

Chapter 2

Degradation of Lignin by Pyrolysis

Abstract Fast pyrolysis is an efficient technique for thermal degradation of lignin to bio-oils containing bio-phenols for the synthesis of adhesives, resins, and polymers. Lignin has a complex structure, and hence a large number of pyrolytic components are generated during the pyrolysis process. The composition of the pyrolytic products depends on the type of lignin, temperature, types of catalyst, and the design of the pyrolysis reactor. It was suggested that the pyrolysis of lignin consists of two steps. In the first step, by thermal cracking of the lignin macro-molecule, vapor of monomeric phenolic compounds is formed during the vapor condensation process, followed by re-oligomerization of the monomeric compounds, forming pyrolysis oils comprising remarkable amounts of dimeric and other oligomeric products. However, the precise mechanism of the pyrolysis of lignin is not clear due to the complexity of the process.

Keywords Fast pyrolysis of lignin • Degradation of lignin • Bio-oils • Bio-phenols • Adhesives • Resins • Polymers

2.1 Pyrolysis Technology

Pyrolysis is a thermochemical process operated in the absence of oxygen, which can be divided into three categories according to the process conditions (heating rate): slow pyrolysis, intermediate pyrolysis, and fast pyrolysis [1, 2]. The conditions of each process are shown in Table 2.1. Slow pyrolysis is conducted at a low temperature for a longer vapor residence time, leading to producing more charcoal and noncondensable gases. Intermediate pyrolysis operates at moderate temperatures and residence time. In contrast, fast pyrolysis is conducted at a high temperature and a short residence time, to produce more liquid fuels that can be used as fuels and chemicals [1, 3].

Table 2.1 Typical modes of pyrolysis, modified from Refs. [1, 2]

Types of pyrolysis	Residence time	Temperature (°C)	Yield (%)		
			Liquid	Char	Gas
Slow	Hours/Days	400	30	35	35
Intermediate	10–30 s	500	50	25	25
Fast	~ 1 s	500	75	12	13

2.2 Fast Pyrolysis of Lignin

Fast pyrolysis of biomass is a promising technology for generation of liquid bio-fuels from lignocellulosic biomass. In general, the pyrolysis of biomass consists of two steps: production of free radical fragments by thermal cracking of the biomass components (cellulose, hemicellulose, and lignin) via the cleavage of covalent bonds, and combination of free radical compounds to form pyrolysis products [4]. The liquid (pyrolysis oil) yield depends on various parameters including biomass types, temperature, residence time, char separation, and ash content of biomass [1]. Among three main components of a lignocellulosic biomass, lignin has a significant effect on the pyrolysis behavior of biomass [5]. As described in Chap. 1, lignin is a natural aromatic polymers comprised of p-hydroxyphenyl, guaiacyl, and syringyl, which are linked by C–O–C ether bonds (β -O-4, α -O-4, 4-O-5) and C–C bonds (β -1, β -5, 5-5) (Fig. 1.3) [5, 6]. The β -O-4 ether bond is the most dominant bonds which made around 46–60% of the total linkages depending on the source of wood [7, 8] and approximate 6–8% of the total linkages occupies by α -O-4 linkages [8]. Due to the complex structure of lignin, the exact mechanism of its pyrolysis remains unknown. In pyrolysis of lignin, it is generally believed that first the cleavage of ether bonds occurs to depolymerize lignin. Subsequently, the side chains cleave from the monolignols via the hemolytic cleavages of O–CH₃ and radical-induced rearrangements [6]. Figure 2.1 shows the evolution of the compounds obtained from thermal pyrolysis of lignin [9].

Pyrolysis of lignin yields up to 40 wt% bio-oil (Tar, such as aromatic and phenolic compounds), 50 wt% biochar, and 10 wt% gaseous species (such as CO, CO₂, CH₄, and H₂) [10–12]. The biochar could be used in various applications such as fuel, soil improver, solid bitumen additive, and as a precursor for activated carbon [11, 13]. The bio-oil has a great potential to be used as a renewable resource of chemicals (such as phenol and polyol) in synthesis of adhesives, resins, and polymers [11, 14–16].

2.2.1 Lignin Pyrolysis Mechanism

A wide variety studies has been conducted on the pyrolysis of lignin to elucidate the pyrolysis mechanism by using advanced analytical techniques such as

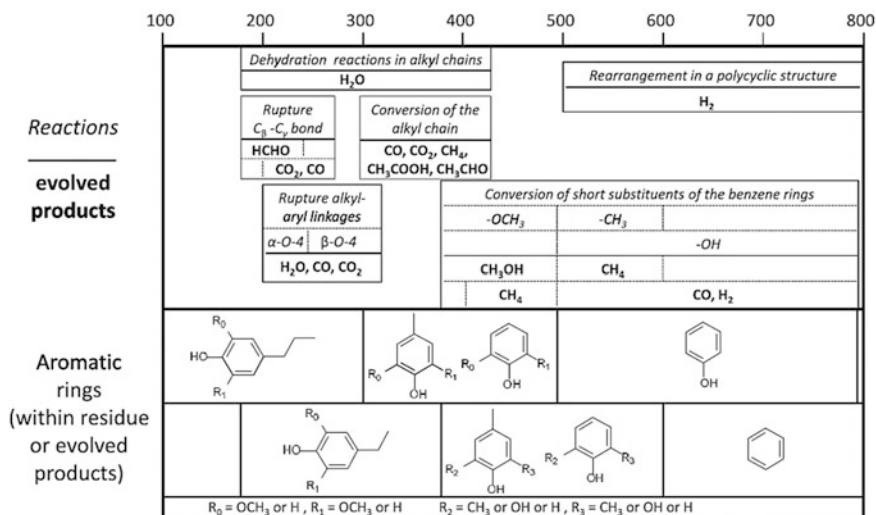


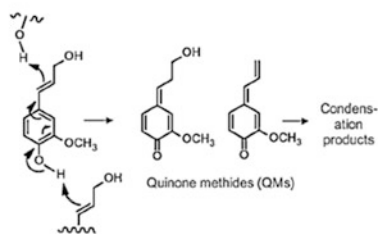
Fig. 2.1 Evolution of the compounds obtained from thermal pyrolysis of lignin, reprinted with permission from Ref. [9]. Copyright (2014) Elsevier

thermogravimetric analysis-Fourier transform infrared spectroscopy (TGA-FTIR) and Pyrolysis-Gas Chromatography/Mass Spectroscopy (Py-GC/MS) [17–21]. Guo et al. [4] modeled kraft lignin pyrolysis by using Boltzmann-Mont Carlo pyrolysis model and validated by the experimental results at temperatures of 400–600 °C. Patwardhan et al. [22] suggested that the pyrolysis of lignin consists of two steps. In the first step, by thermal cracking of the lignin macromolecule vapor of monomeric phenolic compounds are formed such as phenol, 4-vinyl phenol, 2-methoxy-4-vinyl phenol, and 2,6-dimethoxy-phenol, followed by re-oligomerization of the monomeric compounds to produce remarkable amounts of dimeric and other oligomeric products during the vapor condensation process. However, elucidation of detailed mechanism of lignin pyrolysis is very difficult due to the complexity of the lignin structure. Lignin model compounds were commonly used for better understanding the pyrolysis process due to their simple structures and formation similar pyrolysis products [8, 23–28]. Kotake et al. [23] conducted in-depth study on the formation of monomers and oligomers during the pyrolysis of a softwood lignin and coniferyl alcohol (CA) as a model compound in the presence of an aprotic solvent (diphenoxybenzene, DPB) or H-donor (1,2,3,10b-tetrahydrofluoranthene). DPB prevented the polymerization of CA via the inhibition of the proton-transfer, and H-donor promoted the production of the side-chain reduction products as a source of the hydrogen radical. Figure 2.2 presents the proposed mechanism of pyrolysis of CA. It was found that DPB and H-donor played important roles in the formation of monomers (such as dihydroconferyl alcohol and isoeugenol) and oligomers from lignin. At low operation temperature (250 °C), coniferyl aldehyde was the dominant product due to the H-donor/radical balance.

A: Role of DPB

B: Role of H-donor

Neat condition



In DPB

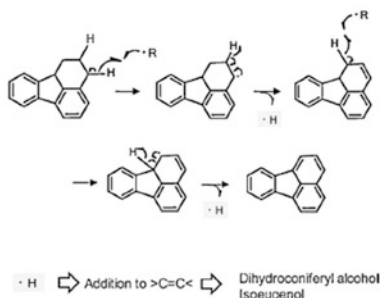
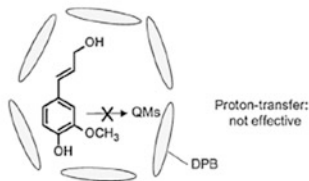


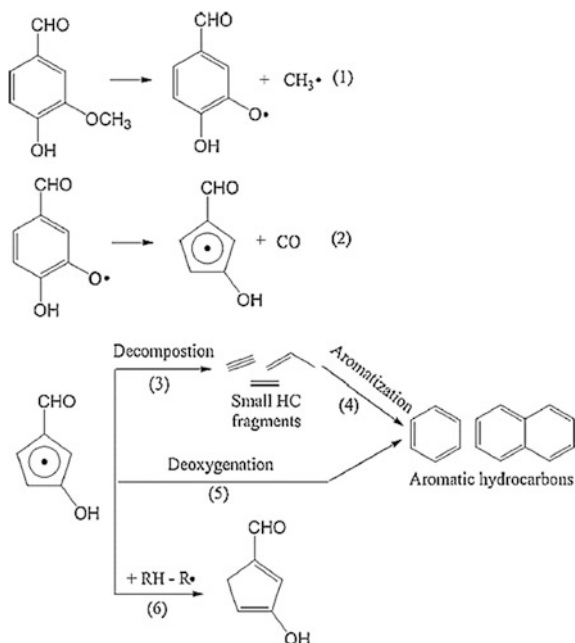
Fig. 2.2 Proposed mechanism of pyrolysis of coniferyl alcohol in the presence of an aprotic solvent (diphenyl ether, DPB) or H-donor (1,2,3,10b-tetrahydrofluoranthene), reprinted with permission from Ref. [23]. Copyright (2014) Elsevier

The following pathway was also proposed by Shin et al. [7, 29] for the pyrolysis of vanillin as a lignin model component to form aromatic hydrocarbons using mass spectroscopy and multivariate analysis (Fig. 2.3).

A β -O-4 type lignin model dimer (1-(4-methoxyphenyl)-2-(2-methoxyphenoxy) ethanol) was also pyrolyzed by Py-GC/MS to explore the mechanism of product formation with respect to temperature [30]. The pyrolysis of lignin model dimer involves three possible pathways: homolysis of the C_{β} -O bond, homolysis of the C_{α} - C_{β} bond, and C_{β} -O concerted decomposition, as illustrated in Fig. 2.4. At a low temperature (300 °C), the pyrolysis process is initiated by homolysis of C_{β} -O due to low dissociation energy (221.4 kJ/mol), producing 4-methoxystyrene and guaiacol. Homolysis of C_{β} -O and C_{β} -O concerted decomposition mainly control the degradation process at a moderate pyrolysis temperature (500 °C), producing 4-methoxystyrene, guaiacol, and carbonyl-containing substances. At a high temperature (800 °C), a wide variety of small molecular compounds are generated from the secondary thermal cracking of the products derived from C_{β} -O homolysis and C_{β} -O concerted decomposition.

A theoretical study was conducted on the mechanism of pyrolysis of lignin dimer model component with α -O-4 linkage by employing density functional theory (DFT) method at B3LYP/6-31G(d, p) level [8]. Figure 2.5 shows the hemolytic cleavages of the α -O-4 linkage lignin dimer and their corresponding bond dissociation energies. According to the calculated bond dissociation energies, there are three possible pathways for pyrolysis of the α -O-4 linkage lignin dimer: (i) the hemolytic cleavage of C_{α} -O bond, (ii) the hemolytic cleavage of O-CH₃, and (iii) the hemolytic

Fig. 2.3 Pyrolysis of vanillin as a lignin model component to form aromatic hydrocarbons, reprinted with permission from Ref. [7]. Copyright (2016) Elsevier



cleavage of $\text{C}_\alpha\text{--C}_\beta$. The major reaction is the breakdown of $\text{C}_\alpha\text{--O}$ bond and the main products are phenolic compounds including guaiacol, p-hydroxyphenyl-ethanol, p-hydroxyphenyl-acetaldehyde, and 2-hydroxybenzaldehyde. Similarly, the mechanism of formation of CO , CO_2 , and CH_4 during the pyrolysis of lignin was theoretically studied in detail by Huang et al. [31] using the DFT method, and it was proposed that CO , CO_2 , and CH_4 could be formed through decarbonylation of phenol (p-hydroxyphenyl, guaiacyl, and syringyl) acetaldehyde, decarboxylation of phenyl (p-hydroxyphenyl, guaiacyl and syringyl) formic acid, and concerted reactions, respectively.

2.2.2 Effects of Types of Lignin

Different types of lignin have different structure, depending on the bioresources of lignin and the methods of isolation [9, 18, 32–39]. Thus, it is needed to investigate on pyrolysis behavior of various types of lignin. For example, Custodis et al. [33] studied the influence of lignin isolation processes on product yields from both catalytic [a commercial Zeolite (H-USY)] and non-catalytic pyrolysis processes. Various types of lignin were extracted from the same soft- and hardwoods by Organosolv-, Klason-, and Dioxane-methods, and they were pyrolyzed at different temperatures. The study revealed that the product yields noticeably depended on the lignin separation methods not on the source of lignin. The highest yield of pyrolysis

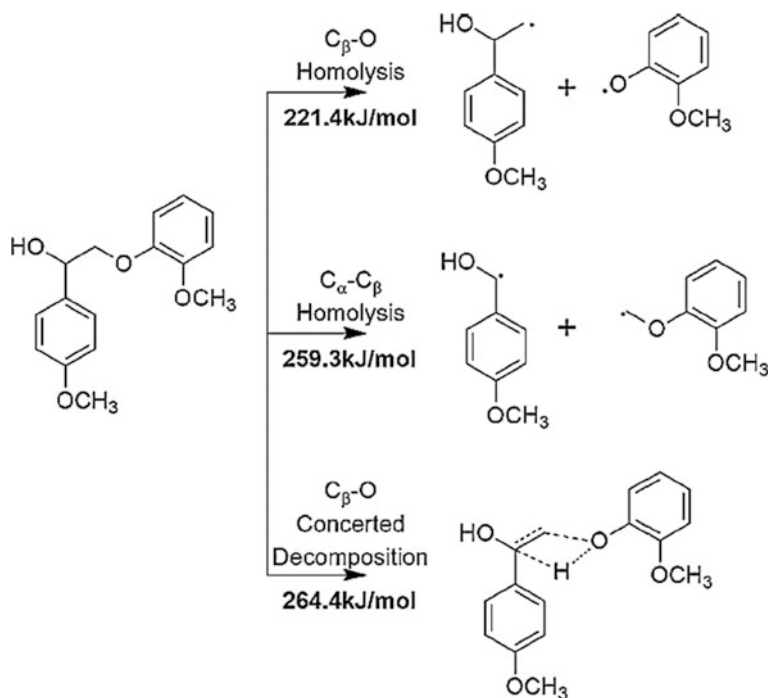


Fig. 2.4 Mechanism of pyrolysis of lignin dimer, reprinted with permission from Ref. [30]. Copyright (2015) Elsevier

oil (66 wt%) was produced from Dixance hardwood lignin at 650 °C. Increasing the temperature enhanced the yield of lignin monomers in the bio-oil, and operation at above 550 °C led to significantly higher gas formation. As discussed in the previous section, at a low temperature the pyrolysis of lignin started with depolymerization via radical formation by homolytic fission or hydrogen abstraction, followed by other reactions such as retro-ene, dehydration-, decarboxylation-, and condensation reactions. A high pyrolysis temperature enhanced the Maccoll reaction of the 2-phenethyl phenyl ether types of compounds, hence the main products changed from phenol alkoxy ketone (rich in the low-temperature pyrolysis oil of lignin) products to phenols. It was also reported that pyrolysis of hardwood lignin produced more liquid products in comparison with softwood lignin, owing to more β-O-4 bonds on the hardwood lignin that are weaker than the C-C bonds in softwood lignin. Figure 2.6 depicts the main pyrolysis products from lignins at different temperatures.

Bahrle et al. [12] observed in situ radical formation from pyrolysis of a softwood and hardwood lignin, respectively by in situ high-temperature electron paramagnetic resonance spectroscopy. For both lignins, the highest radical concentration occurred between 350 and 400 °C, and again more radicals and volatile products were detected with the hardwood lignin than with the softwood lignin.

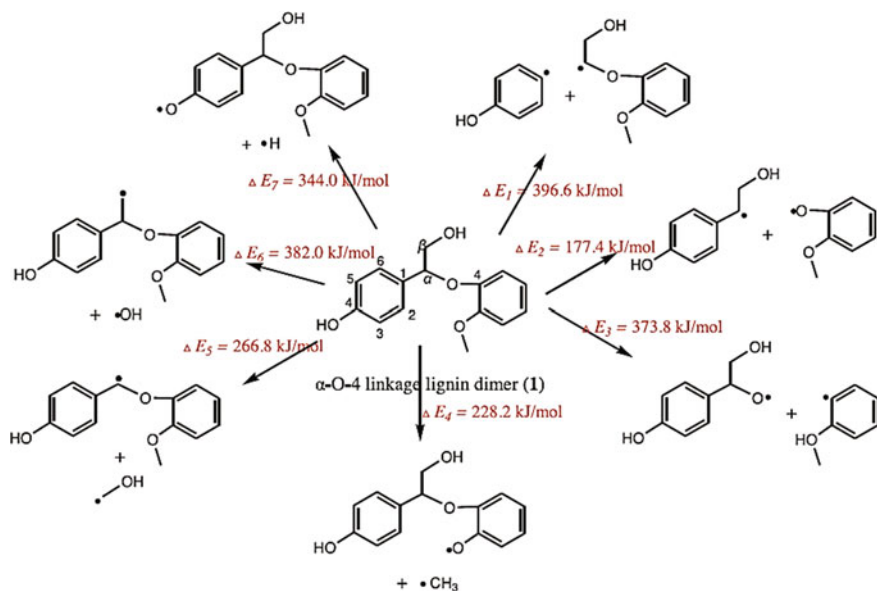


Fig. 2.5 Hemolytic cleavages of the α -O-4 linkage lignin dimer and their corresponding bond dissociation energies, reprinted with permission from Ref. [8]. Copyright (2015) Elsevier

In another study, pyrolysis behaviors of four types of lignin, alkali lignin (AL), klason lignin (KL), organosolv lignin (OL), and milled wood lignin (MWL), isolated from the same pine wood, were studied by TG-FTIR and Py-GC/MS as well as ^{13}C NMR spectroscopy [5]. The ^{13}C NMR results showed that the chemical structure of these isolated lignins is different and the distribution of functional groups is presented in Table 2.2. Ether bonds such as β -O-4 have lower thermal stability and decompose easily at low temperatures. Thus, lignins consisting of more ether bonds would show weaker thermal stability or exhibit a lower temperature at maximum weight loss rate upon heating. This was evidenced by the experimental observation: AL and MWL, due to the presence of more β -O-4 bonds in their structures, have a lower temperature at maximum weight loss rate (346 and 359 $^{\circ}\text{C}$, respectively) than that of OL (396 $^{\circ}\text{C}$) or KL (405 $^{\circ}\text{C}$). Thus, pyrolysis of AL and MWL yielded more phenol compounds at lower temperatures. The dominant products in pyrolysis of these softwood lignins are guaiacyl-type compounds due to lack of syringyl-type unit in the structure of softwood and the maximum of phenol yield was obtained at 600 $^{\circ}\text{C}$.

Pyrolysis behaviors of various lignins extracted from eight different agricultural wastes (e.g., walnut shell, wheat straw, cotton stalk, rice husk, bamboo, rape straw, corncob, and peanut shell) were studied by TG-FTIR and Py-GC/MS [34]. The composition of gaseous products depended on the biomass species. The formation of catechol type fragments (catechol, 3-methylcatechol, 4-methylcatechol, and ethylcatechol) was significant in two types of lignin from peanut shell and cotton

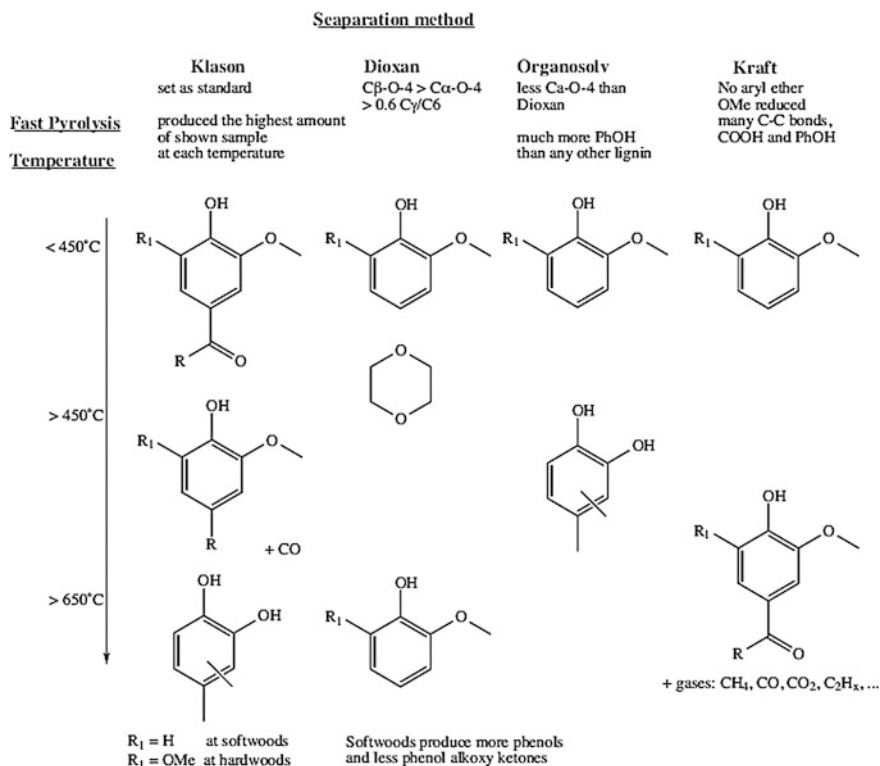


Fig. 2.6 Main pyrolysis products from lignin at different temperatures, reprinted with permission from Ref. [33]. Copyright (2015) Elsevier

stalk and the presence of hemicellulose in these crude lignin samples led to production of styrene and 4-hydroxy-3-methoxystyrene in the pyrolysis oil products. Bai et al. [38] investigated the formation of phenolic oligomers during fast pyrolysis of lignin in a micropyrolyzer. It was reported that more than 500 phenolic compounds with molecular weight less than 504 Da were generated and the most predominant products were monomers followed by dimers, trimers, and tetramers. De Wild et al. [11] pyrolyzed two wheat straw-derived organosolv lignins, Granit lignin (from a mixture of wheat straw and Sarkanda grass) and an Alcell organosolv lignin from hardwood in a bubbling fluidized bed reactor. It was observed that around 80 wt% of the dry lignin was converted into bio-oils and bio-chars. 25–40 wt% of the bio-oil produced was made of phenolic fragments (7–11 wt% monomeric compounds and 14–24 wt% oligomeric compounds). The straw-based lignins including the Granit lignin produced more guaiacol, alkylphenols and catechols and less syringols compared with Alcell lignin from hardwood.

On the other hand, it was also observed that the final residue weights depended on the methoxyl content in the lignin structure: lignins with a higher methoxyl content have lower condensed structural units, resulting in lower thermal stability

Table 2.2 Distribution of functional groups of four kinds of lignin, i.e., alkali lignin (AL), klason lignin (KL), organosolv lignin (OL), and milled wood lignin (MWL), isolated from the same pine wood, reprinted with permission from Ref. [5]

Chemical shift (ppm)	Assignment	Functional group distributions (mol/100 g)			
		AL ^a	KL ^b	OL ^a	MWL ^a
195–190	Carbonyl C=O	0.003	–	0.026	0.017
172	Ester COO-R	0.011	–	0.000	0.003
168	Carboxyl C=O	0.079	–	0.105	0.077
160–140	Aromatic C–O	0.844	1.178	0.753	0.770
140–123	Aromatic C–C	1.086	1.023	1.277	1.055
123–102	Aromatic C–H	0.784	0.899	1.245	1.027
89–57	Aliphatic C–O	0.841	0.960	0.573	0.858
89–78	C _β in β-O-4, C _α in β-5, β-β	0.281	–	0.153	0.271
73–71	C _α in β-O-4	0.112	–	0.046	0.106
64–61	C _γ –OR	0.205	–	0.190	0.273
57–54	–OCH ₃	0.597	0.407	0.622	0.742
31–29	C _α and C _β in –CH ₂ –	0.069	–	0.075	0.043
15	C _γ in –CH ₃	0.011	–	0.088	0.023

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^aData obtained by solution-state ¹³C NMR spectrum

^bData obtained by solid-state ¹³C CP/MAS NMR spectrum

and less char production [5]. Wang et al. [35] investigated pyrolysis behavior and product selectivity for two milled wood lignins from different tree species: Manchurian ash (MA—hardwood) and Mongolian Scots pine (MSP—softwood), respectively. Compared with the softwood lignin, the hardwood lignin (MA lignin) showed less thermal stability and a lower yield of charcoal residue (26 wt%) upon pyrolysis due to the fact that the hardwood lignin has a higher content of syringyl monomer (i.e., a higher methoxyl content).

Alkali lignin contains sodium salts that could be in two forms: organic bond Na salts [phenolic sodium (–CH₂ONa), and carboxylic sodium (–COONa)] or the dissolved salts (NaOH, and Na₂CO₃) [19, 40]. The effect of these dissolved salts on the pyrolysis process of alkali lignin was studied using TGA-FTIR analysis [19]. It was revealed that the production of alcohols and phenols required a higher pyrolysis temperature in the presence of sodium salts, while the formation of aldehydes and ketones was promoted due to the intensive cracking of –CH₂ONa and –COONa bonds.

In order to investigate the role of β-O-4 linkages in the thermal stability of lignin, a milled wood lignin was first treated thermally in the temperature range of 150–300 °C prior to the pyrolysis, and the behaviors was characterized using a pyrolysis-GC/MS analyzer [41]. It was found that the low-temperature thermal treatment produced a thermally stabilized lignin as the β-O-4 linkages were deformed by condensation and charring reactions. As a result, the evolution of

pyrolysis products from the thermally treated lignin was found to be delayed to a higher temperature. For example, the maximum evolution of pyrolytic products was obtained at a high temperature (600 °C) for the lignin sample thermally treated at 300 °C.

Moreover, the pyrolysis kinetics of nine lignins isolated by various methods was investigated by thermogravimetric analysis (TGA) [42]. The obtained activation energies of lignin thermal degradation varied in the range of 130–175 kJ/mol, with the types of lignin.

2.2.3 *Effects of Temperature*

Effects of temperature on distribution of the pyrolytic products of lignin have been studied by many researchers [6, 36, 43–46]. Commonly the maximum bio-oil yields from wood can be obtained at a pyrolysis temperature around 450–500 °C [43]. In pyrolysis of a kraft lignin, char yield decreased from approx. 50 to 47 wt% while increasing the pyrolysis temperature from 470 to 560 °C, accompanied by an increase in pyrolysis oil from ~30 to 38 wt% [43]. For example, an enzymatic/mild acidic hydrolysis lignin from bamboo was pyrolyzed in a tubular reactor at different temperatures, i.e., 400, 500, 600, 700, and 800 °C [6]. It was found that the reaction temperature played a significant role in the yields of pyrolysis products (gas, bio-oil, and char) and the products compositions. With rising the temperature from 400 to 800 °C, the gaseous yield increased from 6.2 to 20.3 wt%, the char formation decreased from 42 to 26.6 wt%, and bio-oil yield increased to a maximum value (57.1 wt%) at 500 °C and then decreased to 53.3 wt% at 800 °C (see Fig. 2.7). The maximum concentration of phenols (G-type and S-type phenols, phenol, p-methylguaiacol, vanillin, etc.) in bio-oil was as high as 79.3% obtained at 600 °C. At lower temperatures (<500 °C), the pyrolysis of lignin was incomplete but at higher temperatures (>700 °C), the secondary reactions such as dehydration, decarboxylation, and demethylation, and radical's rearrangement occurred, generating more gases including CO, CH₄, and H₂. The obtained phenolic bio-oils from lignin could be used as a potential feedstock for synthesis of biopolymers.

Shen et al. [47] reported that the predominant products in non-catalytic pyrolysis of lignin were phenolic compounds and the yield of maximum aromatic monomers (such as guaiacol, phenol, benzene, toluene, etc.) attained at 650 °C also, the portion of guaiacyl-type compounds decreased noticeably with elevating temperature due to the secondary cracking reactions such as demethoxylation reaction. A study was reported by Patwardhan et al. [22] on pyrolysis of cornstover lignin at various temperatures. By increasing the temperature, the char yield decreased from 60 wt% at 300 °C to 22 wt% at 700 °C, accompanied by an increase in the formation of low molecular weight compounds (such as acetic acid), gaseous products, and phenolic products including phenol, 2-methyl phenol, 4-methyl phenol, 2,5-dimethyl phenol, and ethyl phenol, as illustrated in Fig. 2.8.

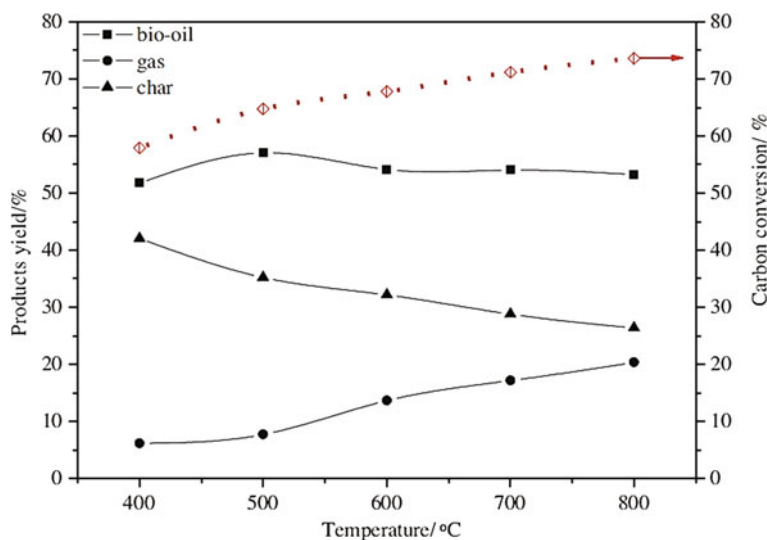


Fig. 2.7 Product yields and carbon conversion derived from pyrolysis of an enzymatic/mild acidic hydrolysis lignin derived from bamboo, reprinted with permission from Ref. [6]. Copyright (2015) Elsevier

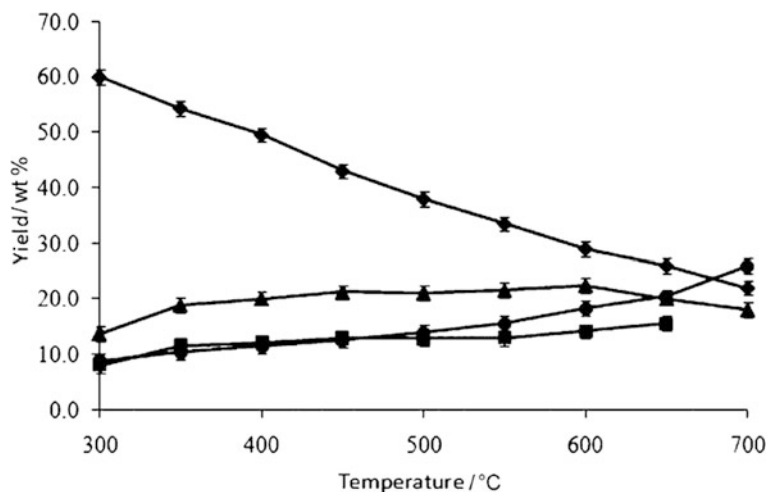


Fig. 2.8 Yields of pyrolytic products of lignin over temperature, Char (♦), Phenolic compounds (▲), low molecular weight compounds (■), and gaseous species (●), reprinted with permission from Ref. [22]. Copyright (2011) John Wiley and Sons

The dependency of pyrolytic products of lignin on temperature in the range of 400–800 °C was investigated on two types of lignin (Alcell lignin and Asian lignin) by Jiang et al. [46]. The maximum yield of phenolic compounds was obtained at

600 °C, being 15.5 and 17.2% for Asian lignin and Alcell lignin, respectively. The main pyrolytic products were 5-hydroxyvanillin at a yield of 4.3% for Alcell lignin, and 2-methoxy-4-vinylphenol at a yield of 4.2% for Asian lignin.

2.2.4 Effects of Catalyst

Various kinds of catalyst such as inorganic metal, transition metal, noble metal, spent FCC, alumina and zeolite have been applied for pyrolysis of lignin [10, 44, 48, 49]. Among these catalyst zeolite is an effective deoxygenation catalyst to produce bio-oil with reduced oxygen content but enriched aromatic hydrocarbons. Beside the type of catalyst, other factors such as catalyst amount, catalyst framework, acidity, and pore size distribution could affect the composition of the pyrolytic products of lignin. Kim et al. [44] investigated the effects of catalyst loading of Zeolite (HZSM-5) (catalyst/lignin ratio from 0.6 to 2 w/w) and catalyst composition (mole ratio of Si/Al from 30 to 280) on the products distribution in pyrolysis of a milled wood lignin. The mole ratio of Si/Al had an inverse effect on the acidity of HZSM-5 catalyst but less effect on the surface areas of the catalysts. A higher acidity of the catalyst increased the production of aromatic hydrocarbons (AH) such as benzene, toluene, xylene, and naphthalene, and the highest yield of AH products was obtained with HZSM-5(30) (2.62 wt%) despite its lowest surface area. It confirmed that the catalyst acidity plays an important role in the yield of AH than the surface area does. The catalyst amount could control the production of pyrolytic products. Additionally, it was observed that the AH production gradually increased with temperature up to 700 °C (~3 wt% of lignin) which could be ascribed to the enhanced thermal degradation of lignin, owing to the improvement of the pore size of HZSM-5, and the decreased energy barrier of the diffusion of large molecules into the catalyst pores at a high temperature [44, 50, 51]. As the coke formation increased above 600 °C, the optimum temperature for lignin pyrolysis was determined to be 600 °C. The effects of acidity, pore size, and structure of the zeolite catalysts on the bio-oil yield and selectivity of the desired products from lignin were investigated by Ma et al. [50]. It was found that a high content of catalyst provides more active sites and could limit repolymerization reactions and minimize the char formation, a low Si/Al ratio for the HZSM-5 catalyst increases its acid sites and promotes the formation of AH products, and large pore size of the HZSM-5 catalyst would facilitate the penetration of large molecules of the lignin degradation products/intermediates and stabilizes the degraded products. Figure 2.9 presents the role of porosity in stabilization of intermediates compounds in fast pyrolysis of lignin.

Two pathways were proposed by Mullen and Boatenge for formation of aromatic hydrocarbons in pyrolysis of lignin in the presence of H-ZSM5 catalyst [18]. These pathways consists of: (i) the scission of the aliphatic linkages of the lignin network to form small olefins, (ii) depolymerization of lignin into alkoxy phenolic monomers. Figure 2.10 shows the proposed pathways of degradation of lignin over H-ZSM5.

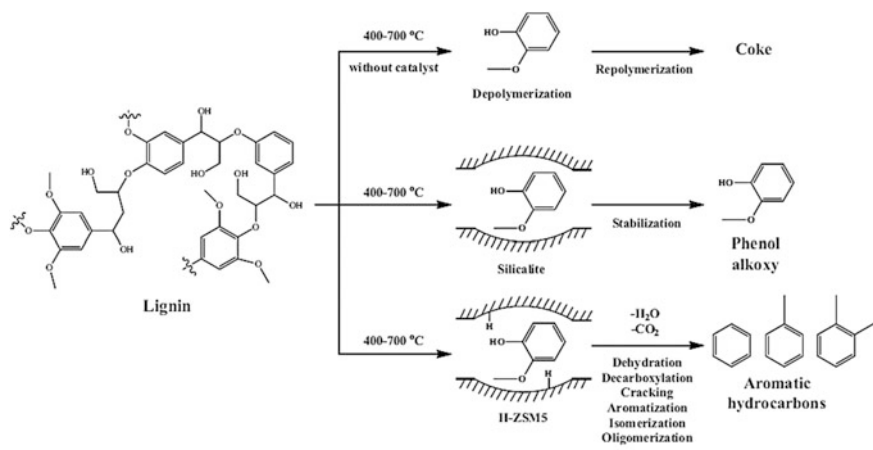


Fig. 2.9 Non-catalytic and catalytic fast pyrolysis of lignin, reprinted with permission from Ref. [50]. Copyright (2012) Elsevier

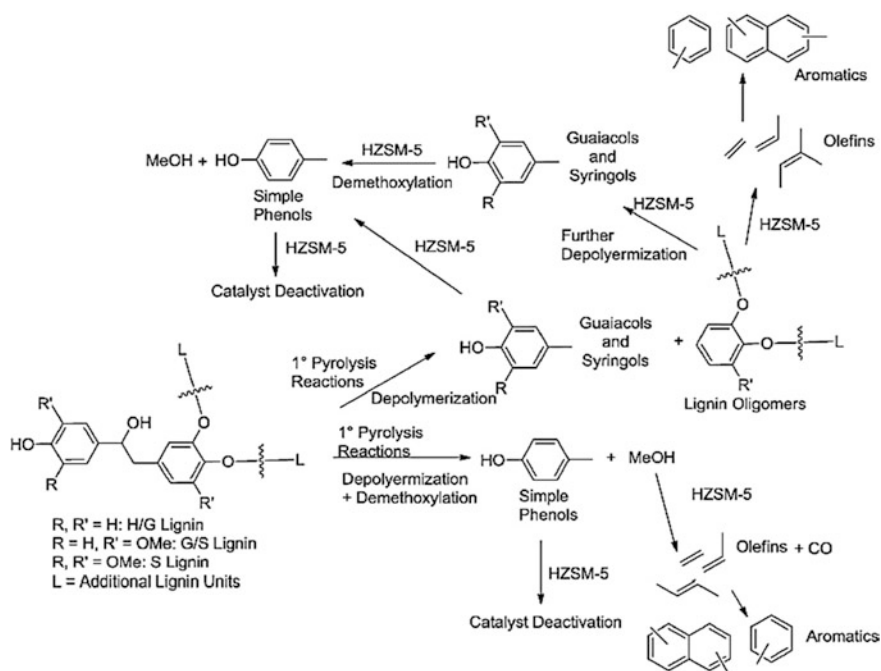


Fig. 2.10 The proposed pathways for depolymerization of lignin in the presence of HZSM-5, reprinted with permission from Ref. [18]. Copyright (2010) Elsevier

Three kinds of catalyst, i.e., HZSM-5, Y-Zeolite, and Pd/C were tested for the catalytic pyrolysis of softwood kraft lignin [52]. HZSM-5 and Y-Zeolite are acidic catalysts which enhanced the production of aromatic hydrocarbons with one to three rings and deoxygenated phenolic structures compared with non-catalytic pyrolysis. Pd/C is a nonacidic catalyst which increased the content of the reduced guaiacyl units. The effects of five different zeolite catalysts (HZSM-5(25), HZSM-5(50), HZSM-S(210), H- β , and H-USY) on the composition of the bio-oil from the lignin pyrolysis was also examined by Shen et al. [47]. The maximum production of aromatic monomers, with different product compositions though, was achieved at 650 °C for both catalytic and non-catalytic pyrolysis of lignin. The zeolite catalysts promoted the deoxygenation reactions to generate more aromatic hydrocarbons. HZSM-5 (25) was found to be the most effective catalyst for producing aromatic monomers due to its strongest acidity (zeolite with a lower Si/Al ratio has a stronger acidity). HZSM zeolites are more effective than other types of zeolites in catalytic pyrolysis of lignin for production of aromatic monomers as HZSM zeolites have MFI orthorhombic structure and a unique three-dimensional pore system, while H-USY showed better deoxygenation performance, forming more aromatic hydrocarbons (benzene, toluene, and xylene) in the bio-oil from lignin pyrolysis. Li et al. [53] pyrolyzed sodium lignosulfonate with and without catalyst (HZSM-5, an aluminosilicate zeolite) from 30 to 650 °C and analyzed the resulting gases by TGA-FTIR to examine the degradation kinetics and product distributions. It was observed that the use of catalysts promoted the cracking of oxygenated products, decreased the molecular weight of pyrolyzed products, and reduced the char yield. The most abundant compounds in the vapor were water, CO, CO₂, aromatics, alkenes, and alkyls. The pyrolysis process could be divided into three stages with the corresponding activation energy of 104, 129, and 169 kJ/mol, respectively. Mullen and Boateng [18] pyrolyzed lignin from four different sources over an acidic zeolite (HZSM-5) and a mixed metal oxide catalyst (CoO/MoO₃). Although both catalysts demonstrated to be effective deoxygenation catalysts, promoting the production of aromatic hydrocarbons from lignin, the acidic HZSM-5 was found to be more active than the CoO/MoO₃.

A recent study by Wang et al. [10] described catalytic pyrolysis of alkali lignin with metal chlorides such as KCl, CaCl₂, and FeCl₃. The addition of CaCl₂ and FeCl₃ noticeably increased the yield of bio-oil with high phenol content. In contrast, the impregnation KCl inhibited the yield of bio-oil and promoted bio-char formation, implying the catalytic effect of KCl on repolymerization of low-molecule fragments derived from lignin pyrolysis. In another study, effects of Na₂CO₃, Na₂CO₃/ γ -Al₂O₃, γ -Al₂O₃ on pyrolysis of lignin were studied using vanillyl alcohol as a lignin model component [7]. Vanillyl alcohol contains three functional groups typical on the structure of lignin derivatives: alkyl group, alkoxy group, and hydroxyl group. Pyrolysis of the model compound over the alkaline Na₂CO₃ catalyst produced a high yield of methoxyphenols. In the pyrolysis over γ -Al₂O₃ catalyst with both Lewis and Bronsted acid sites, however, the condensable phase only contained aromatic hydrocarbons due to the high deoxygenation effects of the acidic catalyst, while the yields of coke and gaseous products were also maximized.

In contrast, with $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$ catalyst, no methoxyphenol was detected and the 67 wt% of the condensable product was phenols. Such results may be explained by the fact that loading Na_2CO_3 onto $\gamma\text{-Al}_2\text{O}_3$ decreased the acidity of $\gamma\text{-Al}_2\text{O}_3$ and basicity of Na_2CO_3 , hence restricting the formation of both aromatic hydrocarbons and methoxyphenols. Aspen lignin was pyrolyzed over two different zeolite catalysts, i.e., HZSM-5 and HY [54]. Similarly, the HY catalyst (with less acidity) produced more phenolic compounds, and HZSM-5 (a more acidic zeolite catalyst) yielded more aromatic hydrocarbons due to the high deoxygenation effects of the HZSM-5 catalyst.

AlCl_3 and ZnCl_2 (both Lewis acids) were used as catalysts by Maldhure and Ekhe [55] for pyrolysis of kraft lignin, it was observed that in the presence of either catalyst the residue (or char) yield decreased, accompanied by increased yields of both liquid (bio-oil) and gaseous products. With respect to bio-oil production from lignin, AlCl_3 demonstrated to be a more active catalyst than ZnCl_2 . Characterization of the lignin pyrolysis products showed that the liquid products mainly contained substituted phenols, cyclic esters, mono- and dicarboxylic acids.

Again the study of Peng et al. [56] confirmed that the presence of alkaline catalysts (NaOH , KOH , Na_2CO_3 , and K_2CO_3) at 10–20 wt% in lignin pyrolysis generated bio-oils composed mainly of 2-methoxy-phenol, 2, 6-dimethoxy-phenol, alkylphenols, and 2-ethoxy-4-alkylphenols, although these alkaline catalysts had negligible effects on the products yields. The hydroxide alkalis (NaOH and KOH) produced more alkylphenols, while the carbonate catalysts (Na_2CO_3 and K_2CO_3) promoted formation of methoxyphenols.

As commonly demonstrated in a number of studies, lignin pyrolysis with an acidic catalyst led to a higher yield of bio-oil rich in aromatic hydrocarbons due to the high deoxygenation effects of the acidic catalyst. Performance and optimum conditions of various acidic catalysts in lignin pyrolysis are compared in Table 2.3.

2.2.5 Pyrolysis Reactors

Pyrolysis technology is the only industrially realized technology for liquefaction of lignocellulosic biomass. Some representative industrial pyrolysis processes include Ensyn's patented RTP[®] technology and BTG (Biomass Technology Group)'s fast pyrolysis technology, both based on fluidized bed reactors, as well as the ABRI-Tech's patented pyrolysis based on augers reactor. It is estimated that 10–15% of the total capital cost of an industrial pyrolysis process allocated to the reactor.

Various types of reactor have been used for lignin pyrolysis, such as bubbling fluidized beds [1, 2, 45, 48, 59] (as schematically shown Fig. 2.11), rotating cone reactors [1], fixed bed reactor [10, 56], centrifuge reactors [60], and circulating fluid beds [1, 2], etc.

Table 2.3 Performance and optimum conditions of various acidic catalysts in lignin pyrolysis

Type of lignin	Catalyst	Catalyst loading (catalyst: lignin w/w)	Optimum temp. (°C)	Performance	Refs.
Mill wood lignin	Zeolite (ZSM-5 (Si/Al = 30)	2:1	600	3.6 wt% yield of aromatic hydrocarbon	[44]
Alkaline lignin	W ₂ C/MCM-41 (Si/W = 50)	10:1	750	20.8 wt% yield of arenes (aromatic hydrocarbons)	[57]
Kraft lignin	HZSM-5, Y-zeolite, Pd/C	1:1	600	High yield of aromatic hydrocarbons	[52]
Black liquor lignin	HZSM-5 (Si/Al = 25) or H-USY	2:1	650	Enhance aromatic monomers yields	[47]
Kraft lignin	AlCl ₃ , ZnCl ₂	1:10	500	Lower char yield, and higher bio-oil production	[55]
Aspen lignin	HZSM-5	3:1	600	23 wt% yield of aromatic hydrocarbons (AH), and 28 wt% yield of aggregate sum of AH and phenolic compounds	[54]
Alkaline lignin	Mo ₂ N/γ-Al ₂ O ₃	4:1	700	17.5% yield of aromatic hydrocarbon	[58]

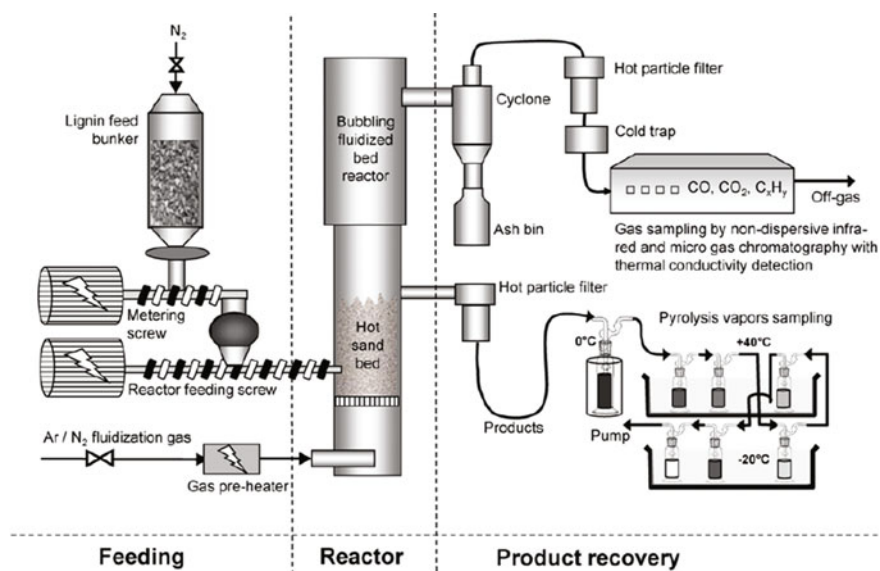
**Fig. 2.11** Bubbling fluidized bed reactor for pyrolysis of lignin, reprinted with permission from Ref. [11]. Copyright (2012) Elsevier

Table 2.4 Product yields of the pyrolyzed Kraft lignin in different bed materials in a fluidized reactor (modified from Ref. [59])

Bed material	Gas yield (wt%)	Bio-char yield (wt%)	Bio-oil yield (wt%)			Yield of organic chemical (wt%)
			Dry bio-oil	Aqueous condensate	Total bio-oil	
Silica sand	30.1	32.6	21.3	16.0	37.3	23.1
Lignin char	26.8	36.0	24.5	12.8	37.3	25.9
Activated lignin char	21.5	35.5	30.4	12.5	43.0	31.3
Birch bark char	31.8	36.0	19.8	12.5	32.3	21.2

In bubbling fluidized-bed pyrolysis reactors, the bed materials, normally silica, olivine sand or other catalyst particles, serve as the heat transfer medium and (if catalyst is used) catalyze the pyrolysis process to alter the products distribution and in situ upgrade the bio-oil products. For example, effect of various bed materials in a bubbling bed reactor (silica sand, lignin char, activated lignin char, birch bark char, and foamed glass beads) were investigated on the yield and quality of bio-oil from the pyrolysis of kraft lignin at 550 °C [59]. The bed materials were found to not only facilitate the heat transfer during the pyrolysis process but also can have a catalytic effect to change the products yields and enhance the quality of the generated bio-oils, as displayed in Table 2.4. Among these bed materials, the activated lignin char provided the higher total bio-oil yield of 43% with a lower molecular weight, a higher phenolic concentration, and similar heating value as compared to standard lignin pyrolysis with a sand bed.

Two major challenges of pyrolyzing lignin in fluidized bed reactors were commonly identified in the feeding (due to the low melting points of lignin, in particular organosolv and kraft lignins) and the formation of lignin-foams and agglomeration of bed materials (which could cause de-fluidization of the bed) [61]. To address these challenges, colleagues of the authors at the Institute for Chemicals and Fuels from Alternative Resources (ICFAR) at Western University have developed a novel bubbling bed reactor system for pyrolysis of kraft lignin as illustrated in Fig. 2.12 [59]. In this reactor system, lignin powders are fed into the reactor using a patented feeder using compressed nitrogen and a pinch valve avoids melting of the lignin feedstock. The reactor is equipped with an internal stirrer with blades of Inconel, to prevent and break the lignin-foams/agglomerates of sand and char during the pyrolysis process. The obtained bio-oil vapor passes through a train of three condensers in series to achieve a dry bio-oil product. The condensing system made of two cyclonic condensers kept at a warm and cold temperature, respectively, and an electrostatic precipitator-cum-condenser (C-ESP). The obtained dry bio-oils contain less than 1 wt% water but are rich in phenolic compounds and of improved heating values.

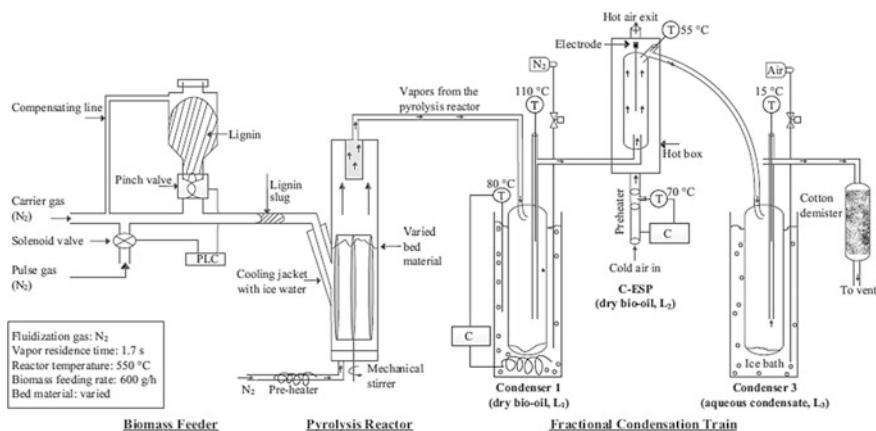


Fig. 2.12 Schematic of a modified bubbling fluidized reactor with an internal stirrer and a three-condenser train, reprinted with permission from Ref. [59]. Copyright (2015) Elsevier

2.3 Summary

Fast pyrolysis of lignin is a promising technology for production of phenolic bio-oil as a potential feedstock to be used as a renewable energy resource and bioreplacement of phenol in synthesis of adhesives, resins, and polymers. The exact mechanism of pyrolysis of lignin is remained unknown due to its complexity in structure. However, the general pathway of lignin pyrolysis contains two-step process: first, the ether bonds cleave to depolymerized lignin, followed by the cracking of side chains on monolignols through the hemolysis of O-CH₃ and radical-induced rearrangements. The pyrolytic products of lignin consist of phenolic bio-oil, bio-char, and gaseous fragments. The content and combination of the pyrolytic products depend on the type of technical lignin, pyrolysis temperature, type of catalyst, and the reactor design.

Various types of reactor have been used for lignin pyrolysis, such as bubbling fluidized beds, rotating cone reactors, fixed bed reactor, centrifuge reactors, and circulating fluid beds, etc. Fluidized bed reactors are the most common reactor type in the pyrolysis technologies commercially developed by far. Two major challenges of pyrolyzing lignin in fluidized bed reactors were commonly identified in the feeding (due to the low melting points of lignin, in particular, organosolv and kraft lignins) and the formation of lignin-foams and agglomeration of bed materials (which could cause de-fluidization of the bed). Worldwide research is going on to address these challenges.

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