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Dossier

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DOSSIER Edited by/Sous la direction de : **A. Daudin et A. Quignard**

PART 1

Second and Third Generation Biofuels: Towards Sustainability and Competitiveness

Deuxième et troisième génération de biocarburants : développement durable et compétitivité

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Dossier

Second and Third Generation Biofuels: Towards Sustainability and Competitiveness
Seconde et troisième génération de biocarburants : développement durable et compétitivité

Thermochemical Conversion of Lignin for Fuels and Chemicals: A Review

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Résumé — Conversion thermochimique de la lignine en carburants et produits chimiques : une revue — La lignine est une des composantes de la biomasse lignocellulosique potentiellement valorisable comme ressource renouvelable pour la production de carburants ou de produits chimiques. Après séparation de la matrice lignocellulosique, cette macromolécule est de nos jours essentiellement utilisée comme combustible dans l'industrie papetière. Outre cette filière papetière, la production d'éthanol de seconde génération à partir de la cellulose aura comme conséquence la mise à disponibilité d'encore plus grandes quantités de lignine. De nouvelles applications pourront donc être proposées pour l'utilisation de cette bio-ressource. Les différentes voies thermochimiques : pyrolyse, solvolyse, conversion hydrothermale et hydroconversion envisagées pour la valorisation de la lignine sont décrites dans cet article.

Abstract* — *Thermochemical Conversion of Lignin for Fuels and Chemicals: A Review — *Lignin is one of the biomass components potentially usable as renewable resource to produce fuels or chemicals. After separation from the lignocellulosic matrix, this macromolecule is nowadays essentially valorized by combustion in paper mills. If second generation ethanol is produced in the future from lignocellulosic biomass, some increasing reserves of lignin will be available in addition to the ones coming from the paper industry. The main thermochemical ways such as pyrolysis, solvolysis, hydrothermal conversion and hydroconversion considered for the valorization of the lignin are reviewed in this article.*

INTRODUCTION

Lignin is one of the most important lignocellulosic biomass components; its complex aromatic structure is highly dependent on the natural source and on the process used for its extraction and/or separation. Lignin is mainly composed of hydroxyl-phenylpropane units issued from three monomers *p*-coumaryl, coniferyl and sinapyl alcohols differently distributed depending on the vegetal material (softwood, hardwood or grass) (*Fig. 1*). The main lignin linkages (*Fig. 2*) are differently distributed according to the type of wood [1]: the β-O-4 ether linkage is the most important in softwood (50%) and in hardwood (60%). The 4-O-5 and α-O-4 aryl ether bonds are less predominant (respectively around 5 and 8% for both types of wood). Biphenyl linkages 5-5 (18%), phenylcoumaran β-5 (11%), diarylpropane β-1 (7%) and β-β (2%) are present in decreasing amounts. The bond dissociations enthalpies were calculated in lignin structure [2]: as expected ether linkages are easier to cleave compared to C-C bonds. Besides the wood lignins as a by-product of paper production, straw (grass and bagasse) lignins are also of importance but not often considered [3]. However, this ex-straw biomass is the largest renewable source available for the production of bio-product or biofuels. In comparison with wood lignins which contain mainly guaiacyl (G) and syringyl (S) units, herbaceous lignins contain all the three

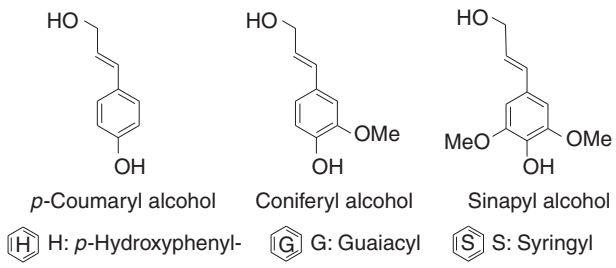

Figure 1

The three alcoholic monomers of lignin.

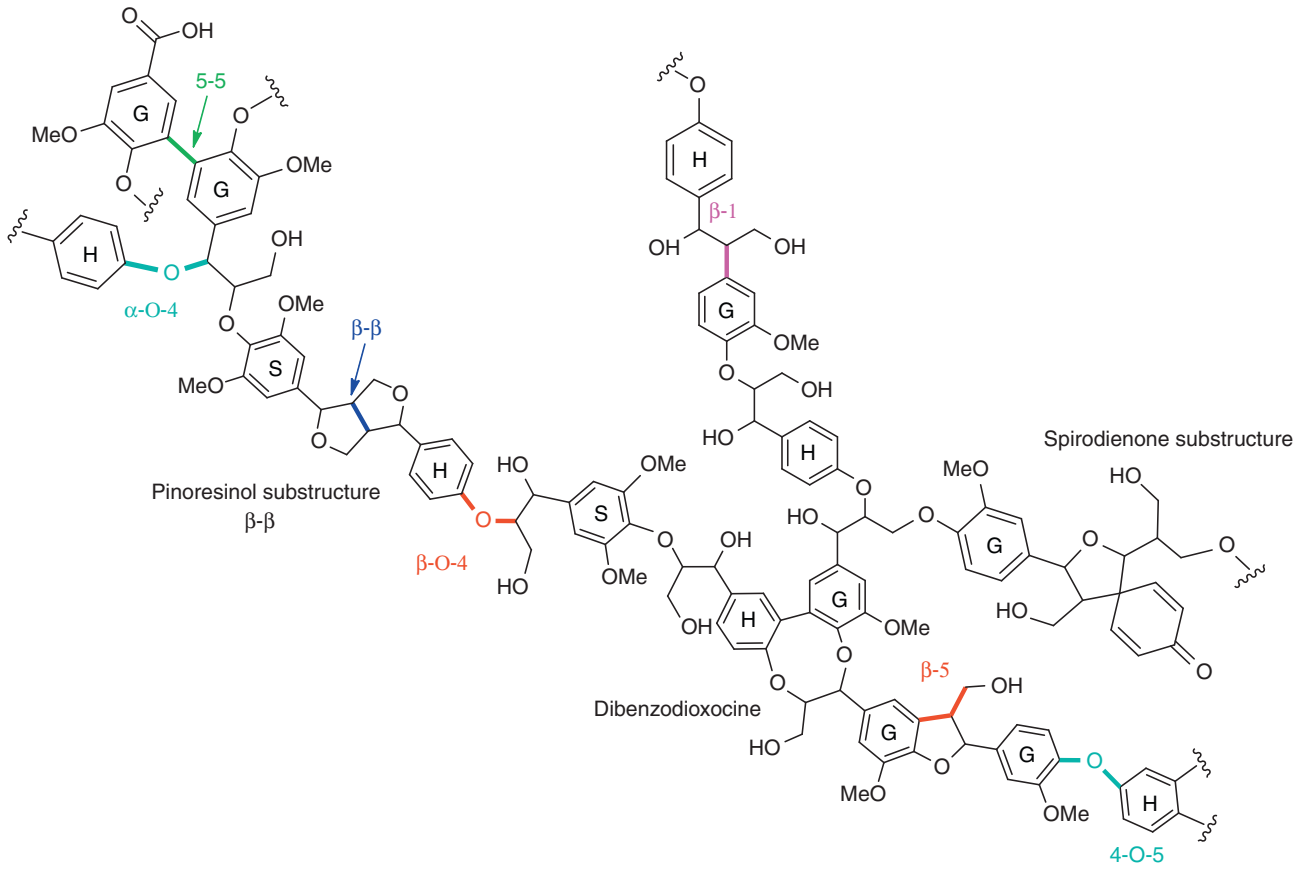

Figure 2

Example of a lignin structure with the typical 5-5, β-β, β-O-4, α-O-4, β-5, β-1 and 4-O-5 linkages.

units: *p*-hydroxyphenyl (H), guaiacyl (G), syringyl (S) in significant amounts [4, 5].

In pulp industry, lignin is separated from cellulose and hemicellulose during the Kraft process (95% of the world quantity of lignin produced per year) and the 55 million tons of lignin co-produced per year are only used as energy source for combustion application [6]. It has been estimated that a significant part of the Kraft-lignin (8 to 11 $Mt.y^{-1}$) could be valorized elsewhere without weakening the industry economy. Furthermore, as the production of second generation bio-ethanol from lignocellulosic materials is under industrial development, it can be planned that more and more lignin will be available as a by-product of bio-ethanol production in a near future [7]. As a consequence, and considering the depletion of the fossil fuels, lignin appears as an interesting alternative resource for aromatic platform chemicals like phenols or aromatics (BTX) but also as raw material for sustainable liquid fuel additives [8-10]. All these developments are often taken into account in the context of integrated biorefineries.

The industrial valorization of lignin into chemicals has been undertaken through two main processes: Noguchi and HRI (or Lignol) processes. The Noguchi process was developed in 1966 in Japan to produce monophenols by catalytic hydrogenolysis after liquefaction by pyrolysis [11]; it was abandoned because of the low yield of targeted products. The Lignol process developed by *Hydrocarbon Research Inc*. is a continuous process involving a heterogeneous catalyst and using the liquid from hydroliquefaction as solvent for the catalytic hydroconversion [12]. It seems also that, in the former USSR, industrial lignin pyrolysis processes from wood saccharification were considered to be valuable for the production of phenolic compounds and activated lignin carbon [13].

The conversion of lignin into added-value products was mostly performed using thermochemical processes. These conversion processes include three sub-categories: gasification (> 900 K), pyrolysis (650-800 K, 0.1-0.5 MPa) and liquefaction (500-600 K, 5-20 MPa) [14].

The purpose of this article is to afford an overview of the principal thermochemical routes (including catalytic and non-catalytic processes) applied to lignin which afford significant amount of bio-liquid potentially utilizable as a source of chemicals or biofuels. In this area, the literature is confusing; pyrolysis is often employed as a generic term for thermal conversion even if it is actually solvolysis (in presence of a solvent) or hydroconversion (conversion in the presence of hydrogen). Therefore, we propose to classify these thermal processes according to the following criteria:

- pyrolysis is performed under inert atmosphere without catalyst at low pressure (with the assistance of a catalyst, it is usually known as catalytic pyrolysis and can be referred as catalytic cracking);
- the conversion in the presence of water is known as hydrothermal processing, using sub-critical or supercritical water (if another solvent is used, it is called solvolysis);
- finally, when hydrogen is used (with or without any solvent including water, such as a H-donor solvent), they are known as hydroconversion type processes which can be assisted with different catalyst types to perform hydrotreatment/hydrodeoxygenation or hydrocracking. The so-called hydropyrolysis process can be considered in this category.

Figure 3 summarizes these different thermochemical routes and the characteristic temperature/pressure ranges of working conditions.

As numerous studies dealing with lignin model molecules conversion can be found in the literature and provide mechanistic information, this review will be focused on the use of lignin as feedstock and the description of products distribution.

The lignin oxidation, which is an alternative route of conversion also described in the literature [15] will not be addressed here.

This article will not detail analytical methods. However, the evolution and application of characterization methods to lignin and lignin products deserves to be briefly introduced. In fact, describing the physical and chemical properties of lignins represents a real challenge from an analytical point of view since the chemical composition of these macromolecules varies over a large range, depending on the vegetal material (wood or grass) but also on the way or the process they are coming from. In order to characterize the structure of various lignins, many analytical techniques have been developed and provide essential information to describe the relationship between structure and reactivity of lignins. For example, the thermal behavior of lignins is described by Differential Thermogravimetry Analysis (DTA/DTG) [16] but also by pyrolysis coupled with Gas Chromatography Flame Ionization Detector (GC-FID) [17]. Size Exclusion Chromatography (SEC) mostly performed in tetrahydrofurane (THF) provides relative molecular weights distribution [18], lignin being often acetylated before GPC analysis in order to increase its solubility in the elution solvant [19]. Nuclear Magnetic Resonance (NMR) is a precious technique to get information on the lignin structure since ^{13}C or ^{1}H NMR analyses afford the proportion of typical functional groups [20]. For instance, detailed quantification of the different functions can be achieved by the two-dimensional ^{13}C,^{1}H-correlated Heteronuclear Single Quantum

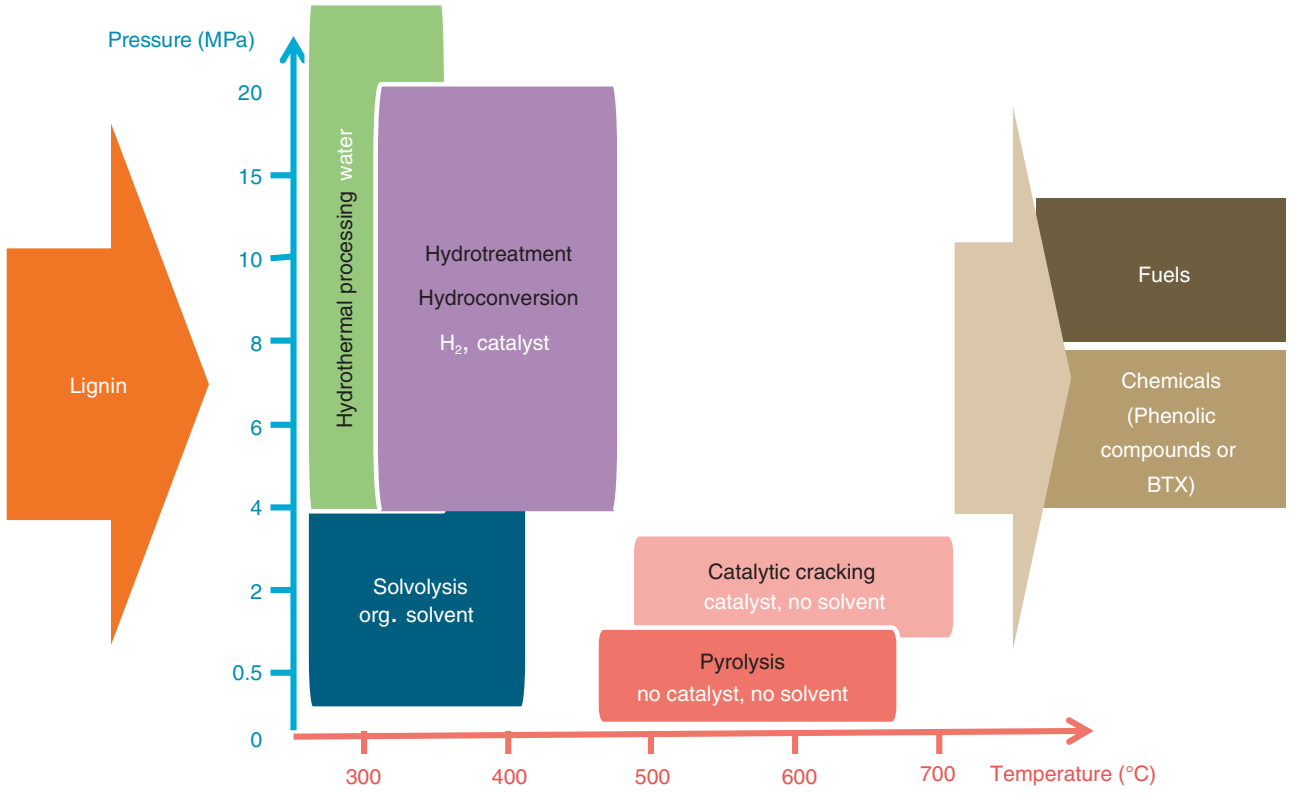

Figure 3

Thermochemical ways and (*P*, *T*) parameters range for the conversion of lignin into liquid.

Coherence (2D-HSQC) technique [21]. The hydroxyl functions from guaiacyl, syringyl or phenolic groups can also be distinguished and quantified by ^{31}P NMR spectroscopy after phosphitylation [22]. Fourier Transformed Infrared (FT-IR) technique also provides information about chemical functions present in the lignin structure [23]. These analytical techniques were often applied to characterize different types of lignin in order to follow their conversion and to find new ways of valorization. More scarcely, Matrix-assisted laser desorption ionization-time of flight mass spectrometry (Maldi-TOF-MS), Laser Desorption/Ionization Time-of-Flight Mass Spectrometry (LDI-TOF-MS) and Pyrolysis Field Ionization Mass Spectrometry (Py-FIMS) techniques were also used to afford complementary structural information [24].

1 CONVERSION OF LIGNIN BY PYROLYSIS OR CATALYTIC CRACKING

As pyrolysis is a classical route to obtain bio-oils from biomass [25], this technique was also applied to lignin. When performing fast pyrolysis (600-1 000°C, 0.5-10 s, 10-200°C/s, in the absence of oxygen), on lignocellulosic biomass, char can be minimized and higher yields of liquids can be generally reached [26, 27]. However as regards fast pyrolysis of lignin, a minimal temperature of 400-450°C is necessary to proceed to the macromolecules decomposition; moreover lignin thermoplastic behavior causes some trouble for the feeding and specific procedures are necessary [28]. The yields to pyrolytic liquids are generally around 40-60 wt% while gases represent 8-20 wt%. Several authors have investigated the experimental conditions and in a lesser extent their impact on the oil composition [29]. The pyrolytic liquids are mainly composed of water, unsaturated compounds, aromatic oxygenated compounds (phenols) and char is formed in large amount (30-40 wt%). Pyrolysis of lignin is generally performed in a wide range of temperatures (400-750°C) despite the fact that thermal degradation starts around 200°C.The first linkages to be cleaved are the weakest α-O-4 ether bonds [30]. Above 400°C, higher yields (40 wt% of liquid products) are obtained but the decomposition is complex and tar formation is observed [31]. Catalytic pyrolysis [32] or hydropyrolysis, in presence

of hydrogen as well as catalytic hydropyrolysis [33, 34] have been carried out to improve the oil yield and quality by deoxygenation and reduction reactions. However, the "hydropyrolysis" term should be restricted to fast pyrolysis using H_2 as gas phase and not mistaken with hydroconversion involving longer residence time (*Sect. 3*).

By using non-sulfided $NiMo/SiO_2$-Al_2O_3 and Cr_2O_3/Al_2O_3 catalysts, for instance, the pyrolytic oil yield was increased and the composition was deeply modified as methoxyphenols products were replaced by phenol, cresols and xylenols by demethoxylation and hydrodealkylation [33]. During fast catalytic pyrolysis, the use of HZSM-5 catalyst (catalytic cracking) improved the yield of non-oxygenated aromatics but not really the liquid yield [35]. Even more recently a liquid yield of 74.9 wt% has been claimed with a selectivity directed towards aromatic hydrocarbons by using a H-USY zeolite for fast pyrolysis in a batch reactor, but huge amount of catalyst was needed, the catalyst-to-lignin ratio being 4 [36]. Furthermore, batch reactor is not adapted for this kind of transformation. $NiCl_2$ and Ni-ZSM-5 exchanged zeolites were also investigated as catalysts, the later promoting deoxygenated products and leading to a less acidic bio-oil more suitable for fuel [37]. Instead of zeolites, calcium formate was also proposed as an effective additive for reducing the oxygen content of the products [38]. At different temperatures, in the range 500-650°C, under atmospheric pressure and with an acidic HZSM-5 catalyst, using acetone as solvent for lignin, a high level of deoxygenation was reached and alkylated aromatic products like toluene and xylenes were predominant (74 to 89 wt%) in the liquid phase [9]. However, at 550°C, the liquid phase represented only 43 wt% of the initial lignin while gases can reach 19 wt% and char/coke 38 wt%.

From these results, it is obvious that doping agents and catalysts enhance deoxygenation and the selective production of aromatic compounds. From an academic point of view, the use of a micro-pyrolyzer coupled with a GC-MS/FID system is becoming popular. It is very useful to identify directly the numerous products formed during lignin pyrolysis [17] but also thanks to short vapor residence time, the secondary reactions were reduced and high mass and carbon balances were achieved to provide mechanism insights on oligomers formation [39]. But the continuous pyrolysis remains a technical challenge when applied to lignin. Several technologies are available to proceed to the pyrolysis of biomass: shallow fluidized-bed reactors, vacuum pyrolysis reactors, ablative reactors, and circulating fluidized-bed reactors [40]. In general, fast pyrolysis of lignin in these types of reactors was not adapted and new reactor designs such as entrained-flow were recommended [41]. For instance, bubbling fluidized bed pyrolysis reactors were used to convert a wheat straw-derived Organosolv lignin in the presence of commercial catalyst [42]. Around 80 wt% of the dry lignin was converted into bio-oil (40-60%), and biochar (30-40%). The bio-oil was composed by both monomeric and oligomeric phenol compounds. Moreover, a second stage of conversion is often considered to improve the deoxygenation of the pyrolytic lignin oil [13].

2 CONVERSION OF LIGNIN USING ORGANIC SOLVENTS OR WATER

The conversion of lignin in organic solvents, called solvolysis, and the hydrothermal processing, in water under subcritical or supercritical conditions, are described here separately, the operating conditions being very different. Mixtures of water and solvents are also often investigated. Up to 50/50 ratio, we will consider the reaction as hydrothermal.

2.1 Solvolysis (in Organic Solvents)

By analogy with coal liquefaction studies, the use of a H-donor solvent [43] for the liquefaction of lignin was proposed in order to improve the hydrogenation and the yield into liquid products. Tetralin is the solvent most often used in this type of study due to its reversible hydrogenation/dehydrogenation capability [44-46]. Besides, its organic solvent properties, this brings the advantage of stabilizing radicals and limit the formation of condensed products and chars. The cleavage of CH_3-O, β-5', C_α-C_β, C_{aro}-C_α bonds has been observed during hydroliquefaction of lignin or model molecules at 400°C [44]. Mixture of solvents might have a beneficial effect on the conversion. For instance, addition of m-cresol during the solvolysis of 4-propylguaiacol was found to increase the yield of phenols [47].

According to Vuori [48], when conversion of lignin was performed at 345°C, the yields into liquids were still low and high quantities (20-30%) of condensation products, precursors of coke and chars, were formed after $C_{aliphatic}$-O cleavages. Therefore, these solvents alone cannot provide high selectivity towards liquid products. As an alternative to H donor solvents, ethanolic solvents or glycerol can also be of interest for an environmental point of view and a lower cost. For instance, a mixture of formic acid and ethanol (or isopropanol) solvents proved to be efficient [8], at 380°C, to obtain liquids having high quality, mainly composed of aliphatics hydrocarbons and phenols [49]. Formic acid may also act as a hydrogen source [50]. It has been successfully used to depolymerize various lignins

into hydrodeoxygenated liquids [10, 51]. By adding a Pt/C catalyst and acetic acid into ethanol, even higher yields of monomeric phenols and low amounts of char were reached from a switchgrass lignin [52].

2.2 Hydrothermal Processing (in Water)

Black liquors containing lignin in aqueous alkaline solutions were already used for the production of phenolic compounds in 1943 [53]. In fact, considering the conversion parameters from the literature, lignin can be depolymerized in such aqueous solutions under subcritical or supercritical conditions at relatively low temperature, typically in the range of 280-400°C, from few minutes to few hours, under 20-25 MPa of total pressure with a water-to-lignin ratio generally varying from 2 to 50. The reaction has the significant advantage of not requiring a preliminary drying process. At conditions close to the critical point (22 MPa, 374°C), water has several very interesting properties, such as a high solubility of organic substances and a low viscosity, which makes near to supercritical or supercritical water an excellent medium for fast, homogeneous and efficient reactions [54]. The high concentration of H^+ and OH^- at subcritical conditions accelerates many acid- or base-catalyzed reactions, such as hydrolysis [55]. Both sub- and super-critical conditions present advantages and drawbacks and corrosion remains a critical issue, as well as the very high pressure level from an economic point of view. Even if higher conversion to methoxyphenols or hydroxyphenols were observed under supercritical conditions, subcritical conditions are generally preferred [56, 57]. These types of hydrothermal treatments of lignin have been investigated by many authors in the late 80's [58, 59]. The reaction leads to gas (mainly CO_2), an organic phase, an aqueous phase and sometimes solid chars. The organic phase yield can reach 20% but may depend on the origin of the lignin [60]. During hydrothermal degradation various phenols, catechol, guaiacol and other methoxy phenols are formed by hydrolysis of ether-bonds; these products can also degrade further by hydrolysis of methoxy groups, the benzene ring being stable at these conditions. Additionally to depolymerization, it was also noticed that heavier products were also formed during the reaction leading to condensed phenol and, when high temperatures and/or long residence times are reached, to phenolic bio-char deposits [61] as illustrated in Figure 4. It is also proposed that in the early stage of the hydrothermal treatment, lignin was decomposed to water-soluble fragments and with the increase of the reaction time, the soluble products were transformed to insoluble products by re-condensation reactions [62]. The reaction parameters which determine these routes need to be optimized and the amount of lignin in the mixture should be carefully balanced. Moreover, as early reported by Oasmaa and Johansson [63], catalysts are required in water solvent to avoid coke formation and to increase liquid yield. For instance, K_2CO_3, $Ca(OH)_2$, Na(OH) have been used as catalysts in hydrothermal synthesis. The presence of alkali may modify the reaction routes, facilitate bond breakings and in some cases enhances the formation of formic or acetic acid [64]. It is also assumed that in alkaline supercritical medium, char formation is limited by avoiding condensation/polymerization reactions and lignin solubility is facilitated [65].

The use of a mixture of water with other solvents has also been proposed. Using these mixtures improves the lignin solubility and may prevent cross-linking reactions [60]. Thus, water-phenol [66-68], water-ethanol [69-71], water-acetone [72], and water-formic acid [73] mixtures were used. 50/50 (v/v) water-ethanol co-solvent was proven to be the most effective solvent mixture for degradation of the lignin in terms of yield. Recently, several types of lignins were converted in a mixture containing water, sulfuric acid and $Pt(1\%)/Al_2O_3$ catalyst under He into valuable H_2, gases and aromatic platform chemicals [74]. Instead of thermolysis or solvolysis, depolymerization of lignin in strong basic media such as NaOH has also been proposed [75].

3 CATALYTIC HYDROCONVERSION OF LIGNIN

As mentioned above, solvolysis by itself can hardly transform lignin into targeted products. Therefore, either metallic, oxide or sulfide heterogeneous catalysts may assist solvents by activating hydrogen and promoting hydrogenation/hydrogenolysis reactions. Hydrocracking, using bifunctionnal catalysts (involving hydrogenation/cracking functions) has also been considered in the literature. The combination of thermal free radical reactions and stabilization of these radicals by H-donor solvents and as well as by hydrogenating catalysts was well known and used in the beginning of the XX^{th} century for the conversion of coal and can be easily adapted to lignin [44, 76]. For this purpose, transition metal sulfide catalysts were often preferred to metallic ones, since the presence of sulfur, in non-negligible amounts in some lignins, may generate H_2S, a well-known strong poison of metal catalysts. Therefore, sulfide catalysts can be used to convert a large variety of lignins. The early works, in the 80's, related to the use of metallic or sulfide catalysts for the conversion of lignin were reviewed by Oasmaa *et al.* [77]. And more recently, a large overview on the catalytic hydrogenation

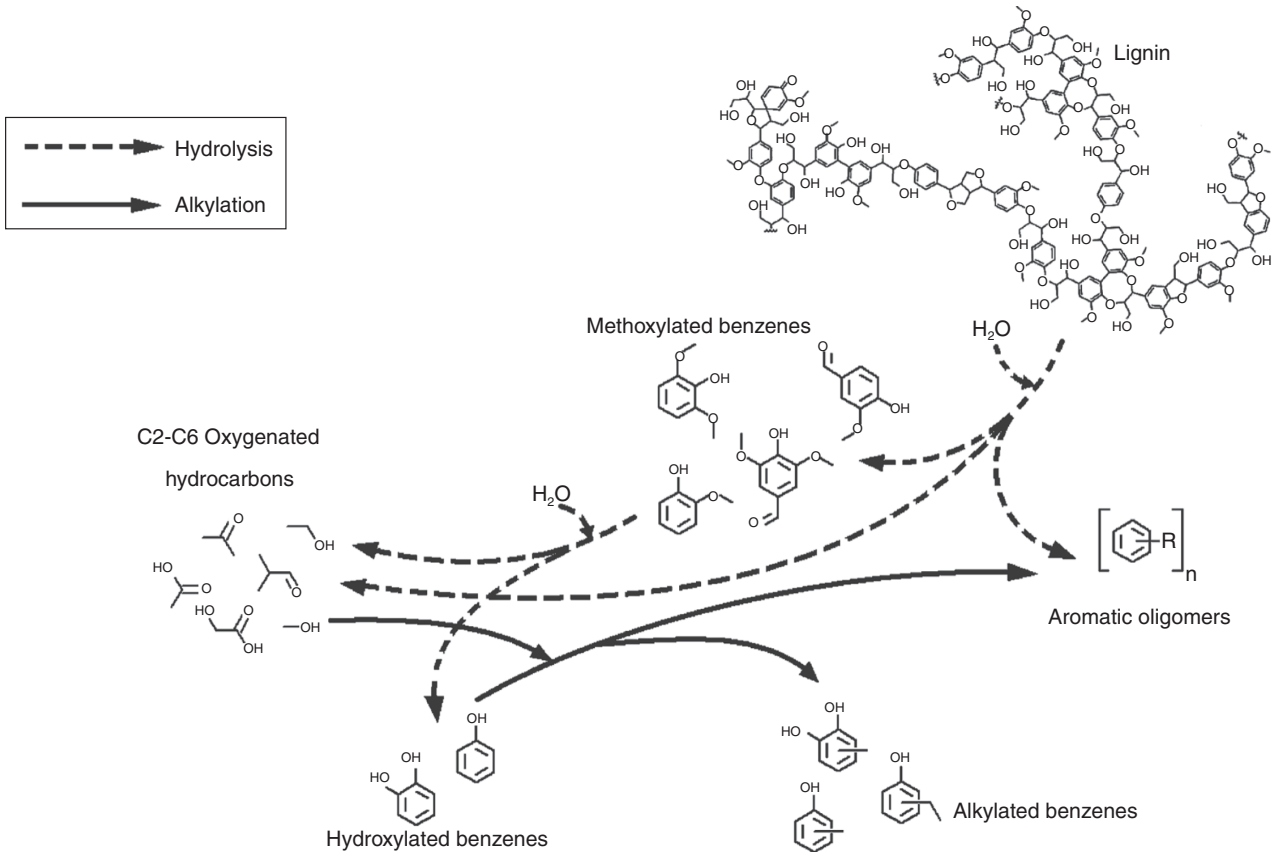

Figure 4

Hydrothermal conversion pathway of lignin from Barbier *et al.* [61].

of lignin was given [15] but mostly focused on model molecules conversion. Typical operating conditions for lignin hydroconversion are using temperatures ranging from 300°C to 500°C, and hydrogen pressure varying from 1 MPa to 15 MPa. Under these conditions high yields in liquid products can be obtained, but they depend on the origin of the lignin.

As already mentioned, noble metal-based catalysts can be used for the hydroconversion of lignin. A two steps process, under typical hydrotreating conditions, was proposed by Yan *et al.* [78] to convert a white birch wood lignin in water using Ru/C, Pd/C, Rh/C, Pt/C catalysts under H_2 pressure into alkanes (C_8-C_9, C_{14}-C_{18}) and methanol. However, H_3PO_4 additive and dioxane as co-solvent were required to get higher yields. While converting by hydrotreating a pyrolytic lignin oil with 5 wt% (based on lignin oil) Ru/C catalyst for a short residence time, it was noticed a high hydrogenation activity of the catalyst, converting phenolic compounds into cycloalkanes, cyclohexanols and alkanes [79]. Ni-W catalysts supported on silica-alumina were used in the hydroconversion of Alcell lignin in tetralin: quite a low conversion was obtained, even if the catalyst decreased the solid residue formation [80]. The complex separation protocol used in this study included several washings, filtrations, and extractions. Finally a part of the products remained in tetralin and were not characterized, while the other part was found in CH_2Cl_2 solubles. On the same way, copper-chromite and supported Ni catalysts suffered from a low catalytic activity and a larger formation of gaseous products [81].

While comparing supported NiMo oxide, Fe oxide, Raney Ni and Pd/C catalysts in a solvent-free hydropyrolysis of Organocell, Kraft and Acetosolv lignins in a batch reactor, Pd/C was found to be the more efficient catalyst to get liquid, followed by NiMo oxide supported on silica-alumina [33].

Several oxide and sulfide counterparts NiMo catalysts were evaluated and compared in the solvent-free

hydrotreatment of Kraft and Organocell lignins [74]. In accordance to earlier results [82], the sulfided counterparts seems to better perform this transformation and 49 to 71% of oil-like products were obtained. The need of a catalyst to prevent coke formation was demonstrated and the comparison with zeolite catalysts showed that NiMoS solids exhibited higher conversion [83]. More recently, γ-alumina-supported sulfided NiMoP commercial catalyst was employed in such solvent-free process and the influence of basic reaction parameters (temperature, hydrogen pressure, catalyst-to-lignin-ratio) was investigated [84]. After work-up, the liquid phase was divided into aqueous and organic phase. The best liquid yield (aqueous + organic) was approximately 35 wt%, which is quite a low value. The solid formation was lowered by a higher severity of these parameters: temperature and H_2 pressure and a high catalyst-to-lignin ratio.

However, the presence of a solvent could undoubtedly afford a beneficial effect to improve the contact between catalyst and lignin and, in the case of H-donor solvent, to provide hydrogen directly in the reacting mixture. Under hydrotreating conditions, the solvent used for the hydroconversion of lignin can be degraded or converted. For that reason, some authors proposed to use as solvent the compounds formed during the conversion (phenols, cresols) or even derived-lignin oil [83, 85]. However, these solvents can undergo undesirable transformation as described for cresol in the liquefaction of a steamed lignin over a NiMoS catalyst supported on alumina [86]. By the same way, the use of methyl-naphthalene previously considered as an inert solvent, with CoMo or NiMo catalysts, indicated that in fact, the solvent reacted during the lignin hydroconversion [87]. Again by analogy with the coal (or lignite) hydroconversion, iron sulfide catalysts were employed to convert a eucalyptus lignin into liquids with different types of solvents [88]. Recent work on the hydroconversion of a wheat straw soda lignin over sulfide NiMo-based catalyst in tetralin showed that a part of lignin residue can be still solubilized in the liquid phase and only a specific product recovery protocol can allow to separate this partially converted lignin fraction [89].

Finally, from these different works, it appeared that sulfided catalysts were often used in the liquefaction of lignin and afforded quite good liquid yields compared to metal catalysts, and could be seriously considered for industrial applications [44, 90, 91]. Patents on two stages processes have been also published for the production of bio-gasoline or additives for gasoline. Thus, Shabtai *et al*. [92] proposed either, the first stage for selective hydrocracking and a second etherification stage to produce reformulated, partially oxygenated, gasoline, or a first stage involving a depolymerization by basic catalysts and further hydroprocessing with the objective to produce alkylbenzenes on sulfide hydrotreating or hydrocracking catalysts [93].

CONCLUSION

As the second most abundant natural polymer in the world, lignin is drawing more and more attention as a potential source of chemicals or fuels instead of fossil resources. Even if, lignin has been studied for more than 100 years, it remains a challenging task to analyze and convert it. In the present paper, we attempted to review the thermochemical pathways that can be used for converting lignin into more valuable products. These pathways are either catalytic or non catalytic and cover a large range of processes from fast pyrolysis to hydrothermal or solvothermal methods or hydroconversion. They lead to complex mixtures of products, with most of the time the objective to obtain monomeric phenols or alkylbenzenes or alkylnapthenes. Depolymerization by cracking or hydrogenolysis and hydrodeoxygenation are the main reactions involved and various catalysts may accelerate these reactions and improve the liquid yield. All the proposed pathways have their own advantages and drawbacks besides any economical considerations. Within the last 10 years, new conversion methods (*i.e.*: mixture of solvants) and catalysts have been applied, improving conversion and selectivities.

Furthermore, many recent characterization methods give nowadays more insights into products distribution, reaction intermediates and mechanisms which can be supported by a recent literature based on model molecules conversion.

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