

*Editorial*

## Utilization of Sub and Supercritical Water Reactions in Resource Recovery of Biomass Wastes

Wahyudiono<sup>1,a</sup>, Siti Machmudah<sup>1,2,b</sup>, and Motonobu Goto<sup>1,c</sup>

<sup>1</sup>Department of Chemical Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan

<sup>2</sup>Department of Chemical Engineering, Sepuluh Nopember Institute of Technology, Kampus ITS Sukolilo, Surabaya 60111, Indonesia

E-mail: <sup>a</sup>wahyudiono@b.mbox.nagoya-u.ac.jp, <sup>b</sup>machmudah.siti@d.mbox.nagoya-u.ac.jp,

<sup>c</sup>mgoto@nuce.nagoya-u.ac.jp (Corresponding author)

**Abstract.** Recently, the utilization of sub and supercritical water has been proposed to recover waste substances from biomass. This is important not only for prevention of environmental issues, but also for rational utilization of natural resources. Sub and supercritical water treatment is one of the most effective methods for this, because water at high temperature and high pressure behaves as a reaction medium with remarkable properties. This sub and supercritical water treatment process can promote various reactions such as oxidation, hydrolysis, and dehydration. Therefore, sub and supercritical water can be used for the conversion of organic wastes to useful chemical compounds, as well as for oxidizing hazardous waste into CO<sub>2</sub> or harmless compounds. This paper presents the concepts of sub and supercritical water and their application in organic waste recycling at temperatures of 423 – 673 K for substances such as lignin and its derived compounds.

**Keywords:** Sub and supercritical water, biomass, waste, lignin, guaiacol, catechol.

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## 1. Introduction

Water is called the universal solvent because more substances dissolve in water than in any other chemical species. It has fascinating properties as a reaction solvent when in its sub and supercritical conditions. Sub and supercritical water reactions involve applying heat under pressure to achieve reactions in an aqueous medium. Subcritical water is an emerging technique based on the use of water as a reaction solvent at temperatures between 373 and 647 K (critical point of water, 647 K and 22 MPa) and at a pressure that is high enough to keep it in the liquid state. When the reaction temperature and/or pressure increase above the critical temperature and pressure, the state of water converts from subcritical to supercritical. Under these conditions, the properties of water are quite different from those of normal liquid or steam at atmospheric pressure. The properties of water, such as density and dielectric constant, can be continuously controlled between gas-like and liquid-like values by varying the temperature and pressure. For example, the dielectric constant decreases from about 78 at 298 K to 27 at 523 K and 2 at 673 K, while at a pressure of 25 MPa. This decrease in dielectric constant gives rise to increased solubility of small organic compounds. Thus, the polarity of water and hence its ability to dissolve various solids, liquids and gases, which are otherwise insoluble or sparingly soluble, can be enhanced significantly by transforming ordinary water into supercritical water. In addition, water at subcritical conditions can act as an acid or base catalyst, whereas supercritical water offers the unique possibility of shifting dominant reaction mechanisms from free-radical to ionic through manipulation of the water density [1-5]. Therefore, both chemical formation and decomposition reactions can occur. Table 1 shows the wide range of variations of physical properties obtained through pressure and temperature changes [3, 6-9].

Table 1. Properties of water under different conditions.

Fluid	Ordinary water	Subcritical water	Supercritical water	Steam	
Temperature (K)	298	523	673	673	
Pressure (bar)	1	50	250	500	
Density (g cm <sup>-3</sup> )	1	0.80	0.17	0.58	0.0003
Dielectric constant	78.5	27.1	5.9	10.5	~ 1
$pK_w$	14.0	11.2	19.4	11.9	-
Heat capacity (kJ kg <sup>-1</sup> K <sup>-1</sup> )	4.22	4.86	13.0	6.8	2.1
Dynamic viscosity (mPa s)	0.89	0.11	0.03	0.07	0.02
Heat conductivity (mW m <sup>-1</sup> K <sup>-1</sup> )	608	620	160	438	55

Biomass is renewable and has great potential as an alternative energy source for generating fuel and valuable chemicals [9-12]. Several technologies and processes have been reported for the utilization of biomass as a raw material for organic materials and for energy applications [13-14]. Due to the distinctive characteristics of water described above, sub and supercritical water reactions are an effective method for the treatment of organic wastes. Sub and supercritical water reactions of biomass can be considered, to a certain extent, as the same process. In both cases, water, biomass and its components are the chemicals present, and a free radical mechanism is initiated [15]. The main difference is the existence of two phases in the subcritical range and only one phase under supercritical conditions. At subcritical temperatures, the production of abundant quantities of dissolved organic matter result [16]. The dissolved organic matter contains significant quantities of volatile acids, which remain in the liquid phase and can be removed at supercritical temperatures. However, if operating conditions in the subcritical range are selected in order to eliminate mass transfer limitations, that difference becomes minimal. Supercritical water also plays an important role as a thermally stable solvent. Various organic reactions such as oxidation and hydrolysis usually proceed without catalysts. Oxidation and hydrolysis reactions are two major reactions whereby organic materials can be completely converted into carbon dioxide, water and nitrogen gas or nitrous oxide. Also, the main products of hydrolysis can be produced in high yield from cellulose under these conditions [2, 17-23]. In comparison to other thermochemical processes such as pyrolysis, hydrogenation or air gasification, aqueous conversion using supercritical water has the significant advantage of not requiring a drying process for feedstock and therefore can be conducted at high moisture content typical for biomass feedstocks [24, 25].

The main components of biomass resources are typically 40-45 wt% cellulose, 25-35 wt% hemicellulose, 15-30 wt% lignin and up to 10 wt% for other compounds [26]. As mentioned above, biomass is an important renewable and alternative source of chemicals, which have been synthesized from carbon dioxide and water using solar energy. Meanwhile, sub and supercritical water as reaction media for biomass waste treatment is widely used to disintegrate organic components by converting the complex organic matter into simpler by-products or harmless end products for discharging into the environment. This review describes the degradation of lignin as a model for biomass waste in sub and supercritical water without catalysts. The discussion of lignin conversion focuses on its derived compounds (phenolic compounds), which are important intermediates in the chemical industry for a diverse range of products, such as pharmaceuticals, dyes, and antioxidants [27]. This process is expected to become a major source of phenolic compounds from lignin due to the many alkylphenol units in its basic structure.

## 2. Thermal Degradation of Lignin

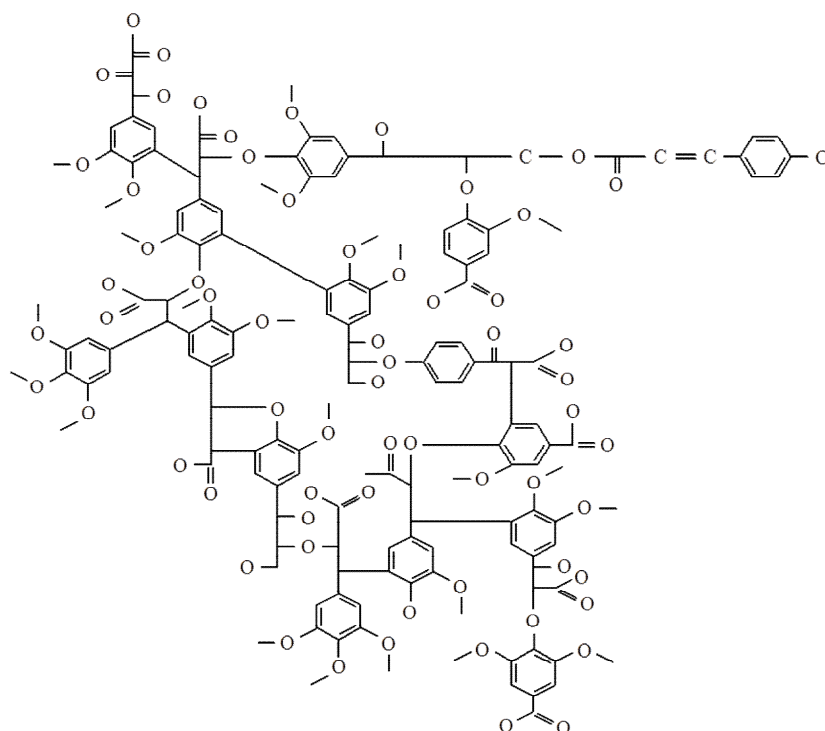


Fig. 1. Structural representation of lignin.

Lignin is a biopolymer in which hydroxyphenylpropane units such as *trans-p*-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol are connected by ether and carbon-carbon bonds (Fig. 1) [26]. Lignin, as a primary component of plant biomass, contains many oxygen functional groups (hydroxyl, carboxyl, carbonyl groups, ether and ester bonds). Due to its complex composition and structure, the thermal decomposition of lignin occurs over a broad temperature range. When lignin is exposed to elevated temperatures, changes can occur in its chemical structure that affect its performance. The thermogravimetric-differential thermal analysis (TG/DTA) of lignin is shown in Fig. 2. TG analysis is an analytical technique used to determine a material's thermal stability and its fraction of volatile components by monitoring the weight change that occurs as a specimen is heated. This behavior could be explained on the basis of heat transfer and medium diffusion, as has been reported by others [28, 29]. The weight loss process of lignin can be divided into several steps [30-31]. Initially, a reaction occurs when the temperature increases up to 373 K due to the release of water. At these regions, gas release also occurs. The cracking of aliphatic hydroxyl groups in the lateral chains generates water. With the release of chemically combined water and CO<sub>2</sub>, the structure of lignin changes to some extent. Upon increasing the pyrolysis temperature, more gaseous products are released. As shown in this figure, the maximum release of low molecular volatiles takes place at 600 K. The weight loss in this region is due to a combination of ether linkage combustion in the main chains in competition with thermal cracking reactions. After 700 K, the

degradation rate of lignin slightly decreases, most likely due to reactions involving combustion of the remaining volatile components and carbon residue.

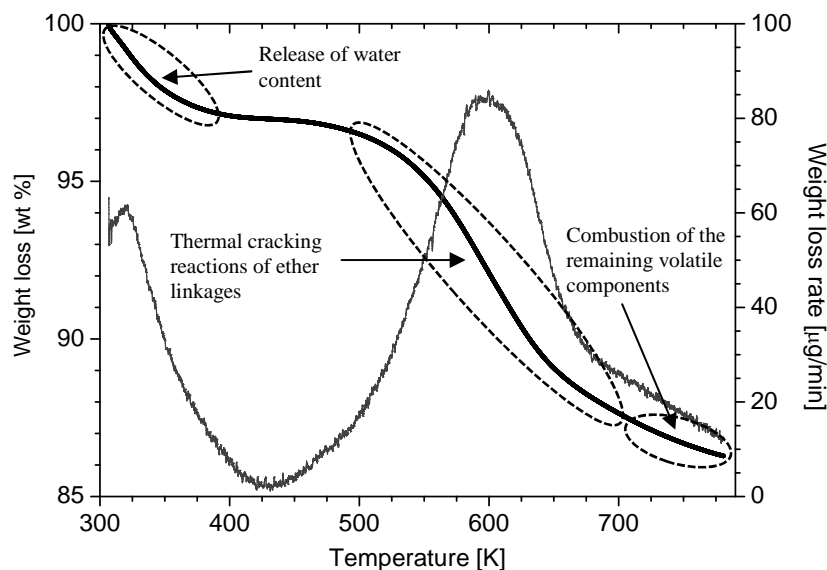


Fig. 2. TG analysis of lignin.

Thermally, the decomposition of lignin takes place over a wide temperature range. Because the various oxygen functional groups in its structure have different thermal stabilities, their scission occurs at different temperatures. The cleavage of these functional groups produces low molecular weight products, while the complete rearrangement of the backbone at higher temperatures leads to char formation 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 more stable products [29, 32-41]. In general, the products from thermal decomposition of lignin can be divided into gaseous hydrocarbons together with carbon monoxide and carbon dioxide, volatile liquids and phenolic compounds. Large amounts of char and complex compounds are also formed. However, the formation of char strongly depends on the thermolysis temperature [26]. Therefore, sub and supercritical water are effective for the treatment of lignin and its derived compounds due to the high reactivity of its functional groups at 423-673 K. In this range of temperatures, degradation of lignin occurs and linkages between the lignin units, of which the  $\alpha$ -O-4 ether bond is the weakest, are cleaved.

### 3. Conversion of Lignin and Its Derived Compounds in Supercritical Water

As a lignin decomposition process, supercritical water has several advantages over conventional processes and even some of the relatively modern processes such as wet-air oxidation and incineration. These advantages arise mainly from the properties of supercritical water itself. As a medium for chemical reactions, supercritical water has both gas-like and liquid-like properties depending on its density. The gas-like low viscosity promotes mass transfer. The liquid-like density promotes solvation processes. The low dielectric constant promotes dissolution of non-polar organic materials. The high temperature increases thermal reaction rates. These properties provide a reaction medium in which mixing is fast, organic materials dissolve well and react quickly with oxygen, and salts precipitate [4, 5, 42].

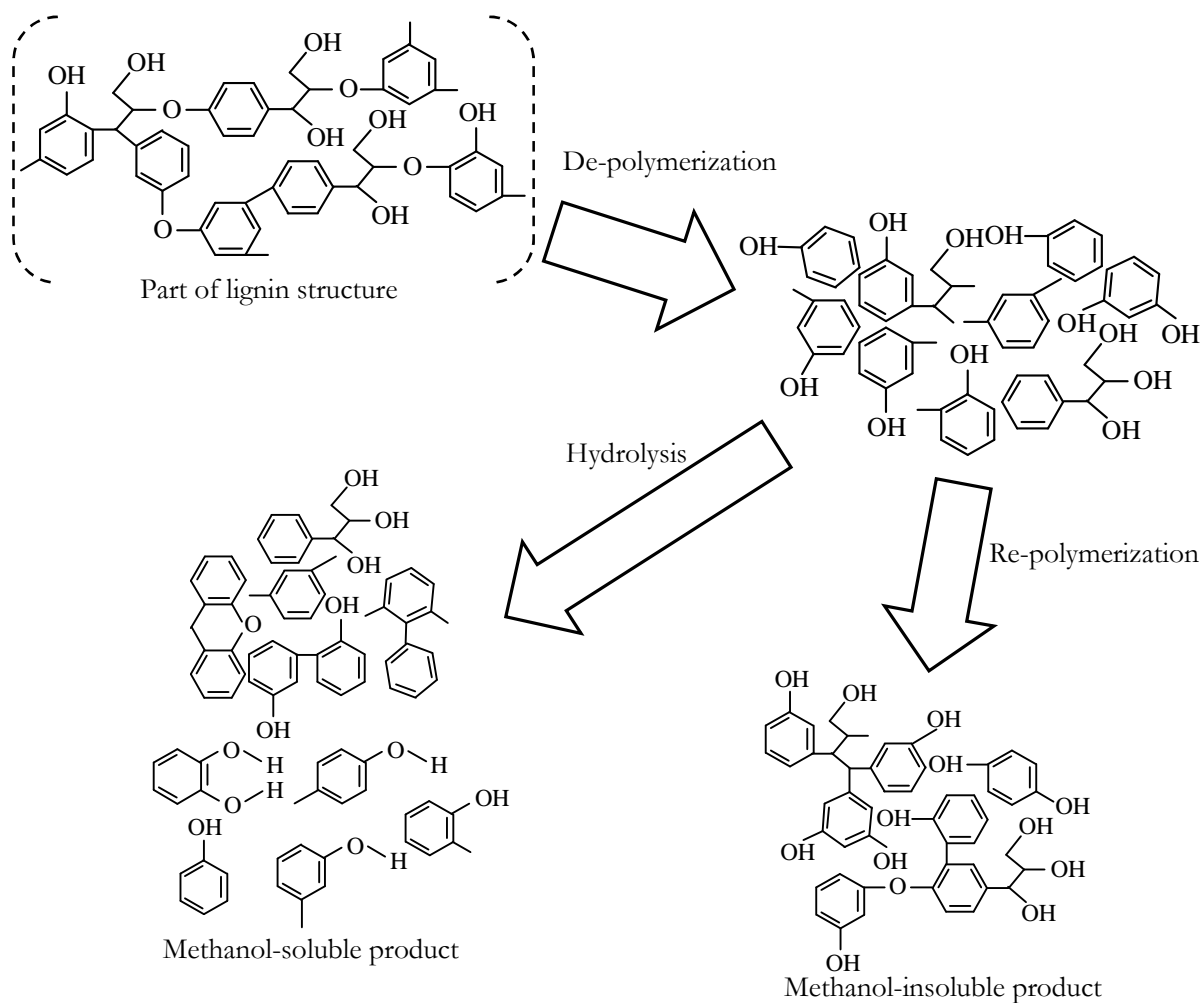


Fig. 3. Plausible reaction pathway of lignin in supercritical water.

Lignin decomposition in supercritical water starts by hydrolysis to form phenolic compounds. Therefore, water density is an important factor in governing the reaction pathway. Figure 3 depicts a schematic of the reaction mechanism for lignin decomposition under supercritical water conditions. A detailed mechanism has not been elucidated because, in principle, every compound can be obtained via different reaction pathways [43]. Most major ether bonds in lignin are between one propyl side chain of a hydroxylphenylpropane unit and the hydroxyl group attached to the benzene ring of another hydroxylphenylpropane unit [26, 43]. Thus, disassembly of ether bonds and carbon-carbon bonds is an important factor in the degradation of lignin. Hydrolysis takes place at ether and ester bonds, cleaving them by the addition of one molecule of water for every broken linkage. This process is accelerated by the high ion product of water. Thus, the lignin macromolecular structure can be partially degraded under hydrothermal conditions [44-46]. Figure 4 shows that the dealkylation of guaiacol as a main structure of lignin gives catechol, which is then hydrolyzed into phenol. After further hydrolysis, *m,p*-cresol and *o*-cresol are obtained. However, these monomers as low molecular weight lignin fragments undergo cross-linking reactions to form heavier compounds that are solid residues [22, 23, 43]. Yokoyama *et al.* 1998 [47] conducted degradation of lignin in near and supercritical water. They reported that the water density has a strong influence on the yield of oil and char. This indicates that, in high-temperature water, especially near the critical temperature, hydrolysis is one of the key reactions that promotes the degradation of biomass. However, the formation of char due to re-polymerization occurs at the same time. This may be the main reason why the yield of chemicals is so low in lignin conversion.

Saisu *et al.* 2003 [48] conducted the decomposition of organosolve lignin in supercritical water with and without phenol at 673 K and a water density of  $\sim 0.5 \text{ g/cm}^3$ . In the absence of phenol, the tetrahydrofuran-insoluble yield decreased and the molecular weight distribution of tetrahydrofuran-soluble products shifted

to lower molecular weights as the water density increased. The products identified as being tetrahydrofuran-soluble were syringols, guaiacols, and catechols, which were derived from the hydrolysis of lignin. However, tetrahydrofuran-insoluble products became heavier as the water density increased. The increase in water density promoted lignin conversion to both lower and higher molecular weight compounds via hydrolysis followed by dealkylation. Okuda *et al.* 2004 [49] also reported that the decomposition of lignin is completed in 0.1 h to form species of around 1000 average molecular weight and other low molecular weight compounds from 100 to 300 amu. With reaction time, the amount of the higher molecular weight compounds decreased and that of lower molecular weight compounds increased without char formation. The presence of phenol as a solvent prevented cross-linking by reacting with reactive sites of the decomposed fragments. Thus, the formation of char may be significantly suppressed by employing a sufficiently high phenol-to-water ratio. This result suggested that rapid depolymerization of lignin without char formation could be accomplished. A study of lignin decomposition in a supercritical water/phenol mixture by Fang *et al.* 2008 [50] also confirmed that addition of phenol inhibited repolymerization. Similar experiments with *p*-cresol and water as solvent under supercritical conditions also resulted in very little insoluble fraction and the molecular weight distribution shifted to remarkably lower values compared to that of the original lignin feedstock [51].

Generally, the reaction pathways that take place during decomposition of wood biomass such as lignin consist of many steps and involve a large number of compounds. In order to investigate the utility of supercritical water in the chemical reactions of lignin, the decomposition reactions of model compounds of lignin were investigated. In this review, guaiacol and catechol have been chosen as model compounds for lignin, because they have been identified as some of the most abundant phenolic compounds found in nature, and contain representative functional groups.

Using guaiacol as a lignin model compound, the reaction pathway of the supercritical water reaction of guaiacol was studied [52-60]. Lawson and Klein 1985 [52] are among the pioneers in the study of guaiacol in supercritical water. They examined the influence of water on guaiacol pyrolysis through a series of pyrolysis experiments spanning reduced water densities from 0.00 to 1.6 at 656 K in batch reactors. They concluded that two competing reactions occurred during the guaiacol reaction in water. The first was neat pyrolysis that led to catechol and high molecular weight material as major products. The second was hydrolysis of guaiacol to catechol and methanol, the selectivity of which was a continuous and increasing function of water density. They also explained that a superposition of free-radical and hydrolysis reaction mechanisms, the latter invoking an ill-defined solvated and caged guaiacol species, allowed formulation of rate expressions that were qualitatively consistent with the temporal variations of observed product yields. Huppert *et al.* 1989 [53] also reported that the reaction of guaiacol in supercritical water was via parallel pyrolysis and hydrolysis pathways. Reaction of guaiacol in the presence of water led to primary hydrolysis products, such as catechol and methanol, as well as neat pyrolysis products. The addition of salts changed the reaction rates and selectivities at a constant density of water. This indicated that the hydrolysis transition state was more polar than the hydrolysis reactants, which implied that supercritical water was able to support polar, ionic-like chemistry in addition to the free-radical chemistry expected in a gas-like phase. DiLeo *et al.* 2007 [58] conducted guaiacol gasification in supercritical water. The reactions were conducted in sealed quartz tubes. At 673-773 K, guaiacol was completely converted in supercritical water, mainly gasified into hydrogen, carbon dioxide, carbon monoxide, and methane, but not all of it was gasified. The rest of the guaiacol decomposed to phenol and *o*-cresol or reacted to form char. The differences in the products can be attributed to the different reaction conditions used. In this case, the pyrolysis rate might be much faster than hydrolysis in supercritical water at low density. Based on the products observed and those reported by a previous researcher, Wahyudiono *et al.* 2007 [59] proposed a simple reaction pathway for guaiacol under supercritical water conditions. Guaiacol was cracked to form catechol (40.73 wt%), phenol (14.18 wt%) and *o*-cresol (4.45 wt%) as main products via three parallel reactions (Fig. 4). The amounts of these products increased with increasing water density at the same temperature. With increasing reaction time, the amounts of guaiacol oligomers and low molecular weight compounds formed increased. At the same time, dehydration reactions of low molecular weight compounds occurred, resulting in the formation of char.

In addition, to improve the understanding of the chemistry of lignin decomposition, Wahyudiono *et al.* also carried out experiments with catechol in supercritical water at 673-693 K [61]. Under these conditions, catechol was decomposed slightly into its derived compounds. By using gas chromatography mass spectrometry (GCMS) analysis, phenol was clearly detected as a decomposition product of catechol. In this work, only phenol was quantified, since this compound was considered to be the main product in the

experiments. However, some other compounds such as cyclopentanone, 2-cyclopentenone, 1,2-benzenedicarboxylic acid, nonylphenol, 1,4-dipropylbenzene, acetophenone, 2,6-di-tert-butyl-naphthalene, 4-butoxyphenol, o-ethoxyphenol, 2-methylterephthalaldehyde, p-diethoxybenzene, and 5-methoxy-2,3,4-trimethylphenol were identified. The conversion of catechol and the formation of phenol increased with an increase in water density almost proportionally to the concentration of water. These results demonstrate that the reaction can be controlled by manipulating the temperature and pressure (water density) in supercritical water [1, 3-5]. They also reported that first-order kinetics were appropriate to describe the catechol decomposition in supercritical water. An Arrhenius plot was used to determine the global rate constant value for catechol decomposition of  $9.0 \times 10^{-4} - 11.0 \times 10^{-4} \text{ min}^{-1}$ . Kruse *et al.* 2000 [62] also reported that catechol could be converted into gases in supercritical water. They calculated the influence of temperature on the gas composition during the decomposition process of catechol at temperatures of 573–1173 K and a pressure of 200 bar. An increase in temperature led to an intense increase in hydrogen and carbon dioxide, a slight increase in carbon monoxide, and a decrease in methane. They explained that although catechol is a stable compound, the C–O linkage can be cleaved under near and supercritical conditions through hydrolysis.

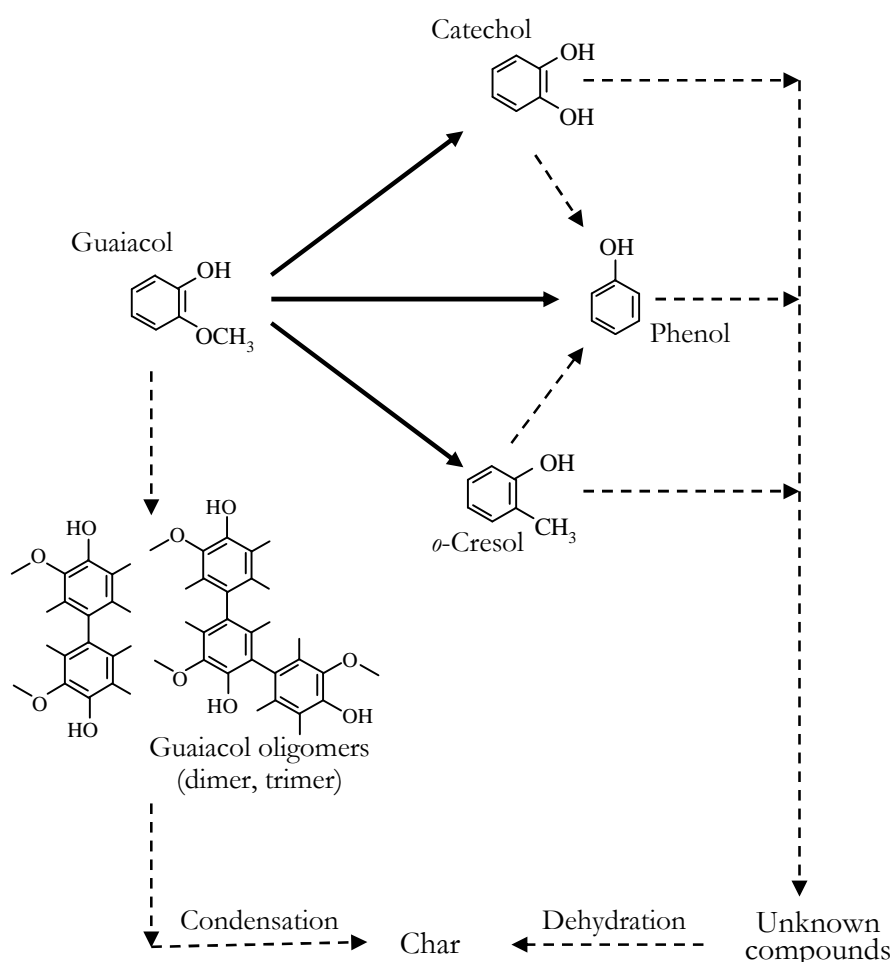


Fig. 4. Simple reaction pathway for guaiacol in supercritical water, adapted from [55].

#### 4. Conversion of Lignin under Subcritical Water Conditions

Organic reactions in water have attracted considerable attention as a way of improving environmentally benign chemical processes, which would obviate the need for harmful organic solvents. One of the major obstacles to this process is the poor solubility of organic compounds in ambient water. However, the properties of water can be tuned to overcome this difficulty by performing the reaction under subcritical water conditions. Below the critical point of water, a vapor and a liquid phase can exist. The equilibrium

composition of gases produced from biomass in this region generally consists of methane and carbon [63]. However, as explained before, the decomposition processes of biomass in subcritical and supercritical water can be considered, to a certain extent, as the same process. These properties make subcritical water a very promising reaction medium for the conversion of biomass. Lignocellulosic materials could be readily decomposed into chemicals by hydrolysis and further reactions. Hence, conducting reactions under subcritical water conditions provides a broad range of possibilities for chemical transformations that are not realized in ambient water.

This section focuses on conversion of lignin by what is often referred to as subcritical water liquefaction. In subcritical water liquefaction, water is an important reactant and catalyst, and thus lignin and its derived compounds can be directly converted without an energy consuming drying step, as in the case of pyrolysis.

The degradation of lignin with molecular oxygen under alkaline conditions was studied by Wu *et al.* in 1994 [64] in a magnetically stirred autoclave. Lignin was degraded at 423-443 K in 8-15 wt% aqueous sodium hydroxide solution under oxygen pressure. The addition of metal oxides resulted in an additional increase in lignin conversion and production of phenolic aldehydes. Aromatic ketones and aldehydes were also obtained, mainly vanillin and syringaldehyde. Similar results were also reported by Xiang *et al.* 2001 [65]. The experiments were carried out in a 55-mL tubing bomb reactor (SS-316 tubing capped with Swagelok end fitting) connected to a pressurized oxygen source (200 psi). The process was based on aqueous alkaline oxidation of lignin with dissolved O<sub>2</sub> in the presence of Fe<sup>3+</sup> and Cu<sup>2+</sup> catalysts at moderate reaction temperatures (433-453 K). Under the conditions used in the alkaline oxygen oxidation of lignin, the syringyl structure in lignin is more sensitive to oxygen pressure and more reactive than the guaiacyl structure. These results showed that the combination of these catalysts (Fe<sup>3+</sup> and Cu<sup>2+</sup>) was most effective in raising the yield of ketones and aldehydes. With the implementation of catalysts, the yields of aldehydes and ketones were improved to the level of 4.6% for vanillin, 9.8% for syringaldehyde, 0.7% for acetovanillone, and 2.6% for acetosyringone. Pecina *et al.* 1986 [66] studied the hydrothermal degradation of poplar lignin in the temperature range of approximately 473 K without catalysts. The GC chromatogram identified seven hydrolysates in the water-soluble phase from hydrothermal degradation of poplar lignin at 488 K that were single-ring compounds (4-hydroxybenzoic acid, vanillic acid, syringic acid, vanillin, coniferyl alcohol, syringaldehyde, sinapyl alcohol). These soluble monomeric and aromatic lignin products were degraded from the syringyl propane (S-element), the guaiacyl propane (G-element) and the *p*-hydroxyphenyl unit (H-element) of the lignin.

Fundamentally, subcritical water liquefaction is pyrolysis, and therefore degradation and polymerization occur. Due to this phenomenon, an increase in temperature is accompanied by effective and efficient decomposition reactions of organic compounds into their derivative compounds. Karagöz *et al.* 2005 [10] obtained phenolic compounds, such as 2-methoxyphenol, 1,2-benzenediol, 4-methyl-1,2-benzenediol, 3-methyl-1,2-benzenediol and phenol from subcritical water treatment of commercial lignin at 553 K. A solid residue was also produced (60%). Wahyudiono *et al.* 2008 [43] studied the degradation of lignin at a temperature of 623 K using a batch type reactor (Hastelloy C-276) without catalysts. The main compounds in aqueous phase products were identified as catechol, phenol, *m,p*-cresol and *o*-cresol. With reaction time, the amount of the lower molecular weight compounds increased. At the same time, the disassembly process of ether and carbon-carbon bonds in lignin and its degradation intermediate occurred. Similar results were obtained in another study [67] on subcritical water treatment of various types of lignin at 647 K. They identified the different compositions of the liquid products from various origins by GC-MS analysis. The liquid products from kraft pine lignin contained mainly guaiacol and methyl-dehydroabietate. The yields were found to be dependent on the composition or structure of the raw materials, which may have resulted from different pretreatment processes. Thus, the composition of liquid products depended on the type of raw materials. In addition, they also suggested that the solid residue was formed by condensation of the phenolic products of the lignin hydrolysis and degradation.

## 5. Summary

Utilization of sub and supercritical water is a prominent method for the treatment of organic wastes such as lignin and its derived compounds and has been attracting worldwide attention of late. Under sub and supercritical water conditions, the decomposition process of biomass can be considered, to a certain extent, to be the same. Due to the composition and structure of lignin, its thermochemical decomposition is a complex process with different pathways, including competitive and/or consecutive reactions. Lignin



thermally decomposes over a broad temperature range due to the existence of various oxygen functional groups, with their scission occurring at different temperatures. Under sub and supercritical water conditions, lignin is decomposed into phenolic compounds as the main products. Unfortunately, the formation of char due to re-polymerization also occurs. In supercritical water, due to the presence of a rapid or direct decomposition pathway, the decomposition reaction of guaiacol as a lignin model compound is favorable. Therefore, supercritical water treatments could be applied as a medium for catechol decomposition even though it is a very stable compound and not known to be easily cleaved under thermal conditions.

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