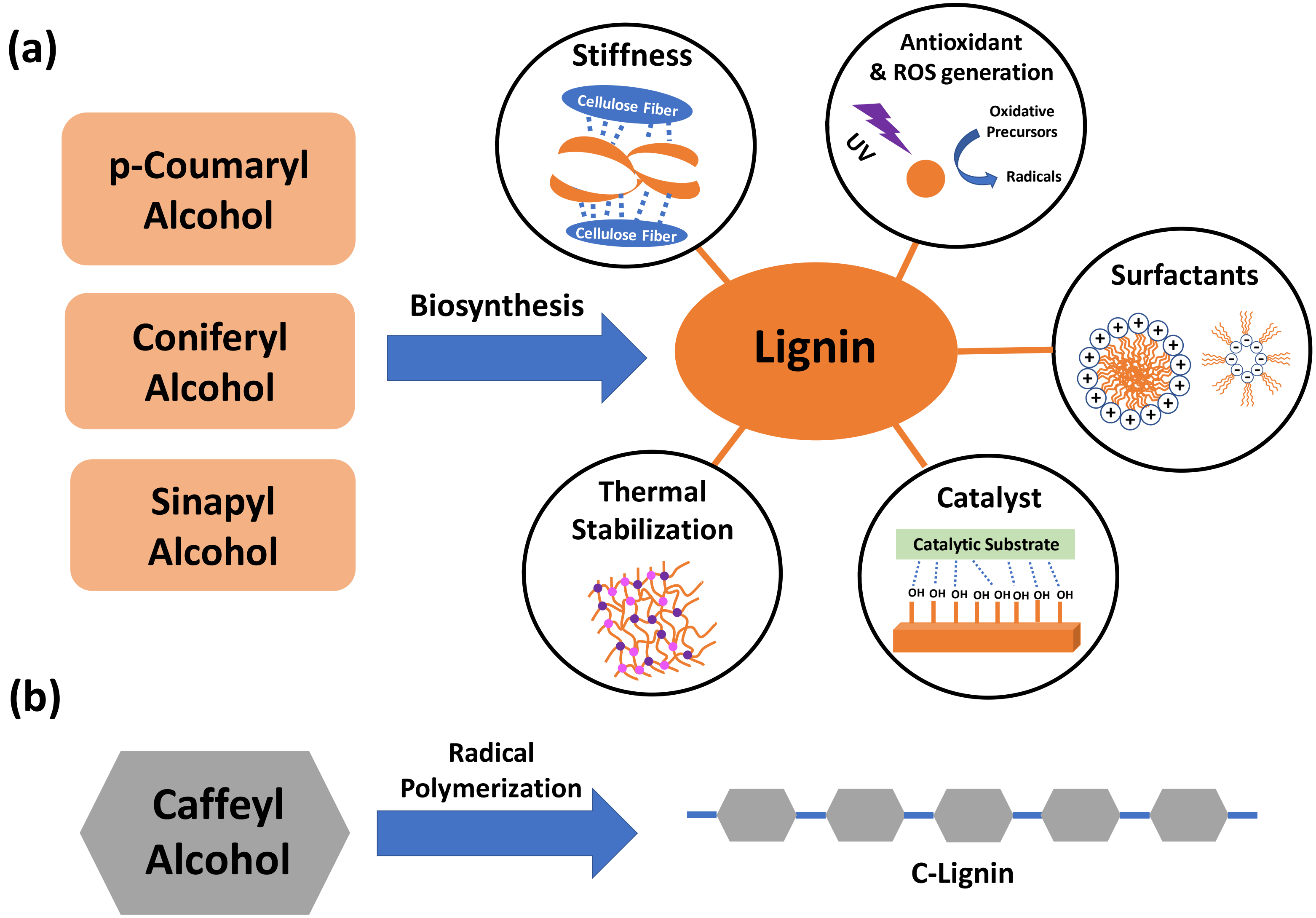


Figure 2. Formation of (a) hetero- and (b) homo- lignin polymers and their key properties for valorization

Figure 3. Roadmap of recent advanced of lignin valorization technologies. Key references for adhesives (Wei et al., 2019); adsorbent (Zhang et al., 2020a); carbon fiber (Bengtsson et al., 2019); plastics/hydrogel (Dai et al., 2020a); electrodes (Chaleawlert-umpon & Liedel, 2017); colored lignin (Zhang et al., 2018a); and pharmaceuticals (Domínguez-Robles et al., 2020)

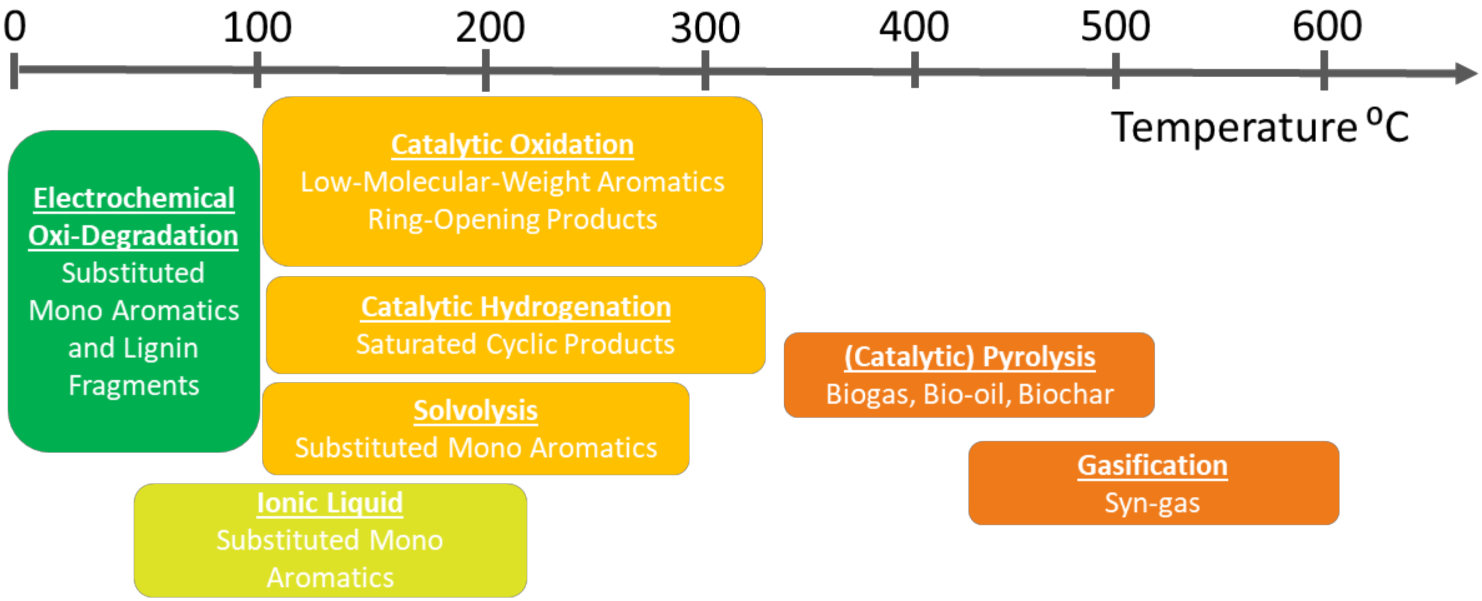


Figure 4. An overview of lignin conversion methods

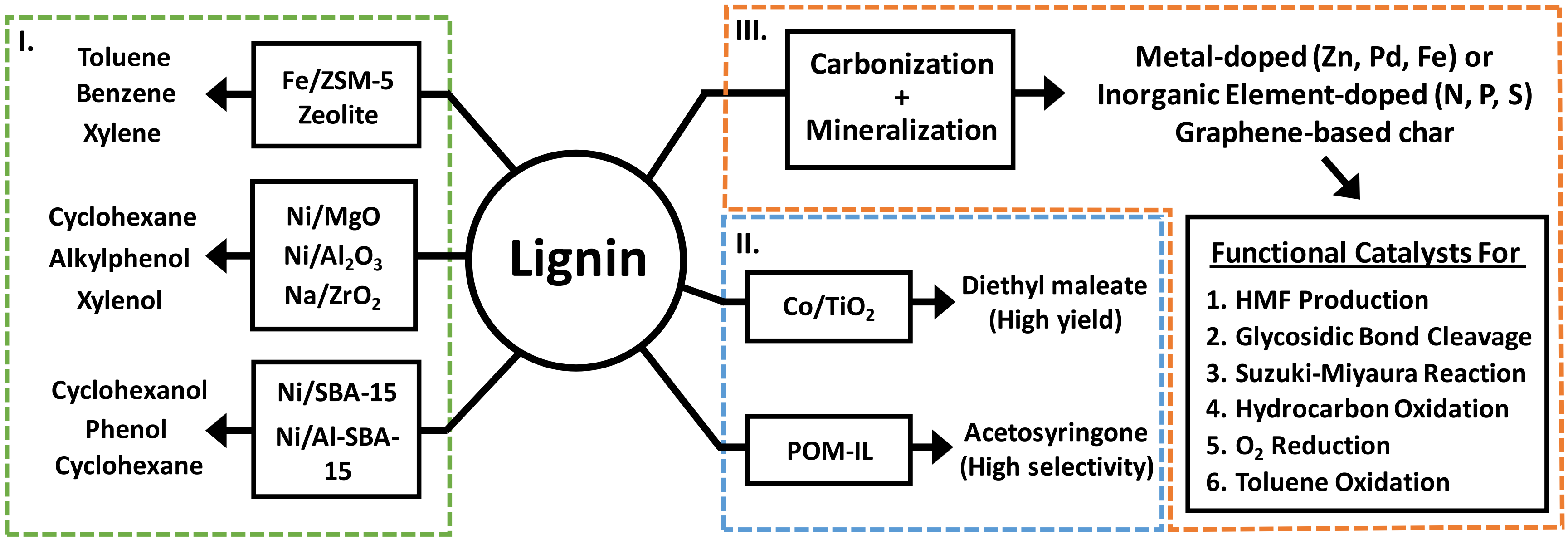


Figure 5. Three thermochemical approaches and the related products of lignin valorization. Type I – Reductive depolymerization (Si et al., 2019; Zhang et al., 2018b). Type II – Lignin derived catalysts (Li et al., 2020). Type III – Oxidative depolymerization (Cai et al., 2019a; Kumar et al., 2020)

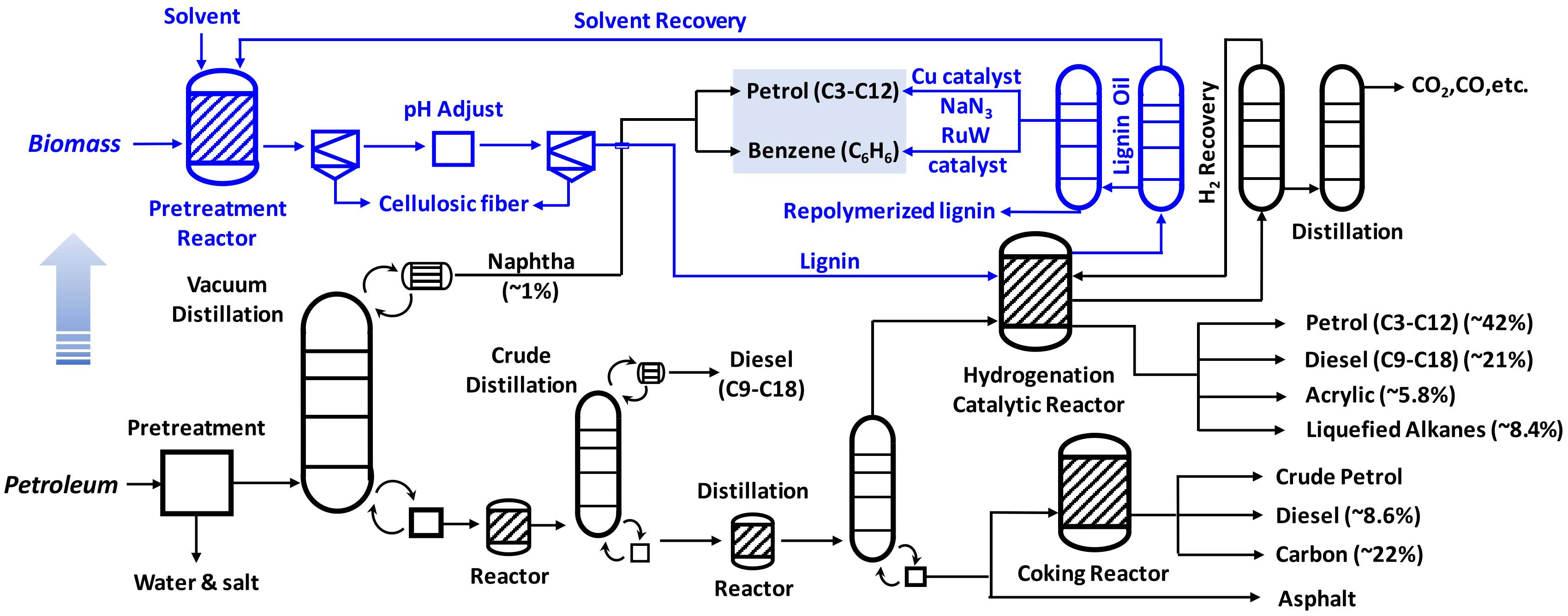


Figure 6. Possible retrofit and related aromatic products (marked in blue) in conventional refinery for lignin valorization. Note that distillation units may be replaced with and some products can only be provided by petroleum refinery.

Table 1. Concentrations of key functional groups in lignin after different pretreatment

Feedstock	Pretreatment method	Aliphatic OH (mmol/g)	Phenolic OH (mmol/g)	Carboxylic (mmol/g)	Average MW (Da)	Ref.
Poplar	Acid	3.25	3.04	0.05	2871	Wang et al. (2021a)
Poplar Wood Chip	Acid/Organosolv	4.55	1.56	0.08	9400	Wang et al. (2020)
Poplar Wood Chip	Acid/Organosolv	1.11	3.05	0.15	3400	Wang et al. (2020)
Poplar	Alkali/Organosolv	1.61	1.69	0.32		Li et al. (2021)
Masson Pine	Alkali/Organosolv	1.29	1.57	0.51		Li et al. (2021)
Softwood	Alkali/Organosolv	2.50	1.53	0.28	3603	Zhong et al. (2020)
Eucalyptus	Organosolv	1.92	2.32		8500	Dong et al. (2019)
Sugarcane Bagasse	Acid/Ionic liquid	0.79	2.84	0.23	956	Ji et al. (2021)
Reed	Ionic liquid	6.59	4.68	048	3962	Zhang et al. (2021b)

Reference

AgileIntel. 2021. Market volume of benzene worldwide from 2015 to 2020, with a forecast for 2021 to 2026 (in million metric tons).

Banu, J.R., Kavitha, S., Kannah, R.Y., Devi, T.P., Gunasekaran, M., Kim, S.-H., Kumar, G. 2019. A review on biopolymer production via lignin valorization. *Bioresource technology*, **290**, 121790.

Barana, D., Ali, S.D., Salanti, A., Orlandi, M., Castellani, L., Hanel, T., 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.

Bawareth, B., Di Marino, D., Nijhuis, T.A., Jestel, T., Wessling, M. 2019. Electrochemical Membrane Reactor Modeling for Lignin Depolymerization. *ACS Sustainable Chemistry & Engineering*, **7**(2), 2091-2099.

Bedia, J., Rosas, J.M., Rodríguez-Mirasol, J., Cordero, T. 2010. Pd supported on mesoporous activated carbons with high oxidation resistance as catalysts for toluene oxidation. *Applied Catalysis B: Environmental*, **94**(1), 8-18.

Bengtsson, A., Bengtsson, J., Sedin, M., Sjöholm, E. 2019. Carbon fibers from lignin-cellulose precursors: effect of stabilization conditions. *ACS Sustainable Chemistry & Engineering*, **7**(9), 8440-8448.

Berstis, L., Elder, T., Crowley, M., Beckham, G.T. 2016. Radical nature of C-lignin. *ACS Sustainable Chemistry & Engineering*, **4**(10), 5327-5335.

Biswas, B., Kumar, A., Kaur, R., Krishna, B.B., Bhaskar, T. 2021. Catalytic hydrothermal liquefaction of alkali lignin over activated bio-char supported bimetallic catalyst. *Bioresource Technology*, **337**, 125439.

Cabral Almada, C., Kazachenko, A., Fongarland, P., Da Silva Perez, D., Kuznetsov, B.N., Djakovitch, L. 2021. Supported-Metal Catalysts in Upgrading Lignin to Aromatics by Oxidative Depolymerization. *Catalysts*, **11**(4).

Cai, C., Zhan, X., Zeng, M., Lou, H., Pang, Y., Yang, J., Yang, D., Qiu, X. 2017. Using recyclable pH-responsive lignin amphoteric surfactant to enhance the enzymatic hydrolysis of lignocelluloses. *Green Chemistry*, **19**(22), 5479-5487.

Cai, P., Fan, H., Cao, S., Qi, J., Zhang, S., Li, G. 2018. Electrochemical conversion of corn stover lignin to biomass-based chemicals between Cu/NiMoCo cathode and Pb/PbO2 anode in alkali solution. *Electrochimica Acta*, **264**, 128-139.

Cai, Z., Long, J., Li, Y., Ye, L., Yin, B., France, L.J., Dong, J., Zheng, L., He, H., Liu, S. 2019a. Selective production of diethyl maleate via oxidative cleavage of lignin aromatic unit. *Chem*, **5**(9), 2365-2377.

Cai, Z., Long, J., Li, Y., Ye, L., Yin, B., France, L.J., Dong, J., Zheng, L., He, H., Liu, S., Tsang, S.C.E., Li, X. 2019b. Selective Production of Diethyl Maleate via Oxidative Cleavage of Lignin Aromatic Unit. *Chem*, **5**(9), 2365-2377.

Chaleawlert-umpon, S., Liedel, C. 2017. More sustainable energy storage: lignin based electrodes with glyoxal crosslinking. *Journal of Materials Chemistry A*, **5**(46), 24344-24352.

Che, Q., Yang, M., Wang, X., Yang, Q., Rose Williams, L., Yang, H., Zou, J., Zeng, K., Zhu, Y., Chen, Y., Chen, H. 2019. Influence of physicochemical properties of metal modified ZSM-5 catalyst on benzene, toluene and xylene production from biomass catalytic pyrolysis. *Bioresource Technology*, **278**, 248-254.

Chen, X., Sun, S., Wang, X., Wen, J., Wang, Y., Cao, X., Yuan, T., Wang, S., Shi, Q., Sun, R. 2020. One-pot preparation and characterization of lignin-based cation exchange resin and its utilization in Pb (II) removal. *Bioresource Technology*, **295**, 122297.

Dai, L., Ma, M., Xu, J., Si, C., Wang, X., Liu, Z., Ni, Y. 2020a. All-lignin-based hydrogel with fast pH-stimuli responsiveness for mechanical switching and actuation. *Chemistry of Materials*, **32**(10), 4324-4330.

Dai, X., Lv, J., Yan, G., Chen, C., Guo, S., Fu, P. 2020b. Bioremediation of intertidal zones polluted by heavy oil spilling using immobilized laccase-bacteria consortium. *Bioresource technology*, **309**, 123305.

Das, L., Xu, S., Shi, J. 2017. Catalytic Oxidation and Depolymerization of Lignin in Aqueous Ionic Liquid. *Frontiers in Energy Research*, **5**, 21.

Deng, Y., Liu, Y., Qian, Y., Zhang, W., Qiu, X. 2015. Preparation of photoresponsive azo polymers based on lignin, a renewable biomass resource. *Acs Sustainable Chemistry & Engineering*, **3**(6), 1111-1116.

Diaz-Baca, J.A., Fatehi, P. 2021. Process development for tall oil lignin production. *Bioresource Technology*, **329**, 124891.

Dier, T.K.F., Rauber, D., Durneata, D., Hempelmann, R., Volmer, D.A. 2017. Sustainable Electrochemical Depolymerization of Lignin in Reusable Ionic Liquids. *Scientific Reports*, **7**(1), 5041.

Domínguez-Robles, J., Cárcamo-Martínez, Á., Stewart, S.A., Donnelly, R.F., Larrañeta, E., Borrega, M. 2020. Lignin for pharmaceutical and biomedical applications–Could this become a reality? *Sustainable Chemistry and Pharmacy*, **18**, 100320.

Dong, C., Meng, X., Yeung, C.S., TSE, H.-Y., Ragauskas, A.J., Leu, S.-Y. 2019. Diol pretreatment to fractionate a reactive lignin in lignocellulosic biomass biorefineries. *Green Chemistry*, **21**(10), 2788-2800.

Duan, D., Ruan, R., Wang, Y., Liu, Y., Dai, L., Zhao, Y., Zhou, Y., Wu, Q. 2018. Microwave-assisted acid pretreatment of alkali lignin: Effect on characteristics and pyrolysis behavior. *Bioresource technology*, **251**, 57-62.

Fan, H., Chang, X., Wang, J., Zhang, Z. 2020. Catalytic pyrolysis of agricultural and forestry wastes in a fixed-bed reactor using K2CO3 as the catalyst. *Waste Management & Research*, **38**(1), 78-87.

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

Gan, L., Lyu, L., Shen, T., Wang, S. 2019. Sulfonated lignin-derived ordered mesoporous carbon with highly selective and recyclable catalysis for the conversion of fructose into 5-hydroxymethylfurfural. *Applied Catalysis A: General*, **574**, 132-143.

Gao, F., Webb, J.D., Hartwig, J.F. 2016. Chemo- and Regioselective Hydrogenolysis of Diaryl Ether C− O Bonds by a Robust Heterogeneous Ni/C Catalyst: Applications to the Cleavage of Complex Lignin- Related Fragments. *Angewandte Chemie*, **128**(4), 1496-1500.

García-Mateos, F.J., Cordero-Lanzac, T., Berenguer, R., Morallón, E., Cazorla-Amorós, D., Rodríguez-Mirasol, J., Cordero, T. 2017. Lignin-derived Pt supported carbon (submicron)fiber electrocatalysts for alcohol electro-oxidation. *Applied Catalysis B: Environmental*, **211**, 18-30.

Garedew, M., Lam, C.H., Petitjean, L., Huang, S., Song, B., Lin, F., Jackson, J.E., Saffron, C.M., Anastas, P.T. 2021. Electrochemical upgrading of depolymerized lignin: a review of model compound studies. *Green Chemistry*, **23**(8), 2868-2899.

Garedew, M., Young-Farhat, D., Jackson, J.E., Saffron, C.M. 2019. Electrocatalytic Upgrading of Phenolic Compounds Observed after Lignin Pyrolysis. *ACS Sustainable Chemistry & Engineering*, **7**(9), 8375-8386.

Garlapati, V.K., Chandel, A.K., Kumar, S.P.J., Sharma, S., Sevda, S., Ingle, A.P., Pant, D. 2020. Circular economy aspects of lignin: Towards a lignocellulose biorefinery. *Renewable and Sustainable Energy Reviews*, **130**, 109977.

Gomes, E., Rodrigues, A. 2020. Crystallization of vanillin from kraft lignin oxidation. *Separation and Purification Technology*, **247**, 116977.

Gomes, E., Rodrigues, A. 2019. Lignin biorefinery: Separation of vanillin, vanillic acid and acetovanillone by adsorption. *Separation and Purification Technology*, **216**, 92-101.

Gordobil, O., Herrera, R., Yahyaoui, M., İlk, S., Kaya, M., Labidi, J. 2018. Potential use of kraft and organosolv lignins as a natural additive for healthcare products. *RSC advances*, **8**(43), 24525-24533.

Gu, X., Kanghua, C., Ming, H., Shi, Y., Li, Z. 2012. La-modified SBA-15/H2O2 systems for the microwave assisted oxidation of organosolv beech wood lignin. *Maderas. Ciencia y tecnología*, **14**(1), 31-41.

Guo, D., Hu, M., Chen, Z., Cui, B., Zhang, Q., Liu, Y., Luo, S., Ruan, R., Liu, Y. 2020. Catalytic Pyrolysis of rain tree biomass with nano nickel oxide synthetized from nickel plating slag: A green path for treating waste by waste. *Bioresource Technology*, **315**, 123831.

Guo, H., Chen, Y., Yang, S., Li, R., Zhang, X., Dong, Q., Li, X., Ma, X. 2021. Lignin-based adsorbent-catalyst with high capacity and stability for polychlorinated aromatics removal. *Bioresource Technology*, **337**, 125453.

Guo, L., Dou, R., Wu, Y., Zhang, R., Wang, L., Wang, Y., Gong, Z., Chen, J., Wu, X. 2019. From lignin waste to efficient catalyst: Illuminating the impact of lignin structure on catalytic activity of cycloaddition reaction. *ACS Sustainable Chemistry & Engineering*, **7**(19), 16585-16594.

He, W., Gao, W., Fatehi, P. 2017. Oxidation of kraft lignin with hydrogen peroxide and its application as a dispersant for kaolin suspensions. *ACS Sustainable Chemistry & Engineering*, **5**(11), 10597-10605.

Hendry, A., Åhlén, M., Fernandes, T., Cheung, O., Sanna, A. 2020. Catalytic cracking of Etek lignin with zirconia supported metal-oxides for alkyl and alkoxy phenols recovery. *Bioresource Technology*, **317**, 124008.

Hu, J., Zhang, Q., Lee, D.-J. 2018. Kraft lignin biorefinery: A perspective. *Bioresource Technology*, **247**, 1181-1183.

Hu, J., Zhang, S., Xiao, R., Jiang, X., Wang, Y., Sun, Y., Lu, P. 2019. Catalytic transfer hydrogenolysis of lignin into monophenols over platinum-rhenium supported on titanium dioxide using isopropanol as in situ hydrogen source. *Bioresource technology*, **279**, 228-233.

Huang, C., Lin, W., Lai, C., Li, X., Jin, Y., Yong, Q. 2019. Coupling the post-extraction process to remove residual lignin and alter the recalcitrant structures for improving the enzymatic digestibility of acid-pretreated bamboo residues. *Bioresource technology*, **285**, 121355.

Huang, K., Fasahati, P., Maravelias, C.T. 2020. System-Level Analysis of Lignin Valorization in Lignocellulosic Biorefineries. *iScience*, **23**(1), 100751.

Islam, M.K., Rehman, S., Guan, J., Lau, C.-Y., Tse, H.-Y., Yeung, C.S., Leu, S.-Y. 2021. Biphasic pretreatment for energy and carbon efficient conversion of lignocellulose into bioenergy and reactive lignin. *Applied Energy*, **303**, 117653.

Islam, M.K., Wang, H., Rehman, S., Dong, C., Hsu, H.-Y., Lin, C.S.K., Leu, S.-Y. 2020. Sustainability metrics of pretreatment processes in a waste derived lignocellulosic biomass biorefinery. *Bioresource Technology*, **298**, 122558.

Ji, H., Lv, P. 2020. Mechanistic insights into the lignin dissolution behaviors of a recyclable acid hydrotrope, deep eutectic solvent (DES), and ionic liquid (IL). *Green Chemistry*, **22**(4), 1378-1387.

Ji, Q., Yu, X., Wu, P., Yagoub, A.E.-G.A., Chen, L., Taiye, M.A., Zhou, C. 2021. Pretreatment of sugarcane bagasse with deep eutectic solvents affect the structure and morphology of lignin. *Industrial Crops and Products*, **173**, 114108.

Jiang, B., Chen, C., Liang, Z., He, S., Kuang, Y., Song, J., Mi, R., Chen, G., Jiao, M., Hu, L. 2020. Lignin as a wood- inspired binder enabled strong, water stable, and biodegradable paper for plastic replacement. *Advanced Functional Materials*, **30**(4), 1906307.

Jin, J., Ding, J., Klett, A., Thies, M.C., Ogale, A.A. 2018. Carbon Fibers Derived from Fractionated–Solvated Lignin Precursors for Enhanced Mechanical Performance. *ACS Sustainable Chemistry & Engineering*, **6**(11), 14135-14142.

Ke, C.-Y., Lu, G.-M., Wei, Y.-L., Sun, W.-J., Hui, J.-F., Zheng, X.-Y., Zhang, Q.-Z., Zhang, X.-L. 2019. Biodegradation of crude oil by Chelatococcus daeguensis HB-4 and its potential for microbial enhanced oil recovery (MEOR) in heavy oil reservoirs. *Bioresource technology*, **287**, 121442.

Khwanjaisakun, N., Amornraksa, S., Simasatitkul, L., Charoensuppanimit, P., Assabumrungrat, S. 2020. Techno-economic analysis of vanillin production from Kraft lignin: Feasibility study of lignin valorization. *Bioresource Technology*, **299**, 122559.

Kim, J.-Y., Moon, J., Lee, J.H., Jin, X., Choi, J.W. 2020. Conversion of phenol intermediates into aromatic hydrocarbons over various zeolites during lignin pyrolysis. *Fuel*, **279**, 118484.

Klinger, G.E., Zhou, Y., Foote, J.A., Wester, A.M., Cui, Y., Alherech, M., Stahl, S.S., Jackson, J.E., Hegg, E.L. 2020. Nucleophilic Thiols Reductively Cleave Ether Linkages in Lignin Model Polymers and Lignin. *ChemSusChem*, **n/a**(n/a).

Kouris, P.D., Huang, X., Boot, M.D., Hensen, E.J.M. 2018. Scaling-Up Catalytic Depolymerisation of Lignin: Performance Criteria for Industrial Operation. *Topics in Catalysis*, **61**(18), 1901-1911.

Kumar, A., Biswas, B., Bhaskar, T. 2020. Effect of cobalt on titania, ceria and zirconia oxide supported catalysts on the oxidative depolymerization of prot and alkali lignin. *Bioresource technology*, **299**, 122589.

Lam, C.H., Deng, W., Lang, L., Jin, X., Hu, X., Wang, Y. 2020. Minireview on Bio-Oil Upgrading via Electrocatalytic Hydrogenation: Connecting Biofuel Production with Renewable Power. *Energy & Fuels*.

Lee, D.-W., Jin, M.-H., Park, J.-H., Lee, Y.-J., Choi, Y.-C. 2018. Flexible Synthetic Strategies for Lignin-Derived Hierarchically Porous Carbon Materials. *ACS Sustainable Chemistry & Engineering*, **6**(8), 10454-10462.

Li, M., Yuan, Y., Zhu, Y., Jiang, B., Wu, W., Wu, S., Jin, Y. 2021. Comparison of sulfomethylated lignin from poplar and masson pine on cellulase adsorption and the enzymatic hydrolysis of wheat straw. *Bioresource Technology*, 126142.

Li, M., Zhang, Q., Luo, B., Chen, C., Wang, S., Min, D. 2020. Lignin-based carbon solid acid catalyst prepared for selectively converting fructose to 5-hydroxymethylfurfural. *Industrial Crops and Products*, **145**, 111920.

Li, Q., Serem, W.K., Dai, W., Yue, Y., Naik, M.T., Xie, S., Karki, P., Liu, L., Sue, H.-J., Liang, H., Zhou, F., Yuan, J.S. 2017a. Molecular weight and uniformity define the mechanical performance of lignin-based carbon fiber. *Journal of Materials Chemistry A*, **5**(25), 12740-12746.

Li, T., Lin, H., Ouyang, X., Qiu, X., Wan, Z. 2019. In situ preparation of Ru@ N-doped carbon catalyst for the hydrogenolysis of lignin to produce aromatic monomers. *ACS Catalysis*, **9**(7), 5828-5836.

Li, Y., Qiu, X., Qian, Y., Xiong, W., Yang, D. 2017b. pH-responsive lignin-based complex micelles: Preparation, characterization and application in oral drug delivery. *Chemical Engineering Journal*, **327**, 1176-1183.

Li, Y., Shuai, L., Kim, H., Motagamwala, A.H., Mobley, J.K., Yue, F., Tobimatsu, Y., Havkin-Frenkel, D., Chen, F., Dixon, R.A. 2018a. An “ideal lignin” facilitates full biomass utilization. *Science advances*, **4**(9), eaau2968.

Li, Y., Yang, D., Lu, S., Lao, S., Qiu, X. 2018b. Modified lignin with anionic surfactant and its application in controlled release of avermectin. *Journal of agricultural and food chemistry*, **66**(13), 3457-3464.

Liu, S., Das, L., Blauch, D.N., Veronee, C., Dou, C., Gladden, J., Sun, N., Socha, A.M. 2020a. Statistical design of experiments for production and purification of vanillin and aminophenols from commercial lignin. *Green Chemistry*, **22**(12), 3917-3926.

Liu, X., Bouxin, F.P., Fan, J., Budarin, V.L., Hu, C., Clark, J.H. 2020b. Recent advances in the catalytic depolymerization of lignin towards phenolic chemicals: a review. *ChemSusChem*, **13**(17), 4296.

Luo, C., Du, L., Wu, W., Xu, H., Zhang, G., Li, S., Wang, C., Lu, Z., Deng, Y. 2018. Novel Lignin-Derived Water-Soluble Binder for Micro Silicon Anode in Lithium-Ion Batteries. *ACS Sustainable Chemistry & Engineering*, **6**(10), 12621-12629.

Ma, Z., Ghosh, A., Asthana, N., van Bokhoven, J. 2017. Optimization of the reaction conditions for catalytic fast pyrolysis of pretreated lignin over zeolite for the production of phenol. *ChemCatChem*, **9**(6), 954-961.

Mandeep, Kumar Gupta, G., Shukla, P. 2020. Insights into the resources generation from pulp and paper industry wastes: Challenges, perspectives and innovations. *Bioresource Technology*, **297**, 122496.

Marchand, G., Calliste, C., Williams, R., McLure, C., Leroy-Lhez, S., Villandier, N. 2018. Acetylated lignins: A potential bio-sourced photosensitizer. *ChemistrySelect*, **3**(20), 5512-5516.

Martinez- Hernandez, E., Cui, X., Scown, C.D., Amezcua- Allieri, M.A., Aburto, J., Simmons, B.A. 2019. Techno- economic and greenhouse gas analyses of lignin valorization to eugenol and phenolic products in integrated ethanol biorefineries. *Biofuels, Bioproducts and Biorefining*, **13**(4), 978-993.

Matsakas, L., Raghavendran, V., Yakimenko, O., Persson, G., Olsson, E., Rova, U., Olsson, L., Christakopoulos, P. 2019. Lignin-first biomass fractionation using a hybrid organosolv – Steam explosion pretreatment technology improves the saccharification and fermentability of spruce biomass. *Bioresource Technology*, **273**, 521-528.

Meng, X., Parikh, A., Seemala, B., Kumar, R., Pu, Y., Wyman, C.E., Cai, C.M., Ragauskas, A.J. 2019. Characterization of fractional cuts of co-solvent enhanced lignocellulosic fractionation lignin isolated by sequential precipitation. *Bioresource Technology*, **272**, 202-208.

Meng, X., Scheidemantle, B., Li, M., Wang, Y.-y., Zhao, X., Toro-González, M., Singh, P., Pu, Y., Wyman, C.E., Ozcan, S. 2020. Synthesis, characterization, and utilization of a lignin-based adsorbent for effective removal of azo dye from aqueous solution. *ACS omega*, **5**(6), 2865-2877.

Mukundan, S., Chowdari, R.K., Beltramini, J. 2021. External Solvent- Free Catalytic Hydrodeoxygenation of Softwood Lignin to Aromatics over Carbon–ZrO2 Supported Ni/MoS2 Catalysts. *Advanced Sustainable Systems*, **5**(3), 2000243.

Nasrollahzadeh, M., Issaabadi, Z., Varma, R.S. 2019. Magnetic Lignosulfonate-Supported Pd Complex: Renewable Resource-Derived Catalyst for Aqueous Suzuki–Miyaura Reaction. *ACS Omega*, **4**(10), 14234-14241.

Nguyen, N.A., Barnes, S.H., Bowland, C.C., Meek, K.M., Littrell, K.C., Keum, J.K., Naskar, A.K. 2018. A path for lignin valorization via additive manufacturing of high-performance sustainable composites with enhanced 3D printability. *Science Advances*, **4**(12), eaat4967.

Otromke, M., Shuttleworth, P.S., Sauer, J., White, R.J. 2019. Hydrothermal base catalysed treatment of Kraft lignin - time dependent analysis and a techno-economic evaluation for carbon fibre applications. *Bioresource Technology Reports*, **6**, 241-250.

Panovic, I., Montgomery, J.R., Lancefield, C.S., Puri, D., Lebl, T., Westwood, N.J. 2017. Grafting of technical lignins through regioselective triazole formation on β-O-4 linkages. *ACS Sustainable Chemistry & Engineering*, **5**(11), 10640-10648.

Patil, S.A., Chigome, S., Hägerhäll, C., Torto, N., Gorton, L. 2013. Electrospun carbon nanofibers from polyacrylonitrile blended with activated or graphitized carbonaceous materials for improving anodic bioelectrocatalysis. *Bioresource Technology*, **132**, 121-126.

Piccinino, D., Capecchi, E., Tomaino, E., Gabellone, S., Gigli, V., Avitabile, D., Saladino, R. 2021. Nano-Structured Lignin as Green Antioxidant and UV Shielding Ingredient for Sunscreen Applications. *Antioxidants*, **10**(2), 274.

Polo, C.C., Pereira, L., Mazzafera, P., Flores-Borges, D.N., Mayer, J.L., Guizar-Sicairos, M., Holler, M., Barsi-Andreeta, M., Westfahl, H., Meneau, F. 2020. Correlations between lignin content and structural robustness in plants revealed by X-ray ptychography. *Scientific reports*, **10**(1), 1-11.

Ponnusamy, V.K., Nguyen, D.D., Dharmaraja, J., Shobana, S., Banu, J.R., Saratale, R.G., Chang, S.W., Kumar, G. 2019. A review on lignin structure, pretreatments, fermentation reactions and biorefinery potential. *Bioresource Technology*, **271**, 462-472.

Prieur, B., Meub, M., Wittemann, M., Klein, R., Bellayer, S., Fontaine, G., Bourbigot, S. 2017. Phosphorylation of lignin: characterization and investigation of the thermal decomposition. *RSC advances*, **7**(27), 16866-16877.

Rajesh Banu, J., Kavitha, S., Yukesh Kannah, R., Poornima Devi, T., Gunasekaran, M., Kim, S.-H., Kumar, G. 2019. A review on biopolymer production via lignin valorization. *Bioresource Technology*, **290**, 121790.

Rehman, S., Islam, M.K., Khanzada, N.K., An, A.K., Chaiprapat, S., Leu, S.-Y. 2021. Whole sugar 2, 3-butanediol fermentation for oil palm empty fruit bunches biorefinery by a newly isolated Klebsiella pneumoniae PM2. *Bioresource Technology*, **333**, 125206.

Renders, T., Cooreman, E., Van den Bosch, S., Schutyser, W., Koelewijn, S.-F., Vangeel, T., Deneyer, A., Van den Bossche, G., Courtin, C., Sels, B. 2018. Catalytic lignocellulose biorefining in n-butanol/water: a one-pot approach toward phenolics, polyols, and cellulose. *Green Chemistry*, **20**(20), 4607-4619.

Renders, T., Van den Bosch, S., Koelewijn, S.F., Schutyser, W., Sels, B.F. 2017. Lignin-first biomass fractionation: the advent of active stabilisation strategies. *Energy & Environmental Science*, **10**(7), 1551-1557.

Sharma, V., Nargotra, P., Bajaj, B.K. 2019. Ultrasound and surfactant assisted ionic liquid pretreatment of sugarcane bagasse for enhancing saccharification using enzymes from an ionic liquid tolerant Aspergillus assiutensis VS34. *Bioresource technology*, **285**, 121319.

Sheng, Y., Lam, S.S., Wu, Y., Ge, S., Wu, J., Cai, L., Huang, Z., Le, Q.V., Sonne, C., Xia, C. 2021. Enzymatic conversion of pretreated lignocellulosic biomass: A review on influence of structural changes of lignin. *Bioresource Technology*, **324**, 124631.

Shuai, L., Amiri, M.T., Questell-Santiago, Y.M., Héroguel, F., Li, Y., Kim, H., Meilan, R., Chapple, C., Ralph, J., Luterbacher, J.S. 2016. Formaldehyde stabilization facilitates lignin monomer production during biomass depolymerization. *Science*, **354**(6310), 329-333.

Si, X., Chen, J., Lu, F., Liu, X., Ren, Y., Lu, R., Jiang, H., Liu, H., Miao, S., Zhu, Y. 2019. Immobilized Ni Clusters in Mesoporous Aluminum Silica Nanospheres for Catalytic Hydrogenolysis of Lignin. *ACS Sustainable Chemistry & Engineering*, **7**(23), 19034-19041.

Singh, J.K., Sharma, R.K., Ghosh, P., Kumar, A., Khan, M.L. 2018. Imidazolium based ionic liquids: a promising green solvent for water hyacinth biomass deconstruction. *Frontiers in chemistry*, **6**, 548.

Song, B., Lin, R., Lam, C.H., Wu, H., Tsui, T.-H., Yu, Y. 2021. Recent advances and challenges of inter-disciplinary biomass valorization by integrating hydrothermal and biological techniques. *Renewable and Sustainable Energy Reviews*, **135**, 110370.

Sorn, V., Chang, K.-L., Phitsuwan, P., Ratanakhanokchai, K., Dong, C.-D. 2019. Effect of microwave-assisted ionic liquid/acidic ionic liquid pretreatment on the morphology, structure, and enhanced delignification of rice straw. *Bioresource technology*, **293**, 121929.

Sun, Q., Khunsupat, R., Akato, K., Tao, J., Labbé, N., Gallego, N.C., Bozell, J.J., Rials, T.G., Tuskan, G.A., Tschaplinski, T.J., Naskar, A.K., Pu, Y., Ragauskas, A.J. 2016. A study of poplar organosolv lignin after melt rheology treatment as carbon fiber precursors. *Green Chemistry*, **18**(18), 5015-5024.

Sun, Z., Cheng, J., Wang, D., Yuan, T.Q., Song, G., Barta, K. 2020. Downstream Processing Strategies for Lignin- First Biorefinery. *ChemSusChem*, **13**(19), 5134-5134.

Sun, Z., Fridrich, B., de Santi, A., Elangovan, S., Barta, K. 2018a. Bright Side of Lignin Depolymerization: Toward New Platform Chemicals. *Chem Rev*, **118**(2), 614-678.

Sun, Z., Fridrich, B., de Santi, A., Elangovan, S., Barta, K. 2018b. Bright side of lignin depolymerization: toward new platform chemicals. *Chemical reviews*, **118**(2), 614-678.

Supanchaiyamat, N., Jetsrisuparb, K., Knijnenburg, J.T.N., Tsang, D.C.W., Hunt, A.J. 2019. Lignin materials for adsorption: Current trend, perspectives and opportunities. *Bioresource Technology*, **272**, 570-581.

Takada, M., Rabemanolontsoa, H., Minami, E., Saka, S. 2018. Characterization of lignin-derived products from various lignocellulosics as treated by semi-flow hot-compressed water. *Journal of Wood Science*, **64**(6), 802-809.

Taleb, F., Ammar, M., ben Mosbah, M., ben Salem, R., Moussaoui, Y. 2020. Chemical modification of lignin derived from spent coffee grounds for methylene blue adsorption. *Scientific Reports*, **10**(1), 1-13.

Thakur, S., Govender, P.P., Mamo, M.A., Tamulevicius, S., Mishra, Y.K., Thakur, V.K. 2017. Progress in lignin hydrogels and nanocomposites for water purification: Future perspectives. *Vacuum*, **146**, 342-355.

Thomas, V.A., Donohoe, B.S., Li, M., Pu, Y., Ragauskas, A.J., Kumar, R., Nguyen, T.Y., Cai, C.M., Wyman, C.E. 2017. Adding tetrahydrofuran to dilute acid pretreatment provides new insights into substrate changes that greatly enhance biomass deconstruction by Clostridium thermocellum and fungal enzymes. *Biotechnology for biofuels*, **10**(1), 1-13.

Tse, H.-Y., Cheng, S.-C., Yeung, C.S., Lau, C.-Y., Wong, W.-H., Dong, C., Leu, S.-Y. 2019. Development of a waste-derived lignin-porphyrin bio-polymer with enhanced photoluminescence at high water fraction with wide pH range and heavy metal sensitivity investigations. *Green Chemistry*, **21**(6), 1319-1329.

Tu, Q., Parvatker, A., Garedew, M., Harris, C., Eckelman, M., Zimmerman, J.B., Anastas, P.T., Lam, C.H. 2021. Electrocatalysis for Chemical and Fuel Production: Investigating Climate Change Mitigation Potential and Economic Feasibility. *Environmental Science & Technology*.

Van, d.B.S., Koelewijn, S.F., Renders, T., Van, d.B.G., Vangeel, T., Schutyser, W., Sels, B.F. 2018. Catalytic Strategies Towards Lignin-Derived Chemicals. *Top Curr Chem (Cham)*, **376**(5), 36.

Vincent, S., Prado, R., Kuzmina, O., Potter, K., Bhardwaj, J., Wanasekara, N.D., Harniman, R.L., Koutsomitopoulou, A., Eichhorn, S.J., Welton, T., Rahatekar, S.S. 2018. Regenerated Cellulose and Willow Lignin Blends as Potential Renewable Precursors for Carbon Fibers. *ACS Sustainable Chemistry & Engineering*, **6**(5), 5903-5910.

Walch, F., Abdelaziz, O.Y., Meier, S., Bjelić, S., Hulteberg, C.P., Riisager, A. 2021. Oxidative depolymerization of Kraft lignin to high-value aromatics using a homogeneous vanadium–copper catalyst. *Catalysis Science & Technology*, **11**(5), 1843-1853.

Wang, A., Song, H. 2018. Maximizing the production of aromatic hydrocarbons from lignin conversion by coupling methane activation. *Bioresource Technology*, **268**, 505-513.

Wang, H., Pu, Y., Ragauskas, A., Yang, B. 2019. From lignin to valuable products–strategies, challenges, and prospects. *Bioresource Technology*, **271**, 449-461.

Wang, J., Xu, Y., Meng, X., Pu, Y., Ragauskas, A., Zhang, J. 2021a. Production of xylo-oligosaccharides from poplar by acetic acid pretreatment and its impact on inhibitory effect of poplar lignin. *Bioresource Technology*, **323**, 124593.

Wang, W., Lee, D.-J. 2021. Lignocellulosic biomass pretreatment by deep eutectic solvents on lignin extraction and saccharification enhancement: a review. *Bioresource Technology*, 125587.

Wang, W., Li, X., Ye, D., Cai, L., Shi, S.Q. 2018. Catalytic pyrolysis of larch sawdust for phenol-rich bio-oil using different catalysts. *Renewable Energy*, **121**, 146-152.

Wang, W., Wang, F., Zhang, C., Tang, J., Zeng, X., Wan, X. 2021b. Versatile value-added application of hyperbranched lignin derivatives: Water-resistance adhesive, UV protection coating, self-healing and skin-adhesive sensing. *Chemical Engineering Journal*, **404**, 126358.

Wang, Y.-Y., Sengupta, P., Scheidemantle, B., Pu, Y., Wyman, C.E., Cai, C.M., Ragauskas, A.J. 2020. Effects of CELF pretreatment severity on lignin structure and the lignin-based polyurethane properties. *Frontiers in Energy Research*, **8**, 149.

Wei, C., Zhu, X., Peng, H., Chen, J., Zhang, F., Zhao, Q. 2019. Facile preparation of lignin-based underwater adhesives with improved performances. *ACS Sustainable Chemistry & Engineering*, **7**(4), 4508-4514.

Wong, S.S., Shu, R., Zhang, J., Liu, H., Yan, N. 2020. Downstream processing of lignin derived feedstock into end products. *Chemical Society Reviews*, **49**(15), 5510-5560.

Xu, C., Zhang, J., Zhang, Y., Guo, Y., Xu, H., Xu, J., Wang, Z. 2019. Enhancement of high-solids enzymatic hydrolysis efficiency of alkali pretreated sugarcane bagasse at low cellulase dosage by fed-batch strategy based on optimized accessory enzymes and additives. *Bioresource technology*, **292**, 121993.

Yadav, P., Athanassiadis, D., Antonopoulou, I., Rova, U., Christakopoulos, P., Tysklind, M., Matsakas, L. 2021. Environmental impact and cost assessment of a novel lignin production method. *Journal of Cleaner Production*, **279**.

Yan, X., Cheng, J.-R., Wang, Y.-T., Zhu, M.-J. 2020. Enhanced lignin removal and enzymolysis efficiency of grass waste by hydrogen peroxide synergized dilute alkali pretreatment. *Bioresource technology*, **301**, 122756.

Yang, Z., Gleisner, R., H Mann, D., Xu, J., Jiang, J., Zhu, J. 2020. Lignin Based Activated Carbon Using H3PO4 Activation. *Polymers*, **12**(12), 2829.

Yin, L., Leng, E., Fang, Y., Liu, T., Gong, X., Zhou, J. 2020. Effects of KCl, KOH and K2CO3 on the pyrolysis of Cβ-O type lignin-related polymers. *Journal of Analytical and Applied Pyrolysis*, **147**, 104809.

Yoo, C.G., Meng, X., Pu, Y., Ragauskas, A.J. 2020. The critical role of lignin in lignocellulosic biomass conversion and recent pretreatment strategies: A comprehensive review. *Bioresource Technology*, **301**, 122784.

Youssefian, S., Rahbar, N. 2015. Molecular origin of strength and stiffness in bamboo fibrils. *Scientific reports*, **5**(1), 1-13.

Yun, S.I., Kim, S.H., Kim, D.W., Kim, Y.A., Kim, B.-H. 2019. Facile preparation and capacitive properties of low-cost carbon nanofibers with ZnO derived from lignin and pitch as supercapacitor electrodes. *Carbon*, **149**, 637-645.

Zhang, D., Wang, L., Zeng, H., Rhimi, B., Wang, C. 2020a. Novel polyethyleneimine functionalized chitosan–lignin composite sponge with nanowall-network structures for fast and efficient removal of Hg (ii) ions from aqueous solution. *Environmental Science: Nano*, **7**(3), 793-802.

Zhang, H., Chen, F., Liu, X., Fu, S. 2018a. Micromorphology influence on the color performance of lignin and its application in guiding the preparation of light-colored lignin sunscreen. *ACS Sustainable Chemistry & Engineering*, **6**(9), 12532-12540.

Zhang, J., Su, Z., Wu, Z., Wang, P., Xiao, F.-S. 2021a. Basic carrier promoted Pt-catalyzed hydrogenolysis of alkaline lignin. *Catalysis Today*, **365**, 193-198.

Zhang, L., Song, Y., Wang, Q., Zhang, X. 2021b. Culturing rhodotorula glutinis in fermentation-friendly deep eutectic solvent extraction liquor of lignin for producing microbial lipid. *Bioresource Technology*, **337**, 125475.

Zhang, N., Tao, P., Lu, Y., Nie, S. 2019a. Effect of lignin on the thermal stability of cellulose nanofibrils produced from bagasse pulp. *Cellulose*, **26**(13), 7823-7835.

Zhang, R., Du, Q., Wang, L., Zheng, Z., Guo, L., Zhang, X., Yang, X., Yu, H. 2019b. Unlocking the response of lignin structure for improved carbon fiber production and mechanical strength. *Green Chemistry*, **21**(18), 4981-4987.

Zhang, S., Xiao, J., Wang, G., Chen, G. 2020b. Enzymatic hydrolysis of lignin by ligninolytic enzymes and analysis of the hydrolyzed lignin products. *Bioresource Technology*, **304**, 122975.

Zhang, S., Zhang, H., Liu, X., Zhu, S., Hu, L., Zhang, Q. 2018b. Upgrading of bio-oil from catalytic pyrolysis of pretreated rice husk over Fe-modified ZSM-5 zeolite catalyst. *Fuel Processing Technology*, **175**, 17-25.

Zhang, Y., Zhao, Q., Li, L., Yan, R., Zhang, J., Duan, J., Liu, B., Sun, Z., Zhang, M., Hu, W. 2018c. Synthesis of a lignin-based phosphorus-containing flame retardant and its application in polyurethane. *RSC advances*, **8**(56), 32252-32261.

Zhao, J., Xu, Y., Zhang, M., Wang, D. 2020. Integrating bran starch hydrolysates with alkaline pretreated soft wheat bran to boost sugar concentration. *Bioresource technology*, **302**, 122826.

Zhong, L., Xu, M., Wang, C., Shao, L., Mao, J., Jiang, W., Ji, X., Yang, G., Chen, J., Lyu, G. 2020. Pretreatment of willow using the alkaline-catalyzed sulfolane/water solution for high-purity and antioxidative lignin production. *International journal of biological macromolecules*, **159**, 287-294.

Authors' contributions

Khan – constructed Abstract, Graphical Abstract, Chapters 1&3, initiated Figures 1&3;
Lau – constructed Chapter 2, Sections 4.3&4.4, Table 1, initiated finalized Figures 2, 3&5;
Guan – constructed Figure 6;
Lam and Zhao – constructed Chapter 4;
Ji – primary reviewed and edited Chapter 1&3;
Wang – constructed Chapter 5;
Xu and Lee – reviewed and edited Chapter 2, 4, & 5;
Leu – supervised, edited, and revised the manuscript.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: