

THERMAL DEGRADATION OF LIGNIN – A REVIEW

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The review describes recent knowledge acquired in the thermal degradation of lignin as an approach to obtaining valuable chemicals or hydrocarbon fuel. Information on the temperature range, kinetics and mechanism of thermal degradation, as well as on the type of degradation products and on the methods proposed to obtain valuable chemicals is presented.

Keywords: lignin, biomass, pyrolysis, chemicals, fuels

INTRODUCTION

Lignin, a valuable resource for chemicals and energy, is a main component of wood, together with cellulose and hemicellulose. It is the second large source of organic raw material,¹ constituting about 4-35 wt% of most biomass, 16-25 wt% of hardwoods and 23-35 wt% of softwoods.² As the most abundant natural aromatic polymer,³ lignin has a highly branched three-dimensional phenolic structure including three main phenylpropane units, namely *p*-coumaril, coniferyl and sinapyl (Fig. 1). Softwood lignin contains relatively fewer sinapyl units and consists mainly of guaiacyl structures, while hardwood lignin contains guaiacyl-syringyl structures.

As a by-product of the paper industry, lignin is most often used by paper mills as a fuel for the recovery of its energy content. However, due to the very large generated quantities, lignin is increasingly considered as a potential source of chemicals, and studies on its thermal degradation receive much interest. “Pyrolytic lignin”, the organic phase obtained from the pyrolysis of wood or of other biomass resources, consists of a brown tar containing high molecular weight compounds derived from lignin, while the water-soluble fraction, accounting for 60-70 wt% of the whole oil, contains lower molecular weight substances.⁵

Temperature range and kinetics of lignin thermal decomposition

A strong interest has been manifested in the analytical characterisation of lignin, for determining its thermal behaviour.^{6,7}

Many studies were carried out on pyrolysis of lignin alone or on co-pyrolysis of lignin with other materials, such as synthetic polymers,⁸⁻¹² aiming at determining the temperature range and at developing kinetic models of decomposition.¹³⁻¹⁹ Due to its complex composition and structure, the degradation of lignin is strongly influenced²⁰ by its nature, reaction temperature, heating rate and degradation atmosphere, which also affects the temperature domain of degradation, conversion and product yields (Fig. 2).

Lignin decomposes slower, over a broader temperature range (200-500 °C) than cellulose and the hemicellulose components of biomass (Fig. 3). Degradation studies performed on different types of lignin by thermal analysis (DTA) showed²²⁻²⁵ an endothermic peak at 100-180 °C, corresponding to the elimination of humidity, followed by two broad exothermic peaks, the first one from 280 to 390 °C and the second one at higher temperatures, with a peak around 420 °C and a long tail beyond 500 °C. The DTG curves of lignin decomposition show wide and flat peaks with a gently sloping baseline²⁶ that makes it impossible to define an activation energy for the reaction.²⁷⁻²⁹ This is different for the sharper DTG peaks of cellulose and hemicellulose, inducing a flat tailing section at higher temperatures for wood decomposition. Heated up by 10 °C/min, lignin decomposes very slowly (< 0.15 wt%/°C), losing only 40 wt% of its initial mass below 700 °C. The degradation rate slightly increases³⁰ to 0.3

wt%/°C above 750 °C, the mass loss at 850 °C being of ~67 wt%. Thermal degradation of lignin is generally influenced by heat and

mass transfer processes, which significantly affect the activation energy of the process and the pre-exponential factor.

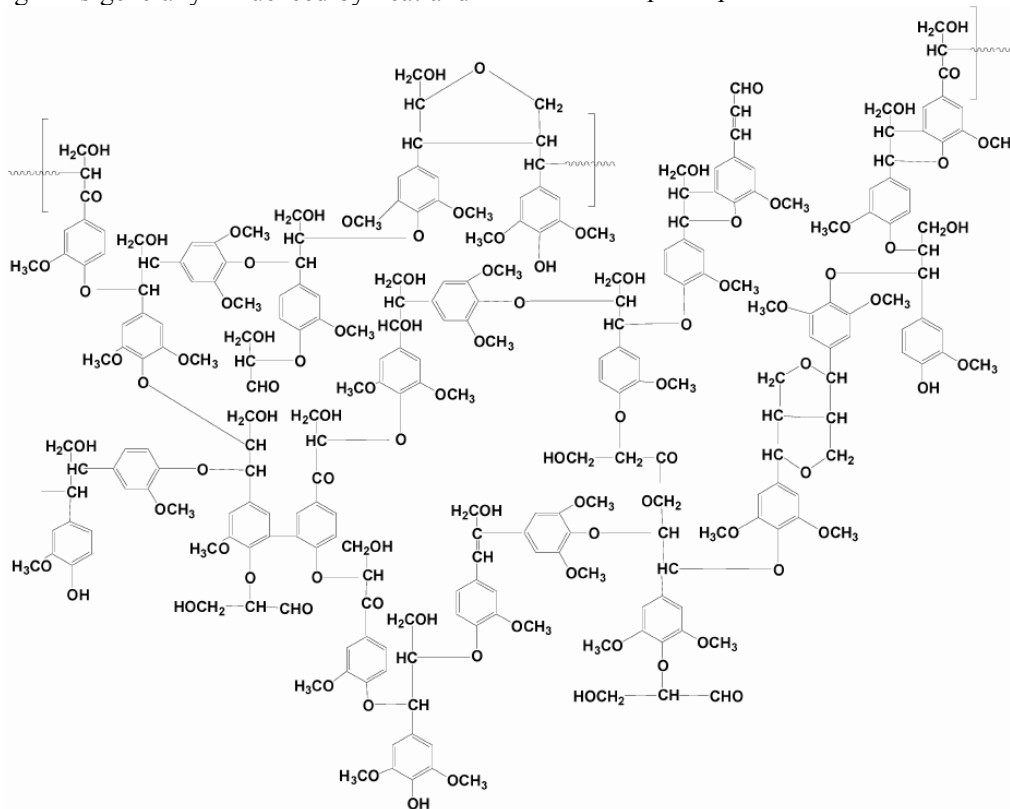


Figure 1: Partial structure of hardwood lignin⁴

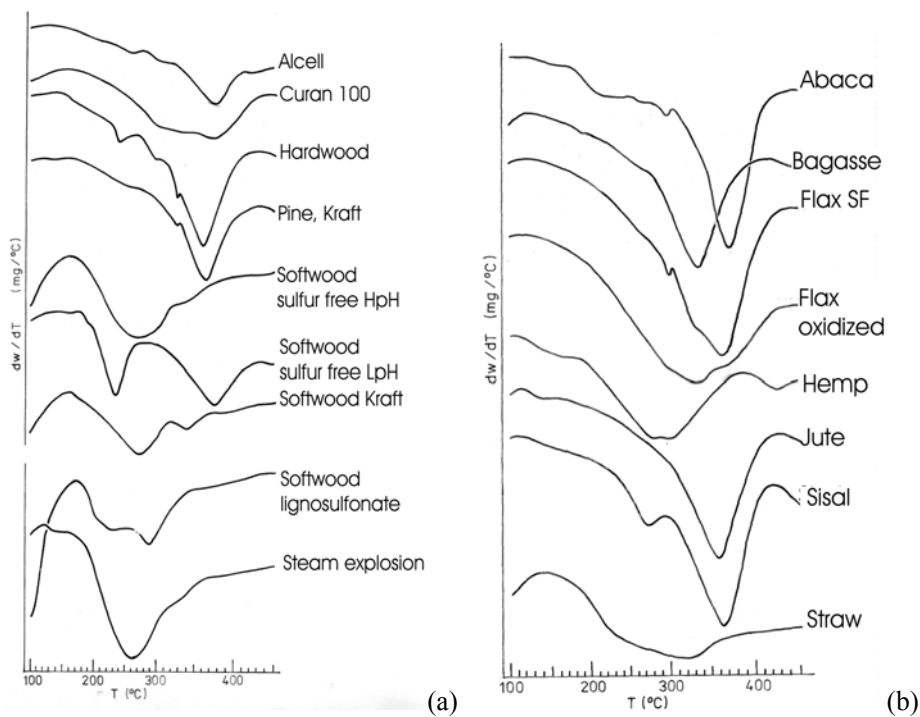


Figure 2: DTG curves of lignin from woody plants (a) and from annual fibre crops (b)²¹

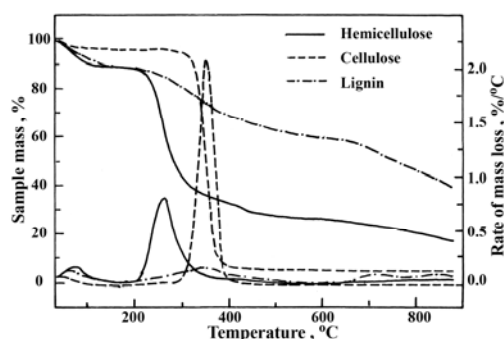


Figure 3: Pyrolysis curves of three biomass components³⁰

The kinetic studies on lignin provided in literature are based on various decomposition models.³¹⁻³⁵ Usually, lignin decomposition^{36,37} is assumed to occur by a single reaction of the first order, with the activation energy varying from 54.34 to 79.42 kJ/mol over a temperature range of 244-309 °C, and increasing to 81.2 kJ/mol, with a frequency factor of $3.39 \times 10^{-5} \text{ min}^{-1}$, over the 327-1167 °C temperature range.³⁸ Lignin decomposition in microwave over a 160-680 °C temperature range was reported³⁹ to have an activation energy of 25.08 kJ/mol and a frequency factor of $4.7 \times 10^{-2} \text{ min}^{-1}$.

A more complex kinetic model, assuming that lignin is formed by “fractions” that decompose only above characteristic temperatures, was proposed by Caballero *et al.*,^{40,41} giving a linearly increasing activation energy from 72.4 to 174 kJ/mol over the 200-600 °C temperature range. TG and DSC studies of Varhegyi *et al.* considered complex networks of parallel, successive and competitive reactions of pseudo-first order, leading to extremely low activation energies, of 34-65 kJ/mol, and a pre-exponential factor of $10^{0.3}$ - 10^3 for the decomposition of a series of milled wood lignins.⁴² Kinetic studies on the pyrolysis of Alcell and Kraft lignins over a 170-630 °C temperature range, in a fixed-bed reactor, showed lower activation energies, of 23-79 kJ/mol and of 17-89 kJ/mol, respectively, which are probably due to a significant mass and heat transfer effect.⁴³ Activation energies of 129-361 and 80-158 kJ/mol, with a frequency factor of 6.2×10^{11} - 9.3×10^{22} and 3.3×10^7 - 1.8×10^9 were reported for the decomposition of Alcell and Kraft lignin, respectively, at heating rates from 5 to 15 °C/min and final decomposition temperature of 800 °C. A high heating rate (15 °C/min) increased conversion to 57 and 65 wt%, for both Alcell and Kraft lignin. Having a higher H/C ratio than the Alcell

lignin, the Kraft lignin gave more gases, and a higher synthetic gas ($\text{H}_2 + \text{CO}$) content, of 68 mol%. Other gases were CO_2 , CH_4 , C_2H_4 and C_2H_6 .⁴⁴ The alkali lignin studied under similar conditions produced⁴⁵ in addition H_2O , CH_3OH and CH_3COCH_3 .

Mechanisms of lignin thermal decomposition

Lignin thermally decomposes over a broad temperature range, because various oxygen functional groups from its structure have different thermal stabilities, their scission occurring at different temperatures (Scheme 1). The cleavage of the functional groups gives low molecular weight products, while the complete rearrangement of the backbone at higher temperatures leads to 30-50 wt% char and to the release of volatile products. The cleavage of the aryl-ether linkages results in the formation of highly reactive and unstable free radicals that may further react through rearrangement, electron abstraction or radical-radical interactions, to form products with increased stability.⁴⁶

Self-condensation by simple coupling of intermediates leads to an initial increase in the molecular mass of the reaction products, with a gradual approach to an equilibrium distribution. Some lignin-derived fragments have molecular weights in the 5000 amu range,⁴ the presence of phenol inhibits self-condensation, thus affecting the molecular mass distribution of the products in an equilibrium state.⁴⁷ The differences in wood species mainly result in different degradation rates for lignin, as well as for the early stages of hemicellulose degradation. Coniferous lignin is thermally more stable than deciduous lignin, the latter producing smaller char yields.⁴⁸

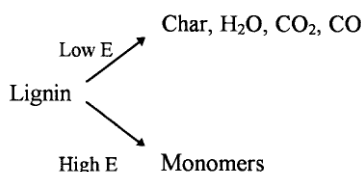
Even small amounts of inorganic salts, such as diammonium phosphate, largely used as a flame retardant for wood, change the

distribution of guaiacols from lignin decomposition and act as catalysts for the scission of the main functional groups.^{49,50} Lignin itself could be used⁵¹ as a flame-retardant for isotactic PP, both alone and in synergism with some phosphate compounds and Al(OH)₃. High and very high salt concentrations (up to 10-20 wt%, commonly used for flame-retardancy) enhance the dehydration reactions, leaving high amounts of char, whose condensed structures are not further degraded into low volatile compounds.^{52,53} Cations such as Na⁺, NH⁺

and Ca²⁺ strongly affect lignin decomposition (e.g. Na⁺ enhances the charring reaction and the formation of gaseous products).⁵⁴⁻⁵⁶

Products of lignin thermal degradation

The decomposition of the polymer structure in lignin starts at relatively low temperatures, of 200-275 °C, the main process occurring around 400 °C, with the formation of aromatic hydrocarbons, phenolics, hydroxyphenolics and guaiacyl-/syringyl-type compounds, most products having phenolic –OH groups.^{57,58}



Scheme 1: Lignin degradation by two competitive reaction pathways³⁴

Table 1
Product yields from aged lime wood pyrolysis⁵⁹

Wood age (years)	Carbohydrate degradation products (%)	Lignin degradation products (%)	Composition of lignins ^a (%)				
			S	S ^b	G	G ^c	S/G
6	77.2	22.8	60.9	37.0	39.1	63.0	0.59
150	70.5	29.5	62.7	38.2	37.3	61.8	0.62
180	66.0	34.0	60.7	36.8	39.3	63.2	0.58
180 (insects)	65.2	34.8	61.5	37.4	38.5	62.6	0.60
270	65.9	34.1	63.8	39.0	36.2	61.0	0.64

^a S: syringyl-type compounds; G: guaiacyl-type compounds

^b Corrected S value = $-59 + 0.704S\%$

^c Corrected G value = $35.4 + 0.707G\%$

The distribution and yields of products are not significantly affected by the heating conditions, being nevertheless strongly dependent on the wood category, age and condition (Table 1). Softwood lignins give mainly guaiacols, while hardwood lignins give both guaiacols and syringols. According to Wittkowski *et al.*,⁶¹ the degradation of the propanoid side chain of lignin occurs in the 230-260 °C temperature range, with formation of methyl-, ethyl- and vinyl-guaiacol and vanillin. Similar results were reported for the degradation at 240-260 °C of the propanoid side chain in ferrulic acid, a lignin model compound.⁶¹ The β–β and C–C linkages between the lignin monomeric units cleave at 275-350 °C, while the recombination of the formed radicals leads to guaiacyl and syringyl compounds.⁶² Guaiacols and syringols are intermediate degradation products, their amount decreasing with increasing pyrolysis

temperature.⁶³ This was confirmed by stepwise laboratory batch vacuum pyrolysis, showing that guaiacol derivatives are formed at lower temperatures, in methylguaiacol, ethylguaiacol, guaiacol order, while syringol derivatives, phenol and catechol are formed at higher temperatures. Catechol and its derivatives, normally not present in natural lignin, are also formed in this temperature range by secondary decomposition reactions of guaiacols, favoured at long residence times.⁶⁴

Highly-substituted phenols are selectively formed by cracking of the phenyl–propane units from the macromolecular lattice of lignin, because the syringyl–propane units are not so linked to the lignin skeleton as the less substituted ones: guaiacyl–propane and phenyl–propane.⁶⁵ The aryl–ether bonds predominate, accounting for more than half of the inter-unit linkages,⁶⁶⁻⁶⁹ and have lower thermal stability, so they may be cleaved^{70,71}

at low temperatures, even below 310 °C. The β -ether linkages have different pyrolytic cleavage mechanisms, as depending on the side-chain structure of lignin.⁷² Methyl-, dimethyl-, ethyl- and vinylphenols are formed from the corresponding guaiacol intermediates by cleavage of the O-C (alkyl) and O-C (aryl) bonds, showing increasing yields at high temperatures.^{73,74} The demethylation of the dimethoxy- groups leads to the conversion of phenols into pyrocatechols at 350-450 °C, when pyrolysis is almost completed.⁷⁵ The cleavage of the aromatic C-O bond in lignin leads to the formation of one-oxygen atom products, while cleavage of the methyl C-O bond forms two-oxygen atom products. The cleavage of the side chain C-C bond occurs between the aromatic ring and the α -C atom.⁷⁶ Low heating rates favour the formation of oxygen-containing compounds, while more hydrocarbons and alkyl-phenol derivatives are formed at fast heating rates.

Due to the prevalent dehydration of lignin, a considerable amount of water is formed, containing many water-soluble pyrolysis products that have to be removed from the waste water, to prevent environmental pollution.⁷⁷ Lignin is more difficult to dehydrate than cellulose or hemicelluloses. The dehydration of the lignin structure gives pyrolysis products with unsaturated side chains, such as styrene derivatives, eugenol and isoeugenol, vanillin and vanillic acid, acetoquaiacone and α -oxypropioquaiacone, coniferyl- (cis-trans) and dihydroconiferyl alcohol, coniferaldehyde and sinapaldehyde, *p*-hydroxycinnamic alcohols.^{78,79} Unsaturated compounds, such as dihydroconiferyl alcohol, vinylguaiacol and cis-isoeugenol are characteristic of pinewood carbonisation, but they are not formed during the pyrolysis of preservative-treated wood.⁸⁰

Acetic acid and non-condensable gases, the main of which are CO, CO₂ and CH₄, are formed during lignin pyrolysis.⁸¹ CO starts evolving from the pyrolysis of lignin around 230 °C, followed by CH₄, both gradually increasing up to about 500 °C, when H₂ starts being released from the rearrangement and condensation of the aromatic rings in the lignin structural units.⁸² The main source of CO at lower temperatures is the ether-bridge joining sub-units, that have low dissociation energy, of 250-290 kJ/mol. The dissociation of the diarylether bonds at higher

temperatures causes additional CO formation. CH₄ is produced from a weakly bonded methoxy group -OCH₃- (bond energy of 250 kJ/mol).⁸³ Secondary reactions beyond 600 °C involve the gradual decomposition of lignin intermediates, char and condensable gases, with the evolution of CO and C₁ - C₃ hydrocarbons, as shown by Py-GC/MS studies (performed at 600-1500 °C) by Boateng *et al.*⁸⁴ The studies of Avni *et al.*⁸⁵ on the pyrolysis of lignin between 150 and 900 °C, coupled with FT-IR analysis, show that the decomposition of the substituted groups and aliphatic structures in lignin leads to CO₂ release from the carboxyl groups, H₂O from the hydroxyl groups, CO from the weakly bound oxygen groups, such as aldehyde groups, and H₂ from the aliphatic and methoxy groups. Tertiary reactions at higher temperatures involve breakage and rearrangement of stronger bonds in aromatic rings, with the evolution of additional H₂ and CO from the tightly bound oxygen functional groups, such as ethers, phenols and other C-C links.

The homolysis of the highly cross-linked structure in lignin and the cleavage of the relatively weak bonds, such as the alkyl-alkyl ether ones, are accompanied by a competition between devolatilisation and charring reactions.^{86,87} Very short residence times result in incomplete depolymerisation of lignin, due to random bond cleavage and inter-reaction of the lignin macromolecule, resulting in a less homogenous liquid product. On the other hand, longer residence times can cause secondary cracking of the primary products, reducing yield and adversely affecting the bio-oil properties. The volatilisation of the branched structures in lignin requires cleavage of the multiple inter-unit linkages, about 40% of which are relatively stable at temperatures below 300 °C. If the inter-unit cleavage rate is low or if the rate of volatilisation of the lignin fragments formed through aryl-ether cleavage is not sufficiently high, as it may occur in low-temperature pyrolysis, crosslinking predominates, resulting in char formation. In the absence of molecular oxygen and at low rates of heat transfer, carbonisation, or condensation, is the main process in the pyrolysis of lignin at low temperatures. While volatilisation is favoured by increased temperatures, the pyrolysis of lignin always gives high amounts of tar and char.⁸⁸ These materials

remain in the reactor and will not be easily decomposed; in catalytic procedures, they stick on the catalyst and prevent the catalytic reaction.⁸⁹

The moisture content of wood favours char formation at 390-460 °C and affects the physical properties and quality of the pyrolysis liquid.⁹⁰ Water has less effect⁹¹ on the hydrogenolysis of both hardwood and softwood lignin between 200 and 400 °C. A higher lignin content in the biomass increases the amount of bio-char.⁹² Lignin chars have low reactivity, compared to those from other biomass constituents, owing to their highly crosslinked nature. The interactions between cellulose and lignin during the pyrolysis of rice straw, rice husk and corncob – studied by TG-MS – contributed to a decrease in tar yields and to an increase in char yields.⁹³ Lignin inhibited the thermal polymerisation of levoglucosan and enhanced the formation of low molecular weight products from cellulose with a reduced yield of the char fraction. Cellulose reduced the secondary char formation from lignin and enhanced the formation of some lignin-derived products including guaiacol, 4-methyl-guaiacol and 4-vinyl-guaiacol.⁹⁴

Pyrolysis strongly affects the propyl chains of the lignin units, as already evidenced, but no demethylation or demethoxylation occurs up to 450 °C, so that the groups attached to the aromatic rings are not altered and the resulted phenols maintain the substitution pattern of native lignin's aromatic ring.⁹⁵ Analytical pyrolysis techniques,⁹⁶ such as pyrolysis coupled with gas chromatography and flame ionisation or mass spectrometry detection Py-GC/FID(MS), could be easily used as a diagnostic tool, to obtain molecular information on lignin,⁹⁷⁻¹⁰⁴ or to determine the lignin composition in wood and pulp.¹⁰⁵⁻¹¹² In contrast, the degradation of cellulose gives carbohydrate-derived compounds more difficult to identify.¹¹³ The combination of pyrolysis with *in situ* methylation could avoid loss of structural information, which might occur in conventional chromatographic techniques applied to lignin decomposition, due to extensive fragmentation and poor chromatographic behaviour of the fragments containing polar functional groups.¹¹⁴⁻¹¹⁷ Multidimensional GC/MS analysis provides more information on the distribution of pyrolytic products, as due to increased chromatographic

separation.¹¹⁸ Ni-Fe and Pt Pyrofoils provide similar structural information on the analytical pyrolysis of lignin, while Au-coated Ni-Fe Pyrofoil could offer additional information, due to pronounced hydrogen-transfer reactions.¹¹⁹ Laser energy could be also used as a pyrolysis source for molecular investigations of the lignin structure.¹²⁰

Lignin as source of chemicals obtained by thermal treatments

Lignin has been proposed as an alternative source of chemicals or hydrocarbon fuels,¹²¹⁻¹²⁵ for saving the fossil resources of coal and petroleum. The complex composition of oils provides the potential for obtaining chemicals, however the challenge lies in economically separating the products for the chemicals market and the liquid fuels. Usually, the volatile yield varies between 61 and 74 wt%, as depending on the nature of lignin. As commonly known, lignin with low methoxy groups from softwood species (guaiacyl lignins) produces a higher char yield than the high methoxy groups.¹²⁶

Old studies of Freudenberg *et al.*¹²⁷ reported that vanillin was produced from lignin by the alkali-nitrobenzene method. Twenty years after, Kashima¹²⁸ converted Kraft lignin in a hydrogen atmosphere of 19.6 MPa at 400-440 °C on an iron oxide catalyst, and obtained 20.2 wt% phenol and 14.4 wt% benzene, from a total amount of 33.6 wt% light oil and 23.3 wt% heavy oil. Kraft lignins were pyrolysed in a "captive sample" reactor over wide temperature ranges (400-600 °C) and reaction times, giving¹²⁹ a maximum yield of phenolic compounds of about 3.22 wt%. Reports on the pyrolysis of Kraft and organosolv lignins in a microwave field showed that the lower fractions of lignin, of only 0.5 wt%, were converted to phenolic compounds.¹³⁰ The formation of monomeric phenols was favoured by the inclusion of molecular oxygen in the fluidising gas, on a bench scale fluidized bed reactor operated at 290 °C. The involvement of molecular oxygen was not associated with a combustion-type process, but it promoted depolymerisation through a free radical mechanism, thus facilitating the formation of free radicals, and/or behaving as a free radical.¹³¹ The presence of water facilitated the oxygen-promoted decomposition of lignin.¹³²

Studies of Meier *et al.*¹³³ have shown that oils with relatively low oxygen contents (about 10 wt%) could be produced from lignin by both batchwise and continuous hydrolysis, at high concentrations of commercial Ni/Mo hydrotreating catalysts. Vacuum pyrolysis (below 2 kPa at 465 °C) of lignin derived from steam-exploded wood yielded 42.7 wt% oil.¹³⁴ Vanillin and syringaldehyde were reported in a total yield of 14.6 wt% from the alkaline oxidation of steam-explosion hardwood lignin.¹³⁵

In lignin hydrocracking, the macromolecular structure typically depolymerizes to a wide variety of products, which can generally be classified into solids, liquids and gases. Product yields and distribution depend on the severity of the reaction conditions and type of catalyst. Under hydrocracking conditions, the β -O-4 aryl ether and unstable C-C bonds from the lignin structure are cleaved, subsequent hydrodealkylation leading to the rupture of the alkyl side chain groups linked to the aromatic rings. Also, it is customary to utilise solvents in amounts ranging from 1 to 3 or more times that of the lignin. When the amounts are equal, excellent hydrocracking solvents, such as phenols, are commonly used. However, these solvents typically react with lignin, especially under hydrocracking conditions, making subsequent analysis of products rather complicated. The advantages of tetralin as a hydrogen-donor solvent include its high boiling point, as well as its ready release of the hydrogen atoms under hydrocracking conditions, leading to the formation of naphthalene, a relatively stable compound. However, the use of lignin as a raw material for chemicals continues to be restricted by the nature of the current commercial delignification processes, which render the lignins thus isolated not reactive for further processing into useful products.¹³⁶

Supercritical water (T_c : 374.15 °C, P_c : 22.1 MPa) has received much attention as an interesting reaction solvent for decomposition of lignin¹³⁷⁻¹³⁹ and of its model compounds, such as guaiacol and 2-isopropylphenol.^{140,141} Most ether bonds present in the lignin structure occur between the propyl side chain and the hydroxyl group on the aromatic ring of the adjacent hydroxyphenylpropane units.¹⁴² Hydrolysis followed by dealkylation is one of the main factors promoting the decomposition of lignin in supercritical water. This leads to the

formation of compounds, such as syringols, guaiacols and catechols, and of low molecular weight fragments with reactive functional groups. Increase of water density usually enhances the hydrolysis reaction. However, the formation of solid products, such as tar or char, also occurs, due to the crosslinking reactions among the reactive degradation fragments and residual lignin, giving higher molecular-weight fragments.^{143,144} Phenol acts as a capping agent for the reactive species from the degradation of lignin and of its model compounds in supercritical water, preventing char formation.¹⁴⁵⁻¹⁴⁷ Therefore, the use of phenol and of water-phenol mixtures is an effective liquefaction technique for lignin, the process proceeding towards lower molecular weights.

Similar to the extraction of coal in supercritical water,¹⁴⁸ Saisu *et al.*¹⁴⁹ proposed possible processes to recover chemicals from lignin, by considering: (1) conversion of lignin in phenol- supercritical water mixtures to obtain low molecular weight phenolic products; (2) reforming of the phenolic compounds by partial oxidation or gasification in supercritical water, to recover the monomeric alkylphenols and phenol; (3) recycling, to feed a portion from the monomeric alkylphenols and phenol.

Near- and supercritical water was also used for lignin gasification,^{150,151} involving fragmentation of the lignin structure into low molecular weight compounds to be further gasified over solid¹⁵²⁻¹⁵⁷ or metal catalysts, such as zirconia¹⁵⁸ or titania- and carbon-supported ruthenium catalysts.¹⁵⁹⁻¹⁶¹ Crosslinking reactions occur between the alkylphenols and the formaldehyde resulted from lignin hydrolysis,¹⁶²⁻¹⁶⁴ producing insoluble solid residues.^{165,166} Carbon dioxide and hydrogen are produced during the early stages of lignin gasification. Methane is formed both by methanation reactions and by dealkylation of the alkyl groups on the alkylphenol structures in lignin. The water molecules participate at gasification as reactants, but their consumption is small, not affecting the water density in the reactor. A low density of the water solution would decrease the contact efficiency between lignin and the catalyst particles, favouring the condensation of lignin degradation fragments to the detriment of their gasification.¹⁶⁷ Sulfur has a poisoning effect on the titania-supported ruthenium catalyst,

affecting the active sites for C–C bond breaking and the methanation reaction, but having no hindering effect on the sites for the gasification of formaldehyde and the water-gas shift reaction.¹⁶⁸

Lignin could be also used to prepare sorbents,¹⁶⁹ activated carbons^{170,171} or carbon fibres¹⁷² with very high surface areas and pore volumes. Pure lignin has a lower adsorption capacity, compared to lignin-based activated carbons, being primarily responsible for the microporosity of the activated carbons obtained from lignocellulosic precursors.¹⁷³ When prepared at lower temperatures, lignin carbon is more stable than the cellulose one, due to its higher content of aromatic structures.¹⁷⁴

CONCLUSIONS

Lignin, as the most abundant aromatic natural polymer and the second richest source of organic raw material, is considered as a potential source of chemicals and energy. The thermal degradation of lignin is a complex process because the materials have many components with different decomposition pathways, including competitive and/or consecutive reactions. Lignin thermally decomposes over a broad temperature range, because various oxygen functional groups from its structure have different thermal stability, their scission occurring at different temperatures. Due to its complex composition and structure, the thermal degradation of lignin is strongly influenced by its nature and moisture content, reaction temperature and degradation atmosphere, heat and mass transfer processes, with considerable effect on conversion and product yields, as well as on the physical properties and quality of the pyrolysis products.

The complex composition of the pyrolysis products provides the potential for obtaining chemicals and/or fuels from lignin, however the challenge lies in economically separating valuable compounds for the market. Therefore, the pyrolysis products need to be well-characterized before selecting the optimum methods for upgrading or for extracting the valuable compounds.

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