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Lignin Hydrothermal Liquefaction into Bifunctional Chemicals: A Concise Review

Yahaya Alhassan, Ursel Hornung and Idris M. Bugaje

Abstract

Lignin, the second largest biomass after cellulose is underutilized. Yet, it remains the only natural source of aromatic, and phenolic compounds. It is imperative to, amidst the expanding interest on biomass conversion, to accord the necessary attention towards lignin degradation into value added chemicals. Specifically, its phenyl, guaiacyl, and syringyl derivatives. Understanding lignin degradation chemistry, goes a long way in its selective valorization into fuels and chemicals via thermochemical routes such as hydrothermal liquefaction (HTL). Therefore, development of technologies targeting value addition of products and by-products from lignin, would undoubtedly give way to emerging markets in the industry. Previous review papers focused on the general HTL of biomass, food waste, algae, and their model compounds. However, review on HTL of lignin is scarcely available. This paper presents the detailed literature analyses of the current trend in lignin degradation via HTL. Effect of HTL conditions including temperature, heating rate and catalyst has been reviewed. In-depth discussion on use of ionic liquids as catalyst for HTL of lignin has also been compiled. Other lignin degradation techniques such as pyrolysis and hydrolysis were also discussed. This is aimed at bringing together an up-to-date information on lignin degradation into selected chemical intermediates.

Keywords: aromatics, catechol, lignin, guaiacol, phenol

1. Introduction

Nowadays, it is evident that, processing lignocelluloses biomass, specifically, lignin into different industrial chemicals via the biorefinery approach; has become economically attractive. Biorefinery, is a pinnacle of simple and advanced technologies, put together; in converting biomass such as lignin into sustainable fuels, intermediates and chemical products [1]. Therefore, lignin processing, including hydrothermal liquefaction (HTL) route is expected to ensure only useful products are produced. Pollutants, waste, and losses are limited, in what is referred to as an atom economy model [2].

Lignin, the second largest biomass after cellulose is largely underutilized. It is largely available in woody biomass, agricultural waste, and as an industrial process by-product from paper milling, and pulping industries [3], and waste stream in organosolv process [4]. It is also the only natural source of aromatic and phenolic compounds. Therefore, development of well-defined technologies targeting value addition of products and by-products from lignin, would undoubtedly give way to emerging markets in the industry.

Detailed literature review papers focused either on the general HTL processing of biomass and algae [5, 6]; HTL of food waste and model compounds [7]. Other areas covered included; the techno-economic, and life cycle assessment of lignocelluloses biomass via thermo-chemical conversion technologies [1]. A few case studies, such as the environmental profile of algae HTL have been reported [8]. However, review on HTL of specific feedstock other than algae and whole biomass are scarcely available; just as the detailed review on HTL of feedstock into specific value-added products, is equally rare. Except for the detailed review on catalytic valorization of lignin for the production of fuels and chemicals [9], such reviews are rare until recently.

It is therefore imperative to, amid the expanding research into biomass conversion, to accord necessary attention towards lignin degradation into value added chemicals, specifically, its hydroxylphenyl derivatives (H-type), guaiacyl derivatives (G-type), and Syringyl derivatives (S-type). In so doing, economically viable, and environmental friendly technology like HTL needs to be explored. This review paper, is aimed at appraising the literature information available on lignin degradation into valuable chemicals, with emphasis on HTL route.
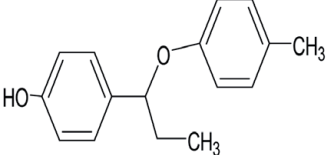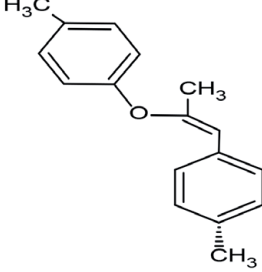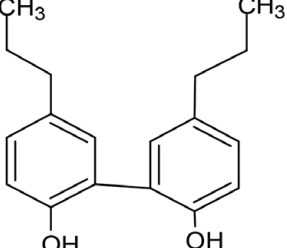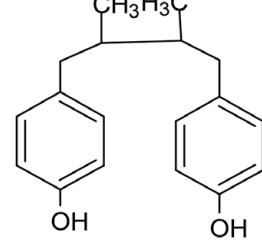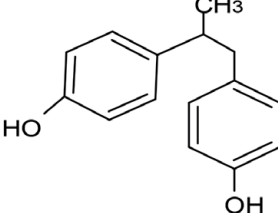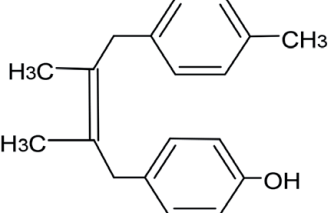
2. Lignin composition and chemistry

Lignin is largely made up of polymerized monolignols (G-type, H-type and S-type), which are interconnected by well-defined benzodioxane linkages in a radical recombination coupling reaction [10]. The chemical structure of lignin according to different authors [11, 12]; suggested that it consisted of complex 4-phenylpropanol macromolecular units. **Figure 1** depicts the monomeric units of lignin. Principally; it consists of phenylpropane monomer units of phenyl, guaiacyl and syringyl geometry (**Figure 1**), linked together via ether bonds (α–O–4; β–O–4; 5–O–4) and carbon–carbon bonds (β–1; β–5; β–β; 5–5). The β–O–4 is the most pointing ether bond in lignin, where different reactions take place.

Authors have reported different simple and complex reactions taking place during lignin degradation. Even though, multitude of reactions are taking place, at this point (β–O–4), it was proposed that at supercritical point of water, for example; less energy intense reactions are a preferentially favored. Greater scheme of reactions take place at the bonds, forming different products depending on the relative thermodynamic stability of the bond, determined by the strength of double bond equivalence.

According to Berstis et al. [10], during lignin HTL, the reactivity of particular bond is depending on its reaction enthalpy, bond strength, and geometry. It was observed that, α–bonds are slightly weaker than their corresponding β–bond counterparts, and similar in strength to that of the conventional β–O–4 linkage. According to Beauchet et al. [13], the α- and β-aryl-ether-bond followed by the
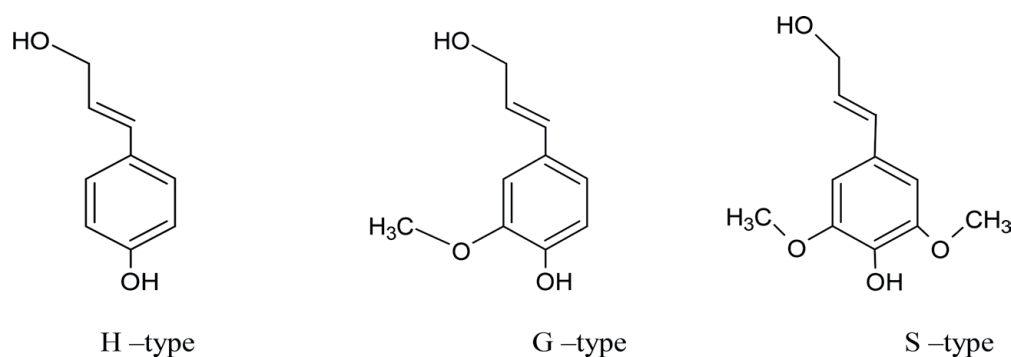
Figure 1.
Different monomeric units of lignin.

Bond type	Structure
α–O – 4 bond	4-[1-(4-methylphenoxy)propyl]phenol
β–O–4 bond	
5–5 bond	
β–β bond	
β–1 bond	
β–β bond	

Table 1.
Types of bonds existing in lignin structure.

aryl–aryl bond, are the weakest bonds in the lignin polymers, thus; hydrocracking, and thermal hydro-deoxygenation have frequently been employed for depolymerisation, targeting these weak bonds. **Table 1** presents the predominant bonds in lignin. According to Forchheim et al. [14], reactions including mild alkylation, hydro deoxygenation, reploymerization, and depolymerisation are predominant in lignin HTL. Liguori and Barth [15], reported reactions like hydro-deoxygenated, demethylated and demethoxylated at the ether bond positions. In addition, radical recombination and decomposition chemistry; are dimensional factors in the reaction rate.

2.1 Lignin as a source of chemicals

Lignin, is the only natural source of phenolic compounds, thus; its liquefaction is increasingly been investigated. Although it was envisaged that the complex nature of lignin makes it valorization a difficult task; recent discoveries in selective bond cleaving of the predominant β–O–4 bond [16], is encouraging further research. The increasing research interest in C_3 and C_5-ortho reactivity and production of genetically modified lignin, have instigated lignin valorization work. The HTL of lignin into substituted Phenol, and aromatic ethers was conducted by Singh et al. [17]. These authors attributed the presence of Phenol, and aromatic ethers from the selective cleaving of β–O–4 and α–O–4 bonds, forming hydroxyl and alkyl groups, respectively. Similarly, Zhou [18] successfully converted Kraft lignin into value-added chemicals, specifically, guaiacol (2-methoxy Phenol), was formed by the degradation of β–O–4 bond. The cleavages of other functional groups including hydroxyl, aromatic, and carbonyl resulted in increased phenolic –OH presence.

3. Lignin degradation technologies

Literature has availed different proposed schemes for lignin degradation. For example, According to Kruse and Dahmen [19], during biomass liquefaction, steam explosion occurs within 140–240°C leading to its structural disruption, just as the hydrothermal carbonization begin to manifest at around 200°C. Finally, liquefaction sets-in, between 300 and 350°C, and gasification reaction completes the liquefaction cycle around 450–600°C; depending on the feedstock. This temperature range was found to be perfect for the thermal degradation range of lignin which is 200–600°C [20]. Apart from HTL route, other biomass conversion techniques found suitable for lignin degradation, including pyrolysis [21, 22], hydrolysis [23], and gasification [24] have been reported.
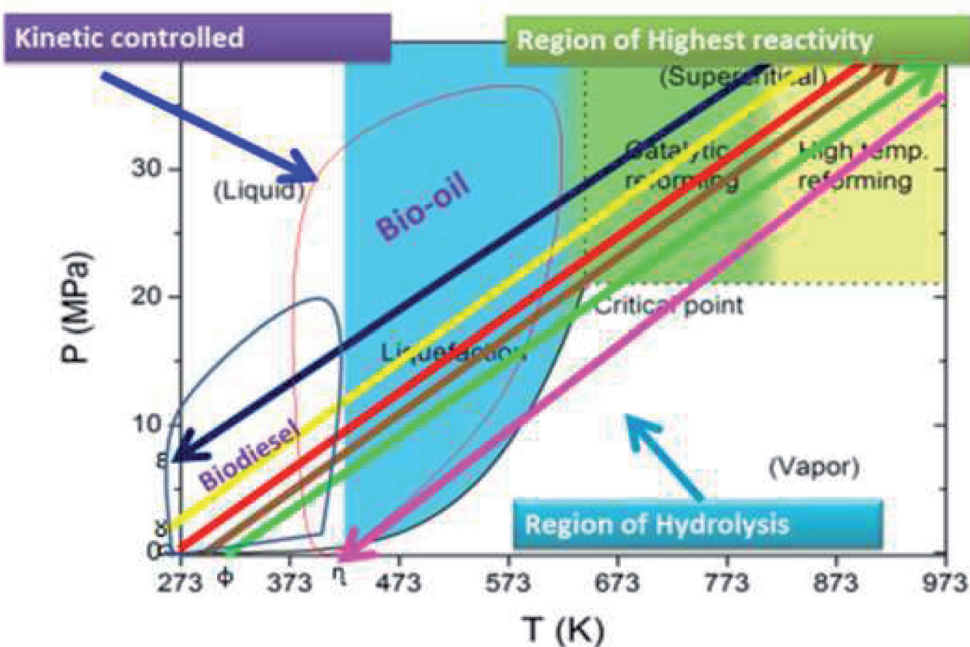
4. Hydrothermal liquefaction technique

Hydrothermal liquefaction (HTL), is one of the emerging biomass conversion technologies gaining desirable attention. This thermo-chemical processing method, has superior advantages in comparison to other processes. **Figure 2** presents the modified vapor pressure curves for HTL processes.

Water, as the solvent in HTL makes the route environmental friendly; in addition to its bifunctional role as catalyst and solvent for multiple reactions taking place [19]. This is because, water, on approaching its supercritical point (above 375°C) exhibits good solvent ability, resulting from its improved properties like polarity, solubility and transportation properties [6, 7].

In economic terms, HTL reduces the energy consumption required during biomass drying, as it is suitable for conversion of high moisture content feedstock into good quality and stable products [7]. For these reasons, HTL has

Figure 2.
Modified vapor pressure curves for hydrothermal conversion process.
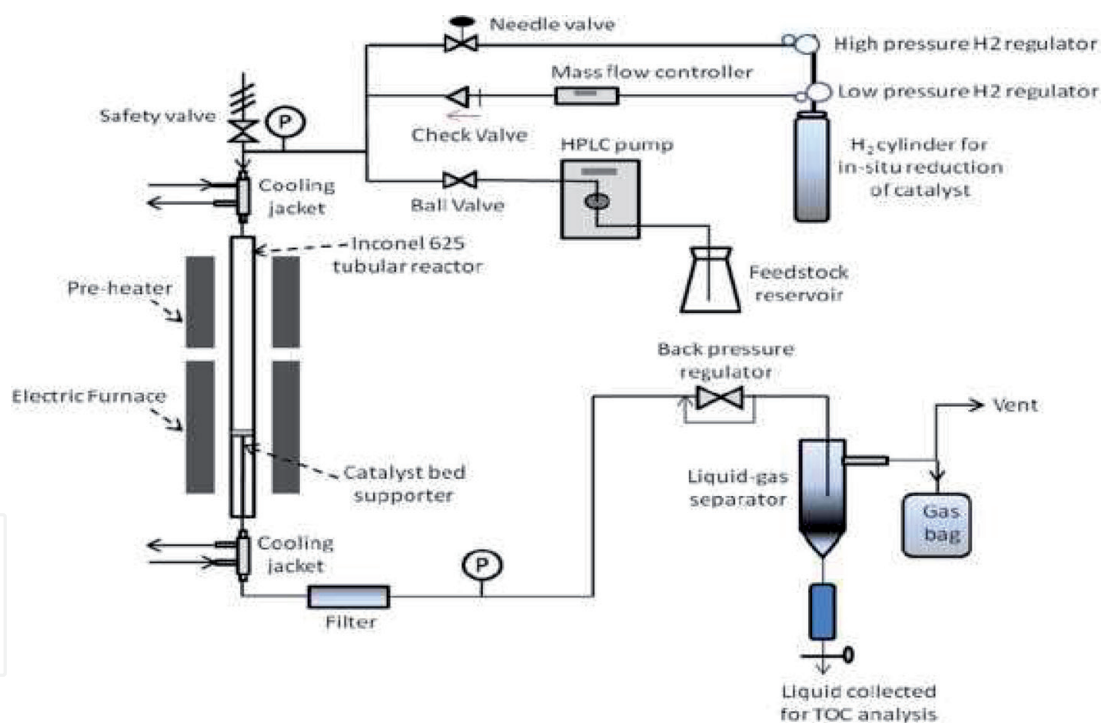
Figure 3.
A semi-continuous process biomass liquefaction flow chart [34].

turned out to be a super-specialty method, found to be appropriate for converting different feedstock. These including cyanobacteria [26]; low-lipid and high protein algae [27]; sewage sludge [28]; bio-cakes [29]; and lignocelluloses model systems [30] etc.; into different targeted products such as protein, lipids, heterocyclic and their derivatives (nitrogenous and sulfur) [31]; phenolic and aromatic compounds [17]; fatty acids and light gases [25]; and nitrogenated compounds [32] etc. Yang et al. [33] identified Phenol and benzene derivatives from Corncob, with the two compounds showing improved active sites than the parent lignin. Thus, making the former suitable substituents in the synthesis of Phenol formaldehyde adhesive.

Lignin source	Liquefaction preview	Yield	Reported biomolecules	Ref.
Organosolv hardwood and wheat straw lignin	The liquefaction involved the preheating of lignin and formic acid in a supercritical fluid consisted of CO_2/acetone/water in molar ratios of 2.7/1/1. The reaction was completed within 3.5 h at 300°C and 10 bar pressure.	10–12% monomeric aromatic compounds	Phenolic oil was obtained consisting monomeric phenol and oligomeric aromatic compounds.	[36]
Agricultural fibrous feedstocks	The reactor was loaded with lignin and ethanol/methanol (1:10 by weight) within 30 min and 200°C.	Liquid products yield (85%) was reported.	Substituted phenol and aromatic ethers.	[15]
Sugarcane bagasse	The biomass loading was fixed at a solid:liquid ratio of 1:10 (w/w) including NaOH.	Not reported.	Major products included phenol, guaiacol and syringol.	[37]
Alkaline lignin	HTL was conducted in a 250 mL autoclave with heating power of 1.5 kW. An alkaline lignin (8.0 g) and 100 mL of water are added and reactor was purged with nitrogen and agitated using a stirrer (200 rpm). The temperature was varied for 30 min.	Not reported.	Isolated products include benzenediols, monophenolic hydroxyl products, weak-polar products, and water-soluble products (low-molecular-weight organic acids, alcohols, etc.).	[38]
Grass silage pressed cake	Lignin is extracted from the solid lignin residue from the mechanically supported enzymatic hydrolysis and subjected to ethanolic organosolv processing, at a reaction temperature and time of 195°C and 80 min, respectively.	Maximum yield obtained was 41–57 wt%.	Not reported.	[39]
Lignin-rich residue from ethanol production	A mixture of lignin and deionized water was added and reactions were carried out at different temperatures (593–653 K). The residence time varied between 15 and 480 min.	Methoxyphenol (12 wt%), catechols (8 wt%) and phenol (15 wt%).	Phenol, catechols and methoxy phenol.	[21]
Enzymatic hydrolysis lignin	The lignin, water and RANEY Nickel (dry matter) were placed in a 5mL autoclave. The autoclave was purged with nitrogen. The reaction mixture was heated at different temperatures for different reaction times.	Varying yields ranging from 3 to 15 mg/g lignin.	Phenol, catechol and guaiacol.	[13]

Lignin source	Liquefaction preview	Yield	Reported biomolecules	Ref.
Kraft lignin	Kraft lignin, heterogeneous catalyst (K2CO3), phenol and deionized water, is uninterruptedly pumped by high pressure diaphragm pump at a flow rate of 1 kg/h. This was a continuous reactor set-up. The reaction temperature was 350°C and 25 MPa.	With respect to dry lignin fed into the reactor, approximately 70 wt% of lignin oil was obtained.	Phenol, alkylphhenols, phenolic dimers, catechol and guaiacol.	[11]
Organosolv lignin	HTL tests were completed in batch autoclave. The reactor was heated with an electric heating jacket. Temperature and pressure were checked online. A 700 mL chilled condenser was connected to the autoclave exit port. Lignin, catalyst, and deionized water with and without catalysts.	Approximately 25 wt% of monomeric phenol.	A complex mixtures of monomeric catechol and methoxylated and alkylated phenol.	[4]
Wheat straw biomass	Sequential biomass pretreatment and followed by room temperature extraction with an activated resin. The biorefinery approach also included supercritical CO2 extraction of phenolic compounds.	Not reported.	High molecular weight phenolic compounds, targeting Tricin.	[40]
Kraft lignin	The treated Kraft lignin, ionic liquid catalyst and, and Pd/C catalyst were placed in a 75 mL autoclave reactor. The reactor was sealed and purged with H$_2$. The reaction was conducted at 200°C at a stirring speed of 800 rpm.	Maximum liquids products yield was 50 wt%, while based on Kraft lignin was 13 wt% yield.	Phenol, catechol and guaiacol.	[24]
Kraft lignin	Kraft lignin and deionized water were reassigned into the reactor. The system was vented with nitrogen three times. For each experiment the reactor was heated in 30 min from ambient to a working temperature of 130°C or 180°C or 230°C, after which the experiment was continued for 15 or 60 min.	Phenolic oil content ranges from 5.4 to 10.6 wt%, with 78 wt% guaiacol.	Guaiacol	[19]

Table 2.
Reviewed HTL of lignin degradation into different bio-chemicals.

The use of co-solvent system in biomass liquefaction and by extension, lignin degradation has been investigated. A co-solvent hydrothermal degradation of alkali lignin into bi-phenolic compounds was investigated by Cheng et al. [12], suggesting an improved yield from the water-ethanol co-solvent system for sub/supercritical conditions. Whereas, time had negligible effect on the yield and quality of liquefaction products, temperature and co-solvent ratio had significant effects on yield and quality of bio-crude oil. Singh et al. [17], employed ethanol and methanol (1:10) co-solvent system for the synthesis of substituted Phenol and aromatic ethers. **Figure 3** presents a semi-continuous process biomass liquefaction flow chart.

Lignin HTL is therefore suitable technology for effectively converting it into useful products with high selectivity, and quality. **Table 2** reviewed the literature works on the HTL of lignin into reported products, highlighting the recounted yields and the major bifunctional chemicals obtained.

5. Factors affecting lignin hydrothermal liquefaction

5.1 Effect of temperature/heating rate

The reaction temperature is the predominant factor in thermo-chemical processes like liquefaction. Lignin HTL is a temperature dependent process, since the degree of liquefaction increases with increasing reaction temperature. A careful selection of the heating rate is desired in reducing the rate, at which, condensation of unsaturated oligomeric phenol occur [39]. Depending on the temperature, HTL is sub-divided into subcritical liquefaction and supercritical liquefaction. **Figure 4** presents the effect of reaction temperature on yield of different feedstock reported in the literature.

From the reported result, degradation temperature for lignin feedstock is between 200 and 300°C. Higher temperature beyond 300°C tends to reduce bio-crude oil yield. According to Hu et al. [43], lignin degradation is temperature dependent, in a manner that, increasing temperature in degradation of black liquor lignin was found to have favored bond cleavage, and elimination of functional groups, and carbonization. To add to this, Yang et al. [33] found that, temperature affected products distribution much more than reaction time.

5.2 Effect of catalyst type/concentration

Different classes of catalysts have already shown positive impact during lignin degradation. From **Table 3**, it could be argued that homogenous catalyst like NaOH, were found suitable [35, 38]. Also, mixed oxide catalysts [12] are increasingly been investigated. However, recent literature trend, suggested a paradigm shift towards ionic liquids.

Ionic liquids [ILs] application in biomass refining has received increasing attention, recently. ILs catalysis in lignin degradation, specifically, have received appreciable attention. Different classes of ILs including biocompatible, bio-renewable, protonic ILs have been investigated [44]. The main factor affecting lignin HTL using ILs as catalysts, and/or co-solvents is their selectivity. This selectivity of ILs revolves around the cationic alkyl chain length, anionic hydrophobicity, temperature and solvent type among others. The catalytic activity of acidic ILs, for example, is largely associated with the Lewis/Bronsted acidity of the alkyl chain length.

Significant acidity of ILs catalysts is derived from inter-molecular bonding interactions. This is in contrast to the acidity of conventional acid catalysts, whose
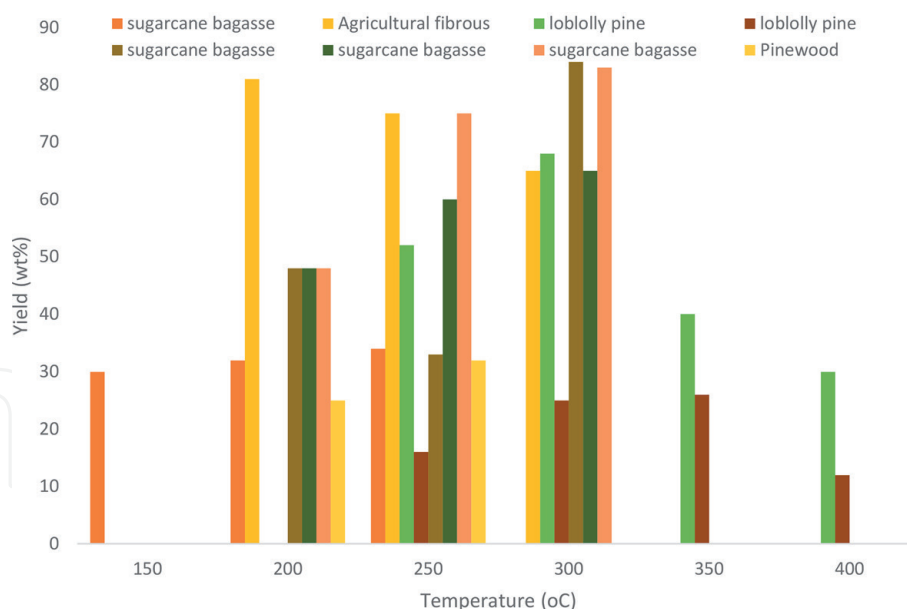
Figure 4.
Effect of reaction temperature on lignin liquefaction for different feedstock. Data obtained from feedstock reported including; sugarcane bagasse [39, 42, 44, 45]; agricultural waste [15]; Loblolly pine [46]; Pinewood [26].

Catalyst	Chemical composition	Feedstock used	Efficiency/findings	Ref.
NaOH	-	Sugarcane bagasse.	The efficiency was achieved using 4% NaOH caused a decrease in ester linked *p*-coumarates in the residues, while at 9% NaOH both *p*-coumarates and ferulates decreased. The last was symbolic for the degradation of particular β–O–4 linkages.	[37]
RANEY Nickel	Nickel (88 wt%) and aluminum (12 wt%).	Enzymatic hydrolysis lignin.	The catalyst produced more carbon dioxide in the gaseous phase at the expense of low C2–C4 and much phenol in the organic phase in comparison to catechol and guaiacol. Low char formation was also observed.	[13]
Raney Nickel 2400, 4200	Nickel (81 wt%), aluminum (6 wt%), iron (2 wt%) and chrome (2 wt%).	Organosolv lignin.	The catalyst favored the production of phenol in all cases. However, the efficiency depends on the Ni/Al ratio and other promoter metallic composition of the catalysts.	[4]
Ionic liquids	1-ethyl-3-methylimidazolium acetate ([emim][OAc]).	Wheat straw	The use of the ionic liquid was effective in selective fractionation of cellulose, hemicellulose and lignin into relatively high purity fractions. The catalyst was also effective in the valorization of the phenolic fraction.	[40]
Dual catalyst (choline-derived ionic liquids and Pd/C).	[Ch][Ace]; [Ch][CF$_3$CO$_2$]; [Ch][H$_2$PO$_4$]; [Ch][Lev], and [Ch]-[MeSO$_3$] with Pd/C.	Kraft lignin	The phenol and catechol production was virtually the same, since the catalytic activity was dependent on the cation and anions combinations	[24]

Catalyst	Chemical composition	Feedstock used	Efficiency/findings	Ref.
K_2CO_3		LignoBoost Kraft lignin	Increasing mass fraction of K2CO3 resulted in remarkable increasing in phenolic oil yield, showing selectivity towards anisole, alkylphenol and catechol	[11]
NaOH	-	Kraft lignin	The base-catalyzed lignin de-polymerization yielded 8.4 wt% monomeric-rich fraction. The catalyst favored deoxygenated aliphatic OH and guaiacyl groups.	[41]
Ionic liquids	The ILs including 1-(4-sulfobutyl)-3-methyl imidazolium hydrosulfate ($[C_4H_8\text{-}SO_3Hmim]HSO_4$), N-methyl imidazolium hydrosulfate. HSO_4), 1-butyl-3-methyl imidazolium hydrosulfate ([bmim] HSO_4), and 1-(2-carboxyethyl)-3-methyl imidazolium chloride ($[C_2H_4COOHmim]Cl$).	Sugarcane bagasse	All ILs studied were very effective towards total degradation of lignin components, showing excellent recyclability up to five times. However, the results into numerous products which caused characteristic separation difficulty.	[42]
Palladium catalysts	Commercially available catalysts, (10%) Pd/C, (30%) Pd/C, Pd(OH)2/C, Pd(OAc)2, Pd-PEPPSI-iPr and Pd/Lindlar.	Spruce lignin; lignin from acidic hydrolysis; enzymatic hydrolysis; acidic hydrolysis; strong acidic hydrolysis; desulfonated Kraft lignin.		[14]
Mixed oxides catalysts	A γ-Al_2O_3 and active carbon (AC) supported metallic (Pt, Ru, and Ni).		It was reported that the metallic catalysts did not have significant change in the yield, generally, but Ni and Ru showed preferential improved yield than Pt	[12]
Ionic liquids	Dialkylimidazolium-based e.g ($[C_4mim]MeSO_3$); ($[C_4mim]OAc$); ($[C_4mim]Cl$).	Regenerated lignin	The pH, IL composition, and IL content were established to significantly affect the degradation and chemical conversion of lignin structure. It was concluded that low pH helped lignin depolymerization nevertheless destroyed the substructure of lignin.	[43]

Table 3.
Effect of catalysts on lignin degradation for different feedstock.

acidity is derived from their protonation. Therefore, the former exhibited the tendency towards eliminating reactor corrosion; a major reaction engineering problem that has been posing serious challenges. It was postulated that, lignin dissolution was aided via a π–π interaction between an alkyl imidazolium chloride catalyst and

the π–bond in the aromatic rings structure of lignin, suggesting the additional dissolution potentials of alkyl based ILs [9]. According to Zhuo et al. [45]; the acidity of 2-phenyl-2-Imidazoline based ILs with shorter-side chain length at C-1, was found to be higher than same ILs having longer-side chain length; and were both lower than –SO₃H functionalized ILs.

Dual-functionalized ILs have even greater acidity. Products distribution is also associated with the acidity of ILs as catalysts/co-solvent medium employed. Highly acidic medium preferentially favored hydrolysis reaction, yielding water-soluble products. While basic medium promotes liquefaction reactions, yielding organic products [23].

However, the most attractive ILs in this field, nowadays, are the deep eutectic solvents (DESs) [46, 47]. Additional properties of DESs including; low volatility, thermal and chemical stability, high selectivity, green characteristic; ease of preparation [29, 48] are among their added advantages of DESs as catalysts. The chemistry of these catalysts suggests that their delignification efficiency was dependent on the acidic amount, its strength, chemical composition of the quaternary salt and the nature of the hydrogen bond acceptor or both [46, 49]. Liu et al. [23], conducted the selective hydrogenolysis of Kraft lignin into mono-phenol, catalyzed by using Choline-derived DESs, in which, [Ch][MeSO₃] showed excellent lignin dissolution, resulting from its strong acidity and better thermal stability.

Accordingly, Wu et al. [47] investigated among others, the lignin extractability of monocarboxylic acids, dicarboxylic acids and polycarboxylic acids based DESs. The authors reported monocarboxylic acids with high acidic strength showed improved lignin extractability, as compared to low acidic monocarboxylic acids and dicarboxylic acids, due to carbon dioxide liberation in case of using dicaroxylic acids. Controversially, the low viscosities of polycarboxylic acids makes their hydroxyl group available for interaction with the etherified hydroxyl components of the lignin, thus; resulting in high lignin extraction [47].

Apart from their general applications in biomass refining including lignin degradation, ILs have been reportedly used in selective production and isolation of biorefinery products such as furfural [48], total reducing sugars [45, 50], and glycerin separation [51]. For example, in place of microwave assisted methylation, the selective oxidation of these benzylic alcohols in lignin into benzylic ketones, prior to the β–O–4 hydrogenolysis treatment has been reported [52].

Technically, two-step lignin depolymerization involving the selective oxidation of primary benzylic alcohols into benzylic ketones on one side and its succeeding β–O–4 cleavage; would have been the most favorable conversion route. However, challenges associated with the low products yields and poor selectivity remained unresolved. Unlike the methylation route, the benzylic ketone (selective oxidation) route, showed low products yield and selectivity as well. In addition, products separation becomes challenging on a large scale [35].

5.3 Effect of reaction time

The effect of reaction time during lignin degradation was studied by Yuan et al. [53]. The authors discovered that; long reaction time was needed to ensure complete degradation of all ether bonds in lignin, and gradual degradation of the stable C–C bonds, afterwards. Long reaction induction period of the intermediates enabled secondary reactions including re-polymerization, cross-linking and rearrangement, thereby forming marginally higher products yields. Reaction time has significantly influenced the properties of individual lignin liquefaction products. According to Chen et al. [12], reaction time had no significant effect on products yield.

5.4 The effect of reaction time

The composition of lignin is yet, another important factor in its degradation. Zhou [18] observed that, the yield of water-soluble hydrocarbons during HTL of Kraft lignin was low as compared to the yield of same components in liquefaction of sawdust. They attributed their finding to the composition of Kraft lignin, having low carbohydrate content. Another important factor in lignin degradation is the composition of the solvent. According to Yuan et al. [53], the composition of solvent greatly influenced the products distribution. They observed that; phenol addition in the reaction medium hindered side reactions like re-polymerization of products intermediates, resulting in low residue formation. Using co-solvent system showed improved lignin degradation, specifically, water-ethanol co-solvent degradation was much effective as compared to individual mono-solvent systems [12].

6. Composition of liquefaction products

As earlier discussed, decomposition of the different classes of lignin components (p-coumaryl, coniferyl and sinapyl alcohols) results in complexing chemical products, intermediates and by-products during liquefaction. Characteristically, p-coumaryl alcohols decomposed into corresponding hydoxyphenyl derivatives (H-type) including Phenol, Phenol-methyl-, Phenol-di-methyl-, Methylphenol and other secondary Benzoic acid hydroxyl- derivatives.

The guaiacyl derivatives (G-type) are largely containing methoxyphenol, methyl methoxyphenol, vinylphenol, methoxy propyl and vanillin. According to Zhou [15], the products distribution from an organosolv liquefaction of Kraft lignin, for example; suggested up to 65 wt% constituted of volatile products, of which 78 wt% was made up of 2-methoxyphenol.
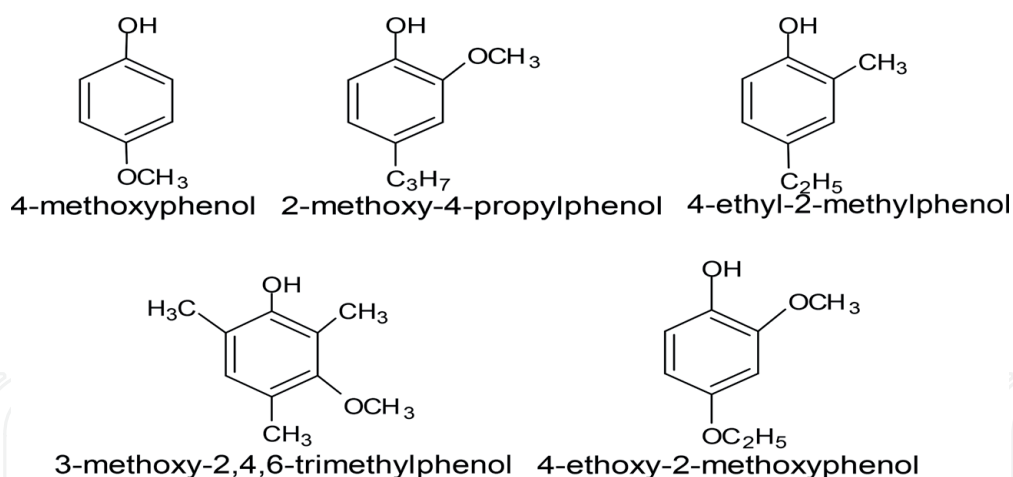
6.1 Phenol

Phenol and its derivatives are probably the most interesting products of lignin liquefaction. Phenol and its derivatives formed the major composition of HTL of lignin and its compounds. Selective cleavage of the different ether bonds (C–O–C), yield highly phenolic products, showing excellent fuel additive properties, when the oxy-aromatic configuration is retained [11]. Phenolic compounds formed the greater composition in bio-crude oil obtained from Corncob lignin degradation. Generally, phenolic products from lignin degradation are classified as G-phenols (methoxy phenols), S-phenols (dimethoxyphenols) and H-phenols (methylphenols).

Khampuang et al. [54], conducted an alkali catalyzed Corncob liquefaction in supercritical water-ethanol, with phenol and its derivatives (phenol, 4-methoxy-acetate; phenol, 2-ethyl-; phenol, 4-ethyl-2-methoxy-; phenol, 2,6-dimethoxy-), constituting major proportion of the bio-crude oil. **Figure 5** presents some selected Phenolic products from HTL of lignin.

Similarly, Riaz et al. [55], confirmed the presence of monomeric phenol as one of the major components of bio-crude oil obtained from the acid hydrolysis lignin degradation in supercritical ethanol. The authors noted that, though, phenol (C_6H_5OH) was the major product, traces of methyl, methoxy, and ethyl groups were equally observed. Base catalyzed HTL of lignin seems to promote phenol formation. According to Nazari et al. [56], phenol derivatives (mainly 2-methoxy phenol), and aliphatic compounds, constituted significant composition of bio-crude oil yield, resulting from the use of base catalyst (KOH). Yuan et al. [53], reported that, higher temperature, and long reaction time increased the phenol combination rate, leading

Figure 5.
Some phenolic products from HTL of lignin.

to re-polymerization, and cross-linking among phenol and the side chains of the degraded lignin. Yang et al. [33], found that, compounds in bio-crude oil had extra active sites than the parent lignin, signifying that the bio-crude oil obtained from lignin degradation was a promising feedstock for industrial synthesis of phenol formaldehyde adhesive. Decomposition of p-coumaryl alcohol (H-type), yield significant bio-crude oil with high amount of phenol.
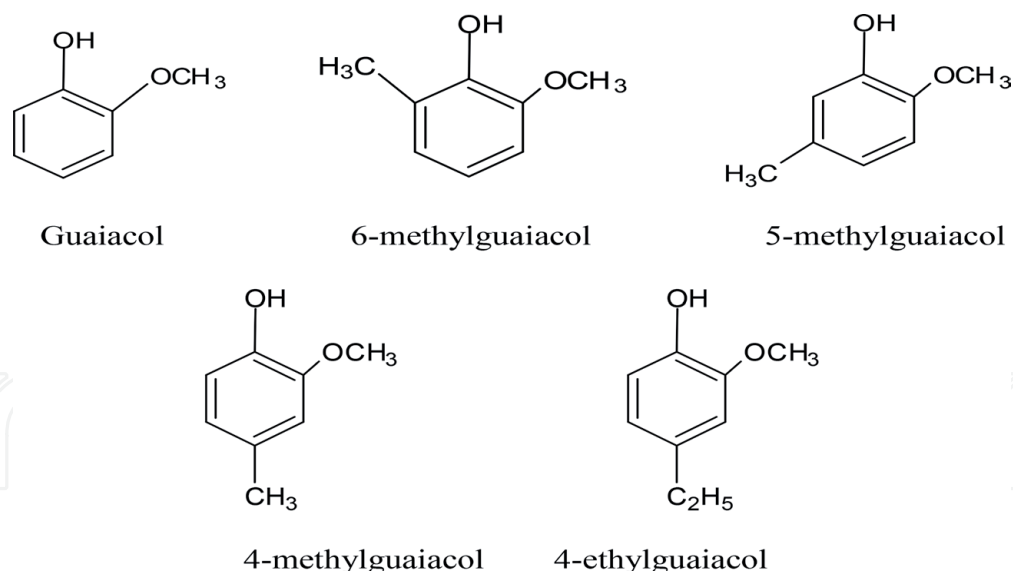
6.2 Guaiacol

The widely accepted mechanism for the production of guaiacol is via β–O–4 bond cleavage. Recalling that, β–O–4 bond is the predominant in lignin structure, large quantity of guaiacol is expected during HTL. The production of guaiacol depends on the cleavage of C–O and C–C bonds during lignin degradation [14]. Increasing reaction temperature reduces the yield of guaiacol-derivatives at the expense of their benzendiol counterparts (Catechol). This was confirmed by the work of Nguyen et al. [11], who reported that, base catalysts, such as K_2CO_3 tend to decrease the yield of guaiacol and increasing the yields of catechol. Zhou [18], conducted the HTL conversion of Kraft lignin, indicating the predominance of guaiacol (19–78 wt%), depending on reaction conditions. The bio-crude oil yield was indicated by improved sum of phenolic –OH groups present in Kraft lignin and, diminished amount of β–O–4 linkages, hydroxyl groups, carbonyl groups, aromatic rings. Thus, suggested that, the guaiacol yield obtained via HTL of lignin was much higher than that obtained from its liquefaction. **Figure 6** presents some Guaiacol derivatives reported from HTL of lignin. **Figure 6** presents the relative distribution of products.
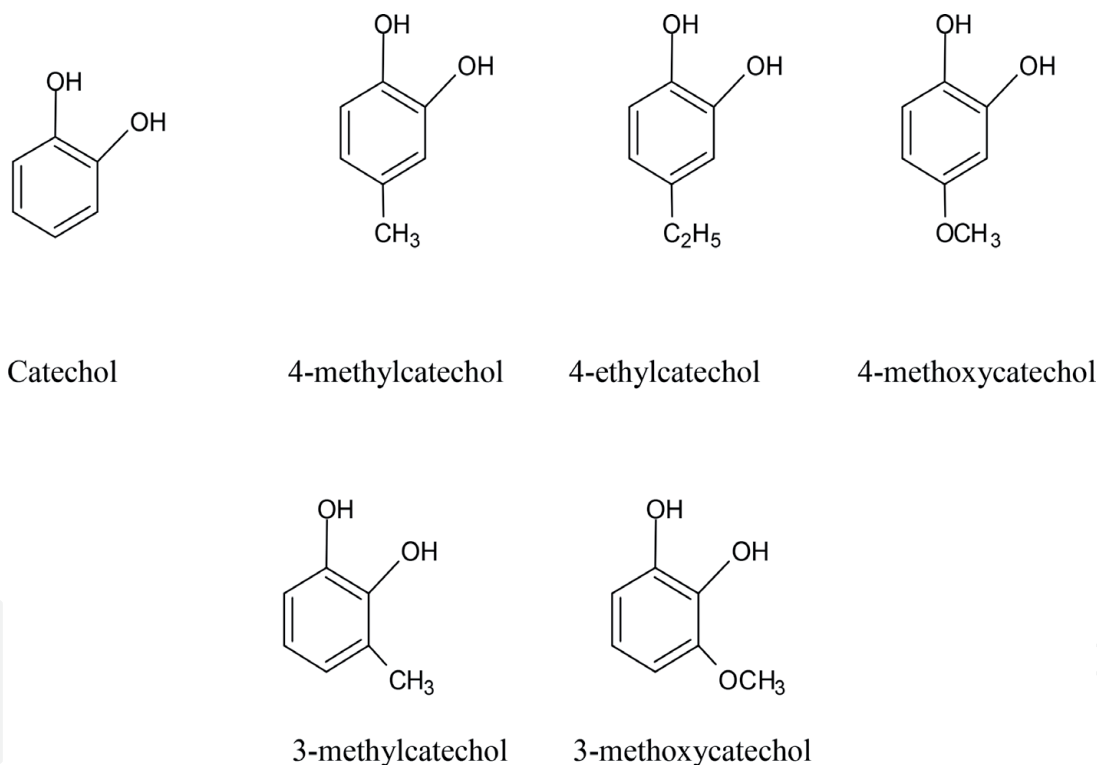
6.3 Catechol

Catechol exists in different monomer forms including pyrocatechol, 3-methylcatechol, 4-methylcatechol, propylcatechol, 4-ethylcatechol and so on. Its production mechanism reported by authors differ. For example, Beauchet et al. [13] proposed the production of pyrocatechol, and methanol via direct hydrolysis of O–CH₃ bond, while its decarboxylation at ether bond of 3-hydroxy-4-methoxybenzeneacetic acid, yielded significant proportion of methylcatechol. **Figure 7** presents some selected catechol derivatives.

Forchheim et al. [14], proposed lignin degradation, and found that, RANEY Nickel catalyst favored ether bond cleavage near critical water condition. Authors also noted the conversion of catechol into phenol as the secondary degradation
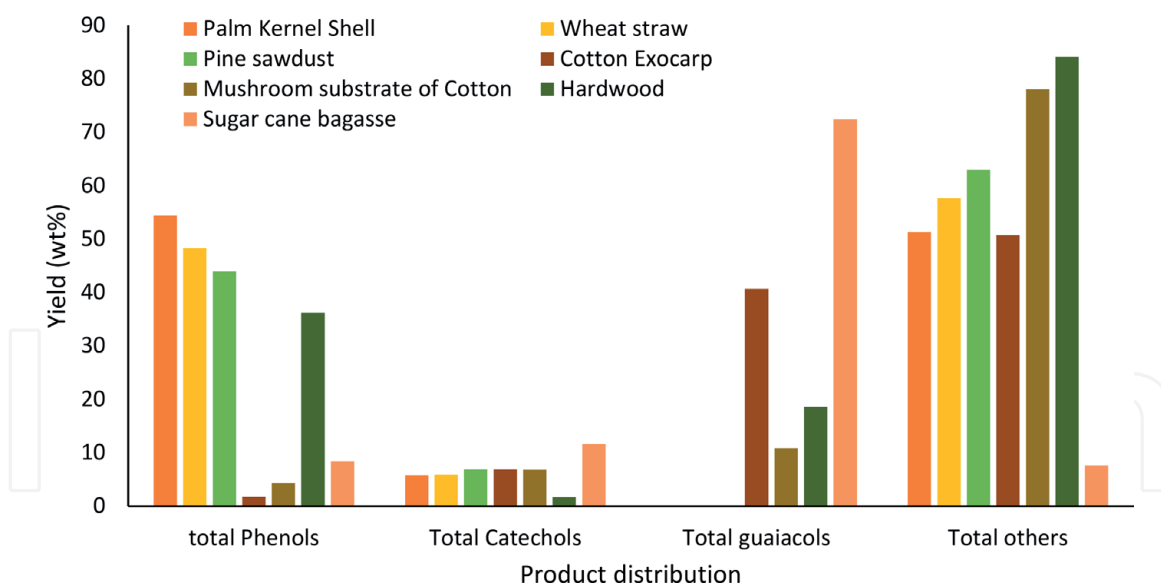
Figure 6.
*Some guaiacol derivatives from HTL of lignin.*

Figure 7.
Structures of some catechols.

product. Guaiacol degradation also yield catechol, whereas, catechol losses one –OH group to form phenol at high temperature [9]. Generally, high-temperature and short time favored the formation of catechol, and subdues the formation of char and gaseous components [14]. Depending on the temperature, HTL is sub-divided into subcritical liquefaction and supercritical liquefaction. **Figure 8** presents the relative products distribution in lignin degradation on yield of different feedstock reported in the literature.

Catechol formation was discussed by Hu et al. [43] suggesting that; it is largely formed by the preferential elimination of methoxyl group depending on the truncated strength of the Aryl–OCH_3 (DBE = 273 KJ/mol) to the Aryl–O–CH_3 (DBE = 416.7 KJ/mol) bond. Specifically, with increasing reaction temperature,

Figure 8.
Relative products distribution in lignin degradation. Palm kernel shell, wheat straw, and pine sawdust [25], cotton exocarp and mushroom substrate of cotton [22], hardwood [36], and sugarcane bagasse [39].
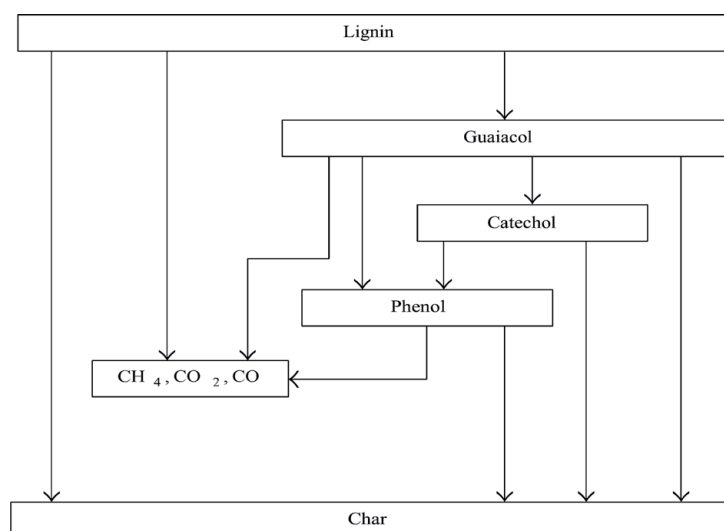
Figure 9.
Proposed reaction pathways for hydrothermal lignin degradation [14].

simultaneous pyrolysis and hydrolysis reactions taking place favored catechol formation. Lignin depolymerisation kinetics designated the decomposition of catechol into phenol, preferentially at high temperature and long reaction time [20]. Berstis et al. [10], demonstrated the use of density functional theory in predicting the relative energetics as well as bond dissociation enthalpies of the different benzodioxane linkages in lignin (C–C, C–S, C–G, C–H).

The index of hydrogen deficiency or double bond equivalence is calculated by the formula proposed by Pedersen and Rosendahl [30] as given below:

$$\Omega = (2 + 2C - H)/2 \qquad (1)$$

Figure 9 presents the relative distribution of products. Guaiacol – catechol – phenol interaction was considered as an important factor in lignin degradation kinetic studied by Forchheim et al. [14], because, phenol has better stability than either of guaiacol or catechol. **Figure 9**, proposed reaction pathways for hydrothermal lignin degradation.

7. Useful compounds and their applications

7.1 Useful compounds obtainable from HTL process

A significant number of chemicals compounds are theoretically and practically obtainable from HTL process. According to the broad literature available, these compounds are classified into phenols, guaiacols and catechols. However, derivatives of these principal groups have been widely reported. For example, lignin phenolic compounds have been produced by different research groups.

HTL products are largely rich in *ortho-methoxyphenolic* compounds which are detected by the presence of $-OCH_3$ in their NMR spectra. This high volume product has chemical and biochemical applications including the manufacture of drugs and in clinical diagnosis. For example, the monitoring of wood smoke exposure by urinary assay was conducted by measuring the *ortho-methoxyphenols*. The production of perfumes, disinfectants resulting from its anti-oxidant properties, and as starting material for the synthesis of guaiacol compounds has been reported. Similarly, 3-methoxyphenol have dual functions as catalyst and building block in synthesis of anti-oxidants. Guaiacol is obtained by destructive distillation of phenol fraction of coal tar.

8. Pyrolysis of lignin

Pyrolysis of lignin has been one of the degradation techniques reported. Wang et al. [57] compared the pyrolytic behavior of different lignin (Manchurian ash and Mangolian Scot pine). The authors concluded that, the differences in pyrolytic behavior of the lignin studied were attributed to variation in their composition, and degradation temperature. High methanol yield was observed from degradation of hardwood, due to its higher methoxy group content, while the secondary methanol yield was attributed to aromatic ring degradation at high temperature.

Although HTL and pyrolysis of lignin are closely related, there exist some fundamental differences in their products. For example, Haarlemmer et al. [7], observed that, bio-crude oil (obtained from HTL) had higher acidity and iodine value as compared to an inverse relationship observed in bio-oil (obtained from pyrolysis) from the same feedstock. According to these authors, HTL oils are very viscous, and had strong black oil smell. It also had higher heating value (35–40 MJ/kg). HTL bio-crude oil is typically proposed as diesel substitute after catalytic upgrading. On the contrast, Pyrolysis oil is often presumed as substitute for fuel oil, and had smoky odor, and is less viscous, with heating value similar to that of the parent biomass. **Table 4** presents the comparative properties of biomass fuels with standards.

Like HTL of lignin, the products distribution during pyrolysis of lignin also depends on the composition of the feedstock. Chang et al. [24], conducted the Py-GC/MS degradation of palm kernel shell. Accordingly, the primary composition of the feedstock indicated the predominance of p-hydroxyphenyl structural units, resulting in high phenolic products, often its degradation. In contrast, pine sawdust and wheat straw contained largely guaiacyl units, and often degradation, yielded significant proportion of methoxy groups. Similarly, Biswas et al. [58], reported the slow pyrolysis of prot, alkali and dealkaline lignin for the production of chemicals. Among these types, alkali lignin was reported to have highest bio-oil yield (34.1%). Bio-oil products showed the presence of guaiacol, syringol, alkylphenols and catechol; depending on the pyrolysis conditions and nature of lignin used.

Standard	Diesel	Biodiesel	Marine heavy fuel oil	Hydrothermal oil	Pyrolysis oil
	NF EN 228	NF EN 14214	NF ISO 8217		In progress
Density at 15°C (kg m^{-3})	820–845	860–900	920–1010	1.14	1.1
Carbon residue (%)	<0.3	<0.3	<2.5–20	17–24	11–13
Total acid number (mg KOH/g)	<0.5	<0.5	ʿ0.5	32–67	45–109
Iodine value (g$_{12}$/100 of fuel)	NA	<120	NA	126–127	147–203
Higher heating value (MJkg^{-1})	45	≥35	NA	27–30	21–30
Water content (%)	<0.02	<0.05	<0.033	<1	8–20
Viscosity at 40°C (mPas)	3–4	<4	8.5–690	67,000	13–70

Table 4.
Comparative physico-chemical properties of different biomass oils [7].

Pyrolysis of lignin-rich biomass from cotton by-product was conducted by Chen et al. [21]. Maximum bio-crude oil yield from fast pyrolysis was 58.13 (wt%) and 45.01 (wt%) at 600°C for cotton exocarp and spent mushroom substrate of cotton by-products, respectively. As compared to cellulose and hemicellulose, lignin degradation occur slowly and within wide temperature range (150–780°C).

9. Hydrolysis of lignin

Raiz et al. [55], conducted the concentrated sulfuric acid hydrolysis of lignin in supercritical ethanol, reporting significant reduction in oxygen content (44 wt%), resulting from improved deoxy-liquefaction. Bio-oil obtained from this work, had higher heating value, improved energy recovery, and energy efficiency.

Like liquefaction, hydrolysis bio-oil was rich in Phenol, esters, hydrocarbons, furan and alcohol. Ji et al. [59], conducted the hydrolysis of wheat straw in a dilute sulfuric acid medium using a continuous reactor. The maximum reducing sugar yield obtained was as high as 60.8 wt%, constituting furfural as the major by-product.

10. Other technologies

A number of emerging lignin degradation techniques are coming up by the day. Recently, a two-step lignin depolymerisation was reported, in which, lignin was methylated using micro-wave irradiation in the presence of benzylic alcohols. The first step of the reaction proceeded via catalytic hydrogenolysis of β–O–4 bond [52]. Similarly, in place of microwave assisted methylation, the selective oxidation of these benzylic alcohols in lignin into benzylic ketones, prior to the β–O–4 hydrogenolysis treatment has been reported [60]. Technically, two-step lignin depolymerization involving the selective oxidation of primary Benzylic alcohols into Benzylic ketones on one side, and its succeeding β–O–4 cleavage; would have been the most favorable

conversion route. However, challenges associated with the low products yields and poor selectivity remained unresolved. Unlike the methylation route, the benzylic ketone (selective oxidation) route, showed low products yield and selectivity as well. In addition, products separation becomes challenging on a large scale [35].

11. Conclusions

Lignin degradation chemistry revolves around its β–O–4 bond cleavage. Products selectivity during its degradation is largely dependent on the catalysts employed, while the yield partly depends on the feedstock and reaction conditions. Temperature is the predominant factor influencing the reaction. Ionic liquids catalysts showed increasing research interest in biomass, and lignin liquefaction, owing to their interaction with lignin structure. Phenolic products are formed from selective cleavage of the different ether bonds (C–O–C). Increasing reaction temperature reduces the yield of guaiacol-derivatives at the expense of catechol. Catechol is formed via hydrolysis of O–CH$_3$ bond, and decarboxylation at ether bonds. Guaiacol – catechol – phenol interaction was considered as an important factor in lignin degradation kinetic studies. Although HTL and pyrolysis of lignin are closely related, there exist some fundamental differences in the products.

Acknowledgements

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