THESIS FOR DEGREE OF LICENCIATE OF ENGINEERING

Catalytic Conversion of LignoBoost Kraft Lignin into Liquid Products in Near-Critical Water

The Effects of K_2CO_3 Concentration and Reaction Temperature

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ABSTRACT

Lignin, one of the three main components of lignocellulosic biomass, is the second most abundant organic polymer found on Earth. Due to its aromatic nature, lignin is recognized as being a potential feedstock for producing transportation fuel and high value-added chemicals. Nowadays, most of the lignin (almost 99%) produced in the Kraft pulping process is used as internal fuel. A modern Kraft mill has an energy surplus and, therefore, the potential of being a large scale biorefinery: one option is to extract lignin from black liquor, make it a new source of specialty chemicals and fuel. Furthermore, a new process, called “LignoBoost”, has recently been developed to extract a high quantity of pure lignin and has gained commercial status. Therefore, in years to come, a huge amount of LignoBoost Kraft lignin is expected to be available for valorisation.

In this work, the catalytic conversion of LignoBoost Kraft lignin into liquid products at near-critical condition in water, using ZrO_2/K_2CO_3 as the catalytic system and phenol as the co-solvent, was carried out in the small pilot unit, developed by, and located at, Chalmers University of Technology in Gothenburg, Sweden. The plant, operated in continuous mode, was fed with lignin slurry at a flow rate of 1 kg/h. The analytical procedure for the reaction products has been developed in order to determine the composition of the liquid products. In addition, the influence of K_2CO_3 concentration and reaction temperature was investigated in order to optimise the yields of the liquid products obtained.

The results show that the K_2CO_3 concentration and reaction temperature exert different effects in terms of the composition and yields of the resulting products. The reaction products obtained from this process consist of water-soluble organics (5–11% on a dry lignin basis), lignin-oil (69–88%) and char (16–22%). The main 1-ring aromatic compounds (found in water-soluble organics and diethyl ether-soluble lignin-oil) are anisoles, alkylphenols, guaiacols and catechols, showing different trends with K_2CO_3 concentration and reaction temperature. In addition, the reaction temperature has a relatively large effect on alkylphenols, whereas K_2CO_3 has a relatively large effect on anisoles. The lignin-oil, being partially deoxygenated, has higher carbon content and heat value, but lower content of sulphur, than lignin in the feed.

Keywords: lignin, LignoBoost, catalytic conversion, hydrothermal conversion, bio-oil, near-critical water.

LIST OF PUBLICATIONS

This thesis is a summary of the following papers, which are appended at the end of the thesis.

I. **Catalytic depolymerisation and conversion of Kraft lignin into liquid products using near-critical water**
Thi Dieu Huyen Nguyen, Marco Maschietti, Tallal Belkheiri, Lars-Erik Åmand, Hans Theliander, Lennart Vamling, Lars Olausson, Sven-Ingvar Andersson
Published in Journal of Supercritical Fluids 86 (2014) 67–75

II. **Effect of temperature on the catalytic conversion of Kraft lignin using near-critical water**
Thi Dieu Huyen Nguyen, Marco Maschietti, Lars-Erik Åmand, Lennart Vamling, Lars Olausson, Sven-Ingvar Andersson, Hans Theliander
In manuscript

Results relating to this work have also been presented at the following conferences:

i. **Catalytic conversion of Kraft lignin in near-critical water**
Marco Maschietti, Thi Dieu Huyen Nguyen, Lars-Erik Åmand, Hans Theliander, Lennart Vamling, Lars Olausson, Sven-Ingvar Andersson
(Oral presentation, presented by Marco Maschietti)
In: Conference proceedings. 9th International Conference on Renewable Resources and Biorefineries, Antwerp, Belgium, June 5–7, 2013

ii. **Catalytic depolymerisation and conversion of Kraft lignin to liquid products using near-critical water**
Thi Dieu Huyen Nguyen, Marco Maschietti, Lars-Erik Åmand, Hans Theliander, Lennart Vamling, Lars Olausson, Sven-Ingvar Andersson
(Oral presentation)
In: Conference proceedings. 21st European Biomass Conference and Exhibition, Copenhagen, Denmark, June 3–7, 2013, pp 485–493

CONTENTS

1. INTRODUCTION AND OBJECTIVES

1.1. Introduction

Natural gas, fossil-oil, and coal are non-renewable resources that are used to produce fuels and chemicals. The ongoing depletion of these resources, together with the ever-increasing emissions of greenhouse gas resulting from their use, has inspired scientists and researchers to find alternative, i.e. renewable, resources. Biomass is a suitable resource that could possibly solve both these problems (Mazaheri et al., 2010; Pandey and Kim, 2011), comprising biological material from living, or recently living organisms, consisting of woody plants (i.e. lignocellulosic biomass), herbaceous plants/grasses, aquatic plants and manure (McKendry, 2002). An advantage of using lignocellulosic biomass is that it does not compete directly with food supplies (Okuda et al., 2004). Wood, which consists of approx. 40–50% cellulose, 20–30% hemicelluloses and 20–30% lignin on a mass basis, is the most common lignocellulosic material found on Earth. Today, about 50% of the wood consumed on a global scale is used as fuel in the production of heat and, to some extent, power. The remaining 50% is used mostly to produce timber-framed constructions and various paper products (Fengel and Wegener, 1989; Gellerstedt, 2009). The dominant method for producing paper pulp is various chemical pulping methods, which include Kraft pulping (generating Kraft lignin), sulphite pulping (generating lignosulfonate) and soda pulping (generating soda lignin). The aim of chemical pulping is to dissolve and remove lignin to liberate wood fibres, although some hemicelluloses are also degraded in the process (Brännvall, 2009). Nowadays, 70 million tons of lignin, which accounts for 90% of total amount produced, comes from Kraft cooking (the most common method). The majority of this type of lignin (almost 99%) is used as internal fuel. There is currently a lignin surplus in the modern Kraft pulping process as pulp mills have become more energy efficient (Lora, 2008). Furthermore, a new efficient process, known as “LignoBoost”, for extracting a high quantity of pure lignin has been introduced recently and has gained commercial status. Thus, in years to come, a huge amount of this type of lignin is expected to be available for valorisation (Theliander, 2008; Tomani, 2010).

Lignin, an amorphous three-dimensional polymer, acts as a binding material in the woody plant cell wall as well as between the cells. Lignin is composed mainly of three monomers, namely *p*-coumaryl, coniferyl and sinapyl alcohol, which are connected randomly with three main types of ether (C-O-C) bonds (i.e. β-O-4’, 4-O-5’ and 1-O-4’) and four types of carbon-carbon (C-C) bonds (i.e. 5-5’, β-5’, β-β’ and β-1’). The dominant bond in native softwood and hardwood lignin is β-O-4’ bond, which accounts for approx. 45–50% of all bonds. During the

Kraft pulping process, more than 95% of this bond is hydrolysed (Henriksson, 2009). Owing to its phenolic nature and the complexity of its structures, converting lignin into more valuable products for use as transportation fuel and chemicals application is a challenge. Therefore, many studies have been carried out to convert lignin into smaller molecular units in the presence, or absence, of the solvents and/or catalysts. Water in super- or near-critical conditions (T_c = 374.1 ^oC and P_c = 22.1 MPa) has many interesting advantages, and it has been suggested that it may have positive effects on the degradation of lignin material into phenolic compounds (Pandey and Kim, 2011). Recently, some authors (Fang et al., 2008; Okuda et al., 2004; Saisu et al., 2003) demonstrated the conversion of lignin without a catalyst in super-critical water (400–600 ^oC) and reported that the yield of phenolic compounds was low. Their results confirmed that the addition of phenol suppressed the formation of char. At near-critical conditions ($100 < T < 374.1$ ^oC and $P > 0.1$ MPa), water exhibits liquid-like behaviour and acts as an effective solvent (Carr et al., 2011; Möller et al., 2011; Toor et al., 2011). In this regard, many other authors (Lavoie et al., 2011; Miller et al., 2002; Schmiedl et al., 2009; Unkelbach et al., 2010) have attempted to degrade lignin in near-critical water using strong bases as the catalyst but high yields of the heavy fraction and char were also obtained. Such lignin conversions give low liquid-product yields and high amounts of oligomeric residues due to the greater ease of formation of a more condensed structure in the re-polymerisation reactions of reactive sites of the decomposed fragments (Azadi et al., 2013; Roberts et al., 2011). In addition, different properties of water are obtained at different temperatures and densities because of its significant variations in the ionic product (increasing from 10^{-12} (at 100 ^oC) to 10^{-11} (at 300 ^oC)) and dielectric constant (decreasing from 27.1 (at 250 ^oC, 5 MPa) to 18.2 (at 330 ^oC, 30 MPa)) at near-critical conditions (Möller et al., 2011). Thus, the influence of solvent, catalyst and operating parameters should be investigated in order to optimise the yields of liquid products (Yong and Matsumura, 2013; Lavoie et al., 2011; Beauchet et al., 2012; Pińkowska et al., 2012). Furthermore, the optimisation of the yields of liquid products becomes especially important in the continuous mode process, since a high yield of solid residues will lead to serious operational problems.

1.2. Objectives

A small high-pressure pilot unit operating in continuous mode for converting LignoBoost Kraft lignin in water solution at near-critical conditions into transportation fuels and chemicals was set up in Chalmers University of Technology (see **Figure 1.1**). The first objective of the present study is to demonstrate the operability of the plant and feasibility of the process using ZrO_2/K_2CO_3 as the catalytic system and phenol as the co-solvent. The second objective is to develop an analytical procedure for the products obtained from this process in order to determine their composition. The third objective is to investigate the effect of K_2CO_3 concentration and reaction temperature on lignin conversion in near-critical water in order to optimise the yields of the resulting liquid products.

Figure 1.1 The high-pressure pilot unit in Chalmers University of Technology.

2. LITERATURE

2.1. Lignin

2.1.1. Structure and properties of lignin

Lignin (derived from *lignum*, Latin word for wood), one of the most abundant amorphous biopolymers found on Earth, has a very complex structure with a mixture of aromatic and aliphatic moieties. Like many other biomass components, it is formed via the photosynthesis reaction (**Figure 2.1**). It is composed mainly of three monolignols (**Figure 2.2**), namely *p*-coumaryl alcohol (without methoxy group attached to the aromatic ring), coniferyl alcohol (with one methoxy group) and sinapyl alcohol (with two methoxy groups). These monomers are connected randomly with a number of different ether (C-O-C) and carbon-carbon (C-C) bonds to form a three-dimensional network. The distribution of these monomers in lignin varies between different trees species (see **Table 2.1**): in softwood there is almost exclusively coniferyl alcohol, although small amount of *p*-coumaryl alcohol is present; in hardwood there are both coniferyl and sinapyl alcohols, with amount of sinapyl alcohol from approx. equal to three times higher, and small amount of *p*-coumaryl alcohol; in grass all three monolignols are present but the amount of *p*-coumaryl alcohol is higher than in other types of lignin.

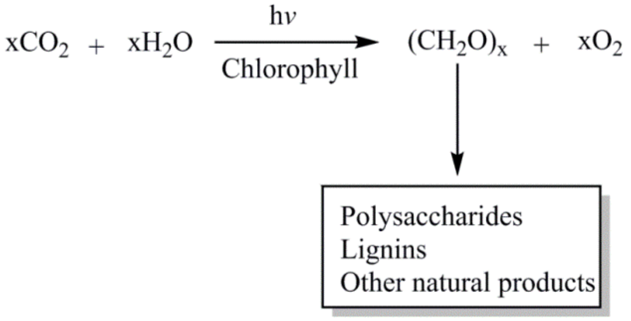
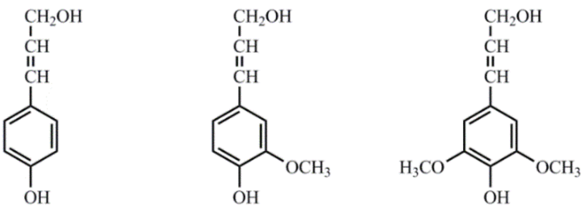


Figure 2.1 Photosynthesis reactions (Gellerstedt, 2008).



p-Coumaryl alcohol   Coniferyl alcohol   Sinapyl alcohol

Figure 2.2 The monomers forming the lignin polymer (Henriksson, 2009).

Table 2.1 Composition (%) of monolignols in different plants (Henriksson, 2009).

Plant type	p-Coumaryl alcohol	Coniferyl alcohol	Sinapyl alcohol
Softwood	<5	>95	0
Hardwood	0–8	25–50	45–75
Grass	5–35	35–80	20–55

The molecular complexity of lignin means that many structural questions still remain to be answered. The dominant bond structures between the monomer units and the various functional groups on these units in lignin have been elucidated by using the methods for identifying the degradation products and the synthesis of model compounds. For instance, Freudenberg (1968) showed the bond structures of softwood lignin (see **Figure 2.3**), constituting of 18 monomer units. The arrangement of these groups is arbitrary due to radical reaction in biosynthesis (Henriksson, 2009).

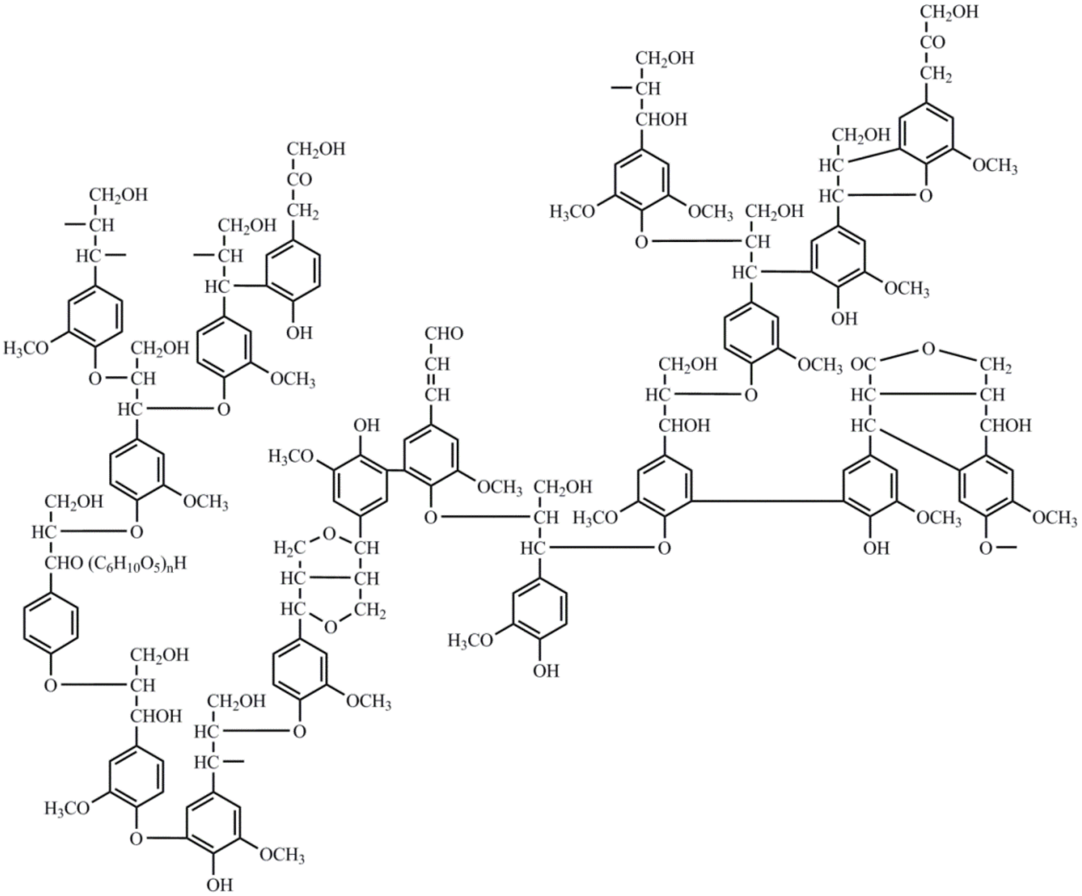
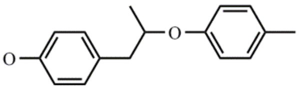
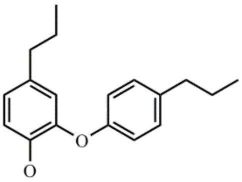
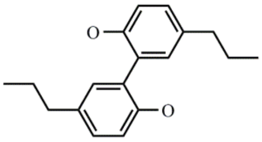
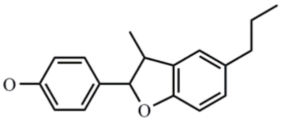
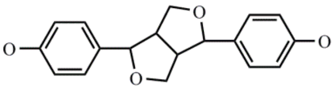
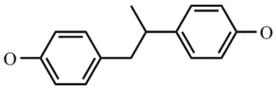
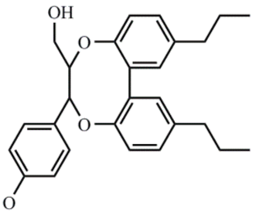
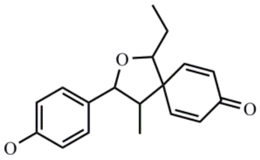
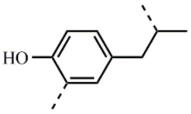


Figure 2.3 The bond structures proposed in softwood lignin (Gellerstedt, 2008).

More than two thirds of the units in native lignin are linked by ether bonds (around 70%) and the rest by carbon-carbon bonds. The carbon-carbon bonds are generally more stable compared to the ether bonds; they are often resistant even in processes such as chemical pulping. The most important types of bond are *β*-O-4’, followed by *β*-5’, 5-5’, *β*-1’ and *α*-O-4’ as reported in **Table 2.2**. The *β*-O-4’ bond is the most common bond in lignin, accounting for about 50% in softwood and 60% in hardwood. The characteristic functional groups in lignin are phenolic hydroxyl groups, methoxyl groups and some terminal aldehyde groups, which are important for the reactivity of the lignin, as shown in **Figure 2.4** (Dimmel, 2010). In addition, some alcoholic hydroxyl groups and carbonyl groups are also present in the lignin polymer. One of the most important functional group is the free phenolic group (i.e. the oxygen in the 4-possition does not form an ether-bond). Free phenols form only 10–13% of the aromatic rings in native lignin (Henriksson, 2009).

Table 2.2 Important bonds as a percent of the total bonds in softwood and hardwood (Gellerstedt, 2009).

Name	**Bonds**	**Structure***	**Softwood**	**Hardwood**
Ether bonds				
β-aryl ether	*β*-O-4’		35–60	50–70
Diaryl ether	4-O-5’		<4	7
Carbon-carbon bonds				
Dihydroxy biphenyl	5-5’		10	~5
Phenyl coumarane	*β*-5’		11–12	4–9
Pioresinol	*β*-*β’*		2–3	3–4

Diaryl propane 1,3-diol	β-1’		1–2	1
Other structures				
Dibenzodioxocin	5-5’-O-4		4–5	Trace
Spiro-dienone	β-1’α-O-α’		1–3	2–3
Free phenol			11	9

*Only the “carbon-skeleton” on the structures is shown.

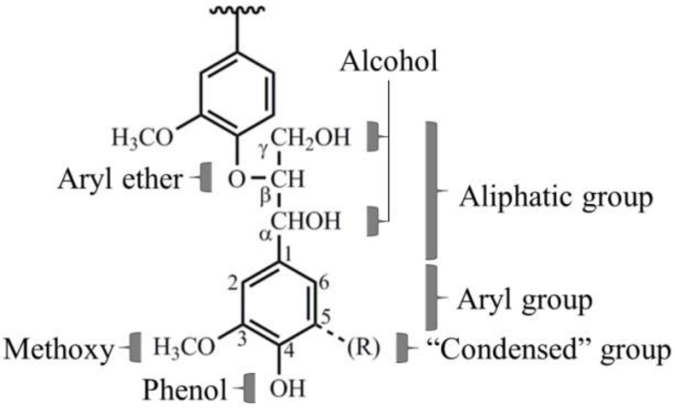


Figure 2.4 Functional groups in lignin (Dimmel, 2010).

2.1.2. LignoBoost Kraft lignin

Today, Kraft pulping is the dominant process for making chemical paper pulp since it gives strong fibres, which make strong paper, and has an efficient chemical recovery process. In the Kraft cooking process, hydroxide ions (OH^-) are used in combination with hydrosulfide ions (HS^-) as the active chemicals to dissolve lignin and liberate wood fibres at 150–170 °C. About 90–95% of the total lignin in the raw material is dissolved in this process. More specifically, not only most of the β-O-4’ structures (>95%) are hydrolysed but also the lignincarbohydrate linkages at Cα-position (i.e. benzylether and benzylester linkages) are hydrolysed, and the resulting lignin fragments are dissolved in the alkaline solution (black liquor). After pulping, the black liquor leaves the digester as an aqueous stream having a solid content of about 15% (i.e. weak black liquor). In **Figure 2.5**, the fragmentation reaction of phenolic β-O-4' structures with free phenol is shown. The fragmentation reaction of these structures depends on the presence of (HS$^-$). In this reaction, an episulfide and a new phenolic end-group are formed. The episulfide structure is instable and is converted into a coniferyl alcohol structure by the elimination of sulphur (S_o). This elimination leads to the formation of Kraft lignin with relatively low sulphur content.

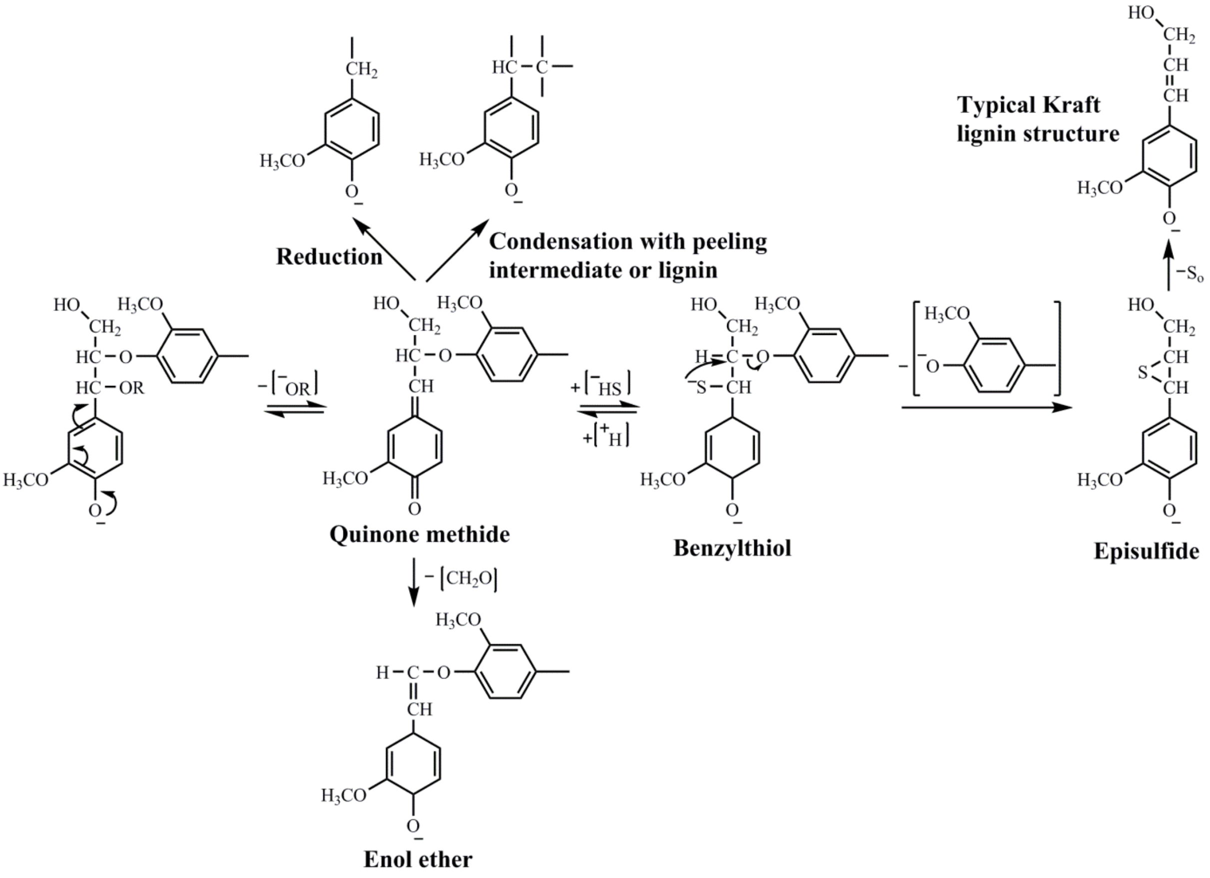


Figure 2.5 Reaction scheme for the cleavage of phenolic β-O-4' structures lignin during Kraft cooking (Gellerstedt, 2009).

Figure 2.6 shows the cleavage of non-phenolic β-O-4' structures which, in contrast to the phenolic type, depends on the presence of (OH$^-$). This reaction results in a cleavage of the β-ether bond and the formation of an epoxide structure, along with the new phenolic lignin end-group. The epoxide is intable and reacts further with (OH^-) in the liquor. As a result of these fragmentation reactions, the solubilisation of lignin is enhanced not only by the formation of new free phenolic groups, which is ionized in alkaline liquor, but also because the molecular weight of the lignin macromolecules has decreased. Furthermore, the competing reactions start from quinone methide involving elimination as well as reduction, and condensation reactions may occur (see **Figure 2.5**). The quinone methide can eliminate the *γ*-hydroxymethyl group to form a stable enol ether structure, cleave the *β*-ether bond or react with other nucleophiles to create new stable carbon-carbon bonds, or reduce the carbon atoms of the methylene type to form the *α*-methylene group (Gellerstedt, 2009). In Kraft pulping, however, the competing reactions are much lower than the reactions between quinone methide intermediate and (HS^-): which would explain the lower content of condensed diphenylmethane and stable enol ether structures observed in Kraft lignin than in soda lignin (Lora, 2008).

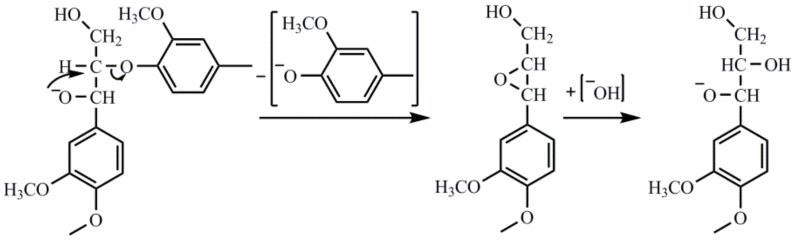


Figure 2.6 Reaction scheme for the cleavage of non-phenolic *β*-O-4’ structures in Kraft cooking (Gellerstedt, 2009).

A schematic diagram of a modern Kraft mill is shown in **Figure 2.7**. Nowadays, such a mill has the potential of being a large scale biorefinery that not only produces market pulp and green electricity but also uses black liquor as a raw material for the production of specialty chemicals and transportation biofuels. The efficient removal of lignin from black liquor can exploit the energy surplus of a Kraft mill and produce a bulk raw material for generating energy or producing of chemicals and fuels. The low solubility of Kraft lignin under acid and neutral conditions in water solutions means that lignin can be separated from black liquor as the pH is being lowered. Other components of the black liquor (i.e. inorganic constituents, carbohydrates and their degradation products), on the other hand, are soluble in water over a wide pH range, which facilitates the recovery of Kraft lignin with relatively low contents of both ash and carbohydrates. In **Figure 2.8**, a schematic diagram of the conventional one-stage process and the new “LignoBoost” process producing lignin from Kraft black liquor are shown. In the conventional process, a filter cake is washed directly after dewatering, resulting in a Kraft lignin with a relatively low dry solid content, high ash (and sodium) content and poor dewatering properties. The LignoBoost process has been developed by researchers at Chalmers University of Technology and Innventia, Swedish research institute. In this process, the filter cake from the first dewatering stage is re-dispersed in low pH liquor with filtrate from a second dewatering/washing stage. The resulting lignin, LignoBoost Kraft lignin, thus has a high level of purity and improved dewatering properties. Furthermore, a higher yield compared to conventional process can be obtained by using the LignoBoost process (Öhman et al., 2007; Tomani, 2009). In 2013 a commercial-scale LignoBoost process was started at a pulp mill in Plymouth, USA. The capacity of this plant is around 75 tonnes per day.

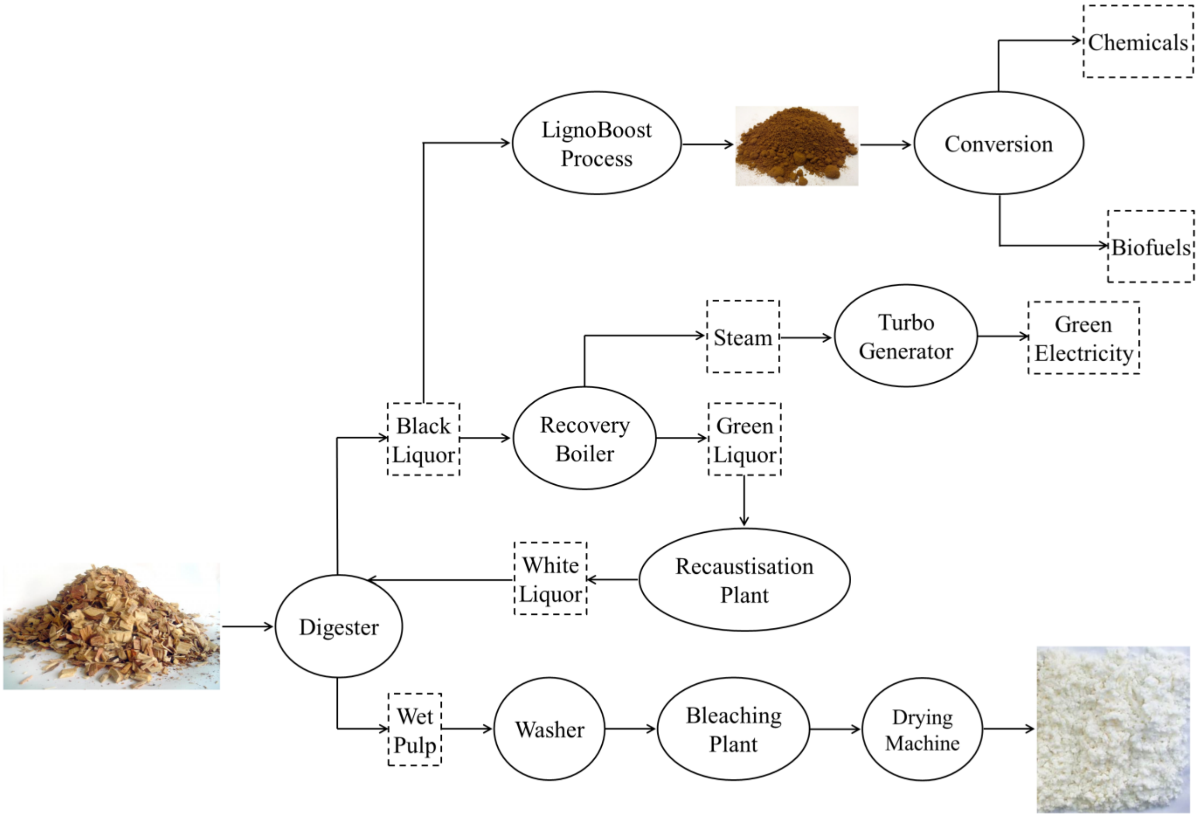


Figure 2.7 A schematic diagram of the modern Kraft mill.

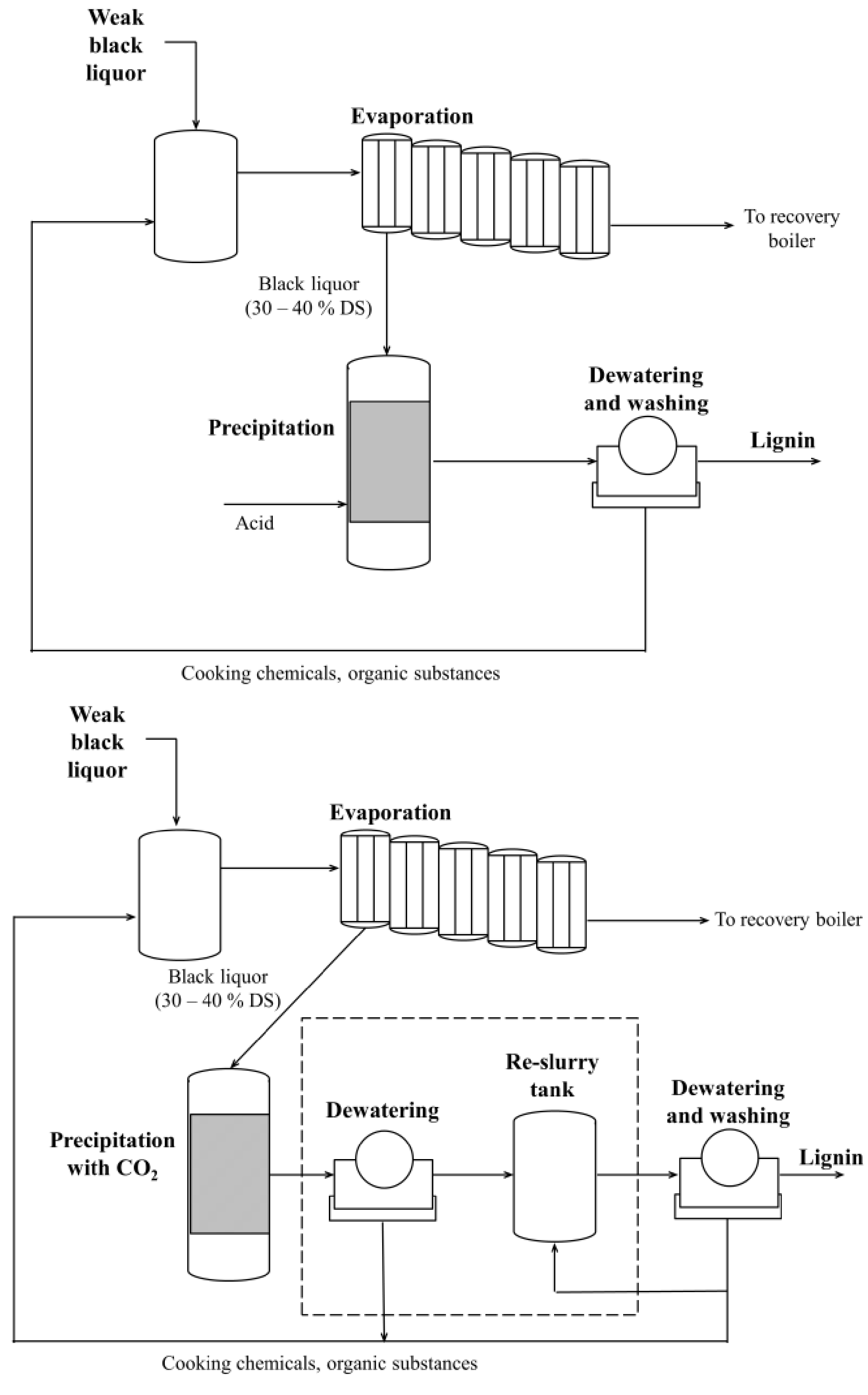


Figure 2.8 Schematic diagram of the conventional one-stage process (up) and the new LignoBoost process (down) for the production of lignin from Kraft black liquor (Axegård, 2008).

2.2. Conversion of lignin

2.2.1. Pyrolysis

Figure 2.9 shows the main lignin conversion processes that are suggested and their potential products are shown. Pyrolysis refers to thermal treatment of the biomass or lignin with or without a catalyst and in the absence of oxygen. At these conditions, the organic substances are broken down into smaller units without any further combustion into carbon dioxide. The pyrolysis of lignin is highly complex in terms of the bio-oil composition and the distribution of obtained products over bio-oil, char and gas. The conversion of lignin occurs over a wider range of temperatures (160–900 ^{o}C) compared to polysaccharides (220–400 ^{o}C) and is affected by several factors, such as the type of feedstock, the severity of the treatment and catalyst used. Of all of the catalysts studied on the pyrolysis of lignin, HZSM-5 zeolites (SiO_2/Al_2O_3 = 30/1) were found to be the most effective in producing aromatic hydrocarbons (Zhang and Moutsoglou, 2014). Lignin degradation begins to cleave the weaker bonds at lower temperatures (160–300 ^{o}C) and the stronger bonds at higher temperatures, proceeding thereafter to crack or condense the aromatic rings at significantly high temperatures (>500 ^{o}C). The obtained bio-oil is a complex mixture of volatile liquids (methanol, acetone and acetaldehyde), monolignols, phenolic aromatics (phenol, guaiacol, syringol and catechol) and other polysubstituted phenols. The bio-oil has high oxygen content and thus cannot be used directly as liquid fuel, making upgrading essential (Ma et al., 2014). A fraction of the lignin is converted into thermally stable products called char. The yield of char can be decreased by increasing the pyrolysis temperature (Pandey and Kim, 2011; Azadi et al., 2013).

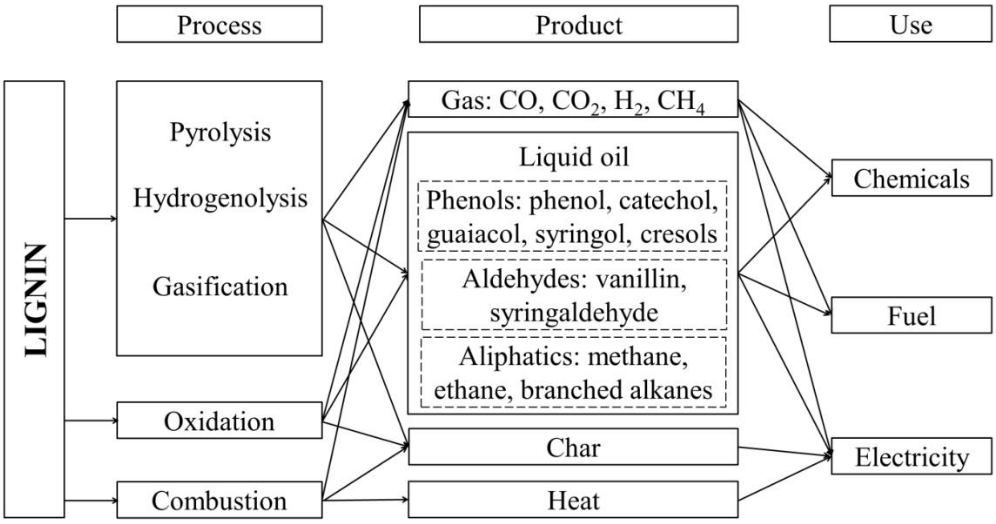


Figure 2.9 The major thermo-chemical lignin conversion processes and their potential products (Pandey and Kim, 2011).

2.2.2. Hydrogenolysis

Hydrogenolysis is pyrolysis in the presence of hydrogen. Hydrogenolysis is carried out at significantly lower temperatures (250–450 ^{o}C) than normal pyrolysis and favours a higher net conversion, higher yields of liquid products (including monomeric phenols) and less char being formed. Another advantage of hydrogenolysis is that it is unnecessary to pre-dry the feedstock, which is an energy demanding process (Kang et al., 2013). Furthermore, the application of a suitable solvent and catalyst can improve the conversion and the yields of products. Thus, hydrogenolysis is probably the most promising method for producing phenols from lignin. In this process, lignin degradation occurs via many chemical reactions, such as the cleavage of the inter-unit linkages, deoxygenation, ring hydrogenation and the removal of alkyl and methoxyl moieties. The result of all these reactions is a quite complex oil mixture. The source of hydrogen for hydrogenolysis can be a hydrogen-donor solvent or pressurised hydrogen gas: examples of hydrogen-donor solvent that may be used are tetralin (Davoudzadeh et al., 1985; Jegers and Klein, 1985; Kudsy et al., 1995; Thring et al., 1993) and formic acid with alcohol as the solvent (Gellerstedt et al., 2008; Kleinert and Barth, 2008; Kleinert et al., 2009). Many authors (Shabtai et al., 1999; Shabtai et al., 2000; Miller et al., 1999; Zmierczak and Miller, 2006) used a hydrogen-donor solvent at supercritical conditions, such as methanol/ethanol (plus water), which resulted in a high liquid yield. In these works, a base-catalysed depolymerisation (BCD) followed by hydrodeoxygenation (HDO) and/or hydrocracking was carried out.

Water in super- or near-critical conditions (T_c = 374.1 ^{o}C and P_c = 22.1 MPa) is also used, and it has been suggested that it has positive effects on the degradation of lignin materials into phenolic compounds (Pandey and Kim, 2011). The main phenolic compounds (such as phenol, *o*-cresol and catechol) recovered from this conversion are important products for the chemical industry (Kang et al., 2013). Recently, many authors (Fang et al., 2008; Okuda et al., 2004; Saisu et al., 2003) demonstrated the conversion of lignin without a catalyst in supercritical water (from 400 to 600 ^{o}C) but reported that the yield of phenolic compounds was low. Their results confirmed that the addition of phenol suppressed the formation of char. At near-critical conditions (100 ^{o}C $< T <$ 374.1 ^{o}C and $P >$ 0.1 MPa), water exhibits liquid-like behaviour and acts as an effective solvent (Carr et al., 2011; Möller et al., 2011; Toor et al., 2011). Also, hydrogenolysis at near-critical condition in water has, unlike other thermo-chemical methods, the potential to create lower-oxygen oil since part of the oxygen presents in small organic compounds hydrolysed by the raw materials would partition into the aqueous phase (Kang et al., 2013). Several other authors (Lavoie et al., 2011; Miller et al., 2002; Schmiedl et al., 2009; Unkelbach et al., 2010) have been working with converting lignin in near-critical water using strong bases as the catalyst, but they obtained high yields of the heavy fraction and char. These lignin conversion systems give low liquid-product yields and high amounts of oligomeric residues due to the ease of formation of a more condensed structure in the repolymerisation reactions of reactive sites of the decomposed fragments (Azadi et al., 2013; Roberts et al., 2011). It has been shown that the use of an organic solvent inhibits char formation. In particular, the addition of phenol or alkylphenols (such as *p*-cresol) facilitates the production of phenolics, while the addition of formic acid or an alcohol is favoured for the production of lignin-derived oils with low oxygen content (Kang et al., 2013).

2.2.3. Gasification

Gasification is a thermal treatment method for converting lignin or biomass into a mixture of small permanent gas molecules: H_2, CO, CO_2 and CH_4. This gas mixture, known as syngas, has been used in industry for a long time for the generation of electricity, pure hydrogen and synthetic liquid fuels and chemicals. However, the primary products of gasified lignin are significantly lower value than the aromatics typically found in a pyrolysed bio-oil; there is also some ash and H_2S formed due to the presence of inorganics and sulphur in the technical lignin. Lignin gasification can be achieved either by conventional gasification in the presence or absence of active agents (i.e. oxygen and/or steam) at high temperatures (around 700 ^{o}C) and near atmospheric pressure; or hydrothermal gasification at moderate temperatures (350 ^{o}C) and high pressures (from 15 to 27.5 MPa). Hydrothermal gasification (supercritical water gasification) is promising technology for the production of hydrogen and methane from organic feedstock with high content of water as there is no need for drying prior to gasification (Azadi et al., 2013). In the case of lignin hydrothermal gasification, there are mainly three categories of catalysts: alkali and alkali salts (NaOH, KOH, Na_2CO_3, CaO, etc.), metals (transition metal or noble metal) and metal oxides (e.g. ZrO_2) (Kang et al., 2013).

2.2.4. Oxidation

Oxidation, which is thermal treatment in the presence of oxygen, is primarily important in converting lignin into aromatic aldehydes (e.g. vanillin, syringaldehyde and *p*-

hydroxybenzaldehyde). The operating temperatures range from 100 to 320 ^{o}C and pressures from 0.5 to 20 MPa (Kang et al., 2013). In fact, of the above named products, vanillin is one of the low-molecular-weight chemicals produced industrially in large quantities from technical lignin by alkaline oxidation in air (Silva et al., 2009). The oxidation of lignin involves the cleavage of the aromatic rings, aryl ether bonds or other linkages; nitrobenzene, metal oxides and hydrogen peroxide are the oxidants most commonly used. The yield and composition of the degradation products vary based on the severity of the reaction conditions. Villar et al., (2001) reported that nitrobenzene and metal oxides could preserve the lignin aromatic ring and produce aldehydes. Furthermore, the yield of aldehydes can be increased when catalysts such as noble metals and transition metal salts are used. Transition metal salts are more suitable for industrial applications due to their low cost (Kang et al., 2013).

3. MATERIALS AND METHODS

3.1. Materials

The Kraft lignin used in this work originates from softwood and was produced in the LignoBoost demonstration plant in Bäckhammar, Sweden. The heterogeneous catalyst used in the reactor was zirconia (ZrO_2) pellets (Harshaw Chemie BV, length: 3 mm, diameter: 3 mm, BET surface area 48 m^2/g). The potassium carbonate (K_2CO_3, ≥99.5%) used as the homogeneous co-catalyst, the phenol (crystallized, ≥99.5%) used as the co-solvent and the 1 mol/L hydrochloric acid (HCl) used in the analytical procedure of the aqueous phase were all sourced from Scharlau. Sigma-Aldrich provided the following chemicals: anisole (≥99.65%), phenol (≥99.5%), *o*-cresol (≥99%), *m*-cresol (99%), *p*-cresol (≥99.0%), guaiacol (≥98.0%), catechol (≥99%), syringol (≥98.5%), 4-methylguaiacol (≥98%), hydrocoumarin (99%) and 4-hydroxybenzaldehyde (98%) used as the analytical standard; Hydranal-Composite 5 and methanol (puriss. p.a. ≥99.8%) used in the Karl Fischer titration; and the tetrahydrofuran (THF, ≥99.9%) and diethyl ether (DEE, ≥99.9%) used as the solvents in the analytical protocol. All chemicals were used as provided, without further purification.

3.2. Apparatus and procedure

A schematic diagram of the laboratory catalytic conversion plant used is shown in **Figure 3.1**. Prior to the start of the experimental run, the system is heated up and pressurized to operating conditions, maintaining a continuous flow of deionized (DI) water. During the run, the feed, composed of lignin, K_2CO_3, phenol and DI water, is pumped continuously by a high-pressure diaphragm pump (Lewa) at a flow rate of 1 kg/h measured by a mass flow-meter (Endress and Hauser, Promass). The lignin slurry is prepared by crushing lignin manually before dispersing it in a solution of K_2CO_3 in DI water. The actual dispersion procedure is performed using an Ultra Turrax disperser (IKA WERK T 45/N) operating at room temperature for approx. 5 min. The feed is made by mixing the lignin slurry with phenol; it is stored in a 10 L feed tank equipped with an impeller, where it is kept at 40 °C. Prior to entering the reactor, the feed is heated to 80 °C using an electric preheater and mixed with a stream recirculated from the reactor; the recirculation pump is of high-temperature and high-pressure type. The recycle-to-feed ratio is kept at approx. 10 for all runs with the exception of that at the highest reaction temperature (i.e. 370 ^oC): the value for this run was set at 2 due to operational reasons. The ratio is estimated by measuring temperatures before and after the mixing point and then applying an energy balance. Recirculation allows the fresh feed to be heated rapidly and mixed before coming into contact with the heterogeneous catalyst in the reactor. There is a second electric heater installed prior to the inlet of the reactor. The reaction mixture comes into contact with the solid catalyst whilst flowing upwards in the 500 cm^3 fixed-bed reactor (Parr 4575; height: 171 mm, internal diameter: 61 mm), composed of Inconel 600 in the high-temperature parts and equipped with an electrical heating jacket. The free volume of the reactor charged with the catalyst is 294 cm^3. At reaction conditions (i.e. reaction temperature in the range of 290–370 °C and pressure of 25 MPa), the reactor residence time (τ) is in the range of 10–13 min.

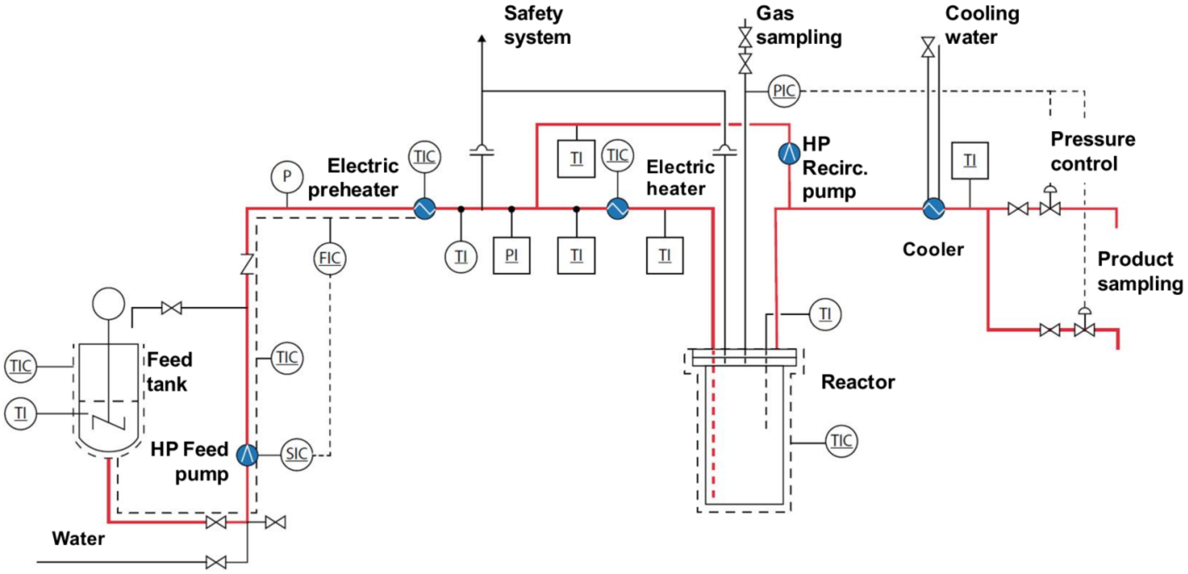


Figure 3.1 Schematic diagram of the pilot plant.

The reaction products are cooled down and depressurised to ambient conditions. Two pressure control valves are used for controlling the system pressure and for depressurising the reaction products. These valves are in parallel, allowing them to be switched over from one to the other in case the valve in operation becomes congested by solid particles. The liquid products are collected continuously in sampling bottles for analysis: each bottle is used to collect the liquid products corresponding to approx. 45 min of operation. The pH of the liquid products in each of the bottles is measured using a pH-meter (Jenway, 370) equipped with a glass electrode (Jenway, 924005), using a 2-point calibration with standard buffer solutions. Gas samples were not taken during the runs that were carried out since no significant amount of gas was collected in the gas sampling bag (Tedlar sample bag, SKC, USA) placed at downstream, on the outlet line exiting the cap of the sampling bottle. Auxiliary lines for cleaning the apparatus in between the runs and safety systems are also installed.

The observation was made that the visual appearance of the products in the sampling bottles changes progressively during the start-up period and shows a progressive darkening; the exception was a single run without lignin in the feed, in which the products consisted of a homogeneous liquid phase showing a steady appearance right from the beginning. After a period of approx. 2 h from the start, the operating parameters of the plant, the pH of the aqueous phase and the visual appearance of the products in the sampling bottles were steady in all runs. In the runs with lignin in the feed, the pH of the aqueous phase in the sampling bottles varied by about 0.5–0.7 pH units during the first 2 h, while it was constant (±0.1) at steady-state condition. The runs lasted for around 4 h, i.e. the steady state period was kept for approx. 2 h before the shutdown operations began. After the end of each experimental run, the plant is cleaned, the reactor disassembled and the char deposited on the catalyst measured.

Several liquid product samples were taken during the steady-state operation. When lignin is fed to the system, the samples were found to consist of two distinct liquid phases: an aqueous and an oil phase. These were separated by means of centrifugation (Thermo Fisher Scientific, Heraeus Megafuge 40R) operating at 492 rad/s for 3 h at 25 °C. This process gives a fairly transparent aqueous phase with a colour ranging from yellowish to dark green (depending on the mass fraction of K_2CO_3 in the feed) and a high-viscosity black oil phase (lignin-oil) that is heavier than the aqueous phase. In order to obtain larger single samples for the analytical procedures, all of the aqueous samples obtained during the steady-state operation were mixed into one single aqueous sample; the same was done with the oil samples. These samples are, thus, representative of an average of the steady-state conditions. The oil was dissolved in THF in order to achieve its complete recovery because of its high viscosity, as well as to facilitate mixing of the samples from different bottles. THF was then evaporated in a rotary vacuum evaporator (Büchi, R) operating at temperatures never exceeding 35 °C.

3.3. Experimental conditions

Table 3.1 shows the operating conditions of the experimental runs. The pressure was kept at 25 MPa in all runs. In the four experimental runs A – D, the mass fraction of K_2CO_3 in the feed was varied from 0.4 to 2.2% while the reaction temperature was kept constant at 350 ^{o}C in order to evaluate the effect of the co-catalyst on the process. In the five experimental runs C and F – I, the reaction temperature was varied between 290 and 370 ^{o}C while the mass fraction of K_2CO_3 in the feed was kept constant at 1.6% in order to evaluate the effect of reaction temperature on the process. In all runs, the ratio of phenol-to-dry lignin was in the range of 0.73–0.75 (mass basis). In Run E, however, the feed was prepared without lignin, with only K_2CO_3 and phenol in DI being dissolved in water: this run was carried out with the aim of studying the hydrothermal process when there is no lignin in the system, and also to demonstrate that the products obtaining in the other runs are in fact derived from lignin.

Table 3.1 Feed data of the mass fraction (%) of each component in all the runs and feed pH.

Input data	K_2CO_3 mass fraction series					Reaction temperature series			
	A	B	C	D	E	F	G	H	I
Reaction temperature (^{o}C)	350	350	350	350	350	290	310	330	370
K_2CO_3 (%)	0.4	1.0	1.6	2.2	1.9	1.6	1.6	1.6	1.6
Dry lignin (%)	5.6	5.5	5.5	5.4	0	5.5	5.5	5.5	5.5
Phenol (%)	4.1	4.1	4.1	4.0	4.7	4.1	4.1	4.1	4.1
pH_f	7.9	8.8	9.1	9.3	9.5	9.1	9.1	9.1	9.1

3.4. Analytical methods

3.4.1. Characterization of lignin

The elemental composition, ash content and heat value of this lignin were all analysed at the national research centre SP (Statens Provningsanstalt, Sveriges Tekniska Forskningsinstitut) in Borås, Sweden. The carbon, hydrogen and nitrogen content were measured according to the method SS-EN 15104, the sulphur and chlorine content according to the methods SS-EN 15289 and SS-EN 15289 A, respectively, and the ash content and heat value according to the methods SS-EN 14775 and SS-EN 14918, respectively.

The moisture content of the lignin was measured prior to each experimental run by a moisture analyser (Sartorius MA30). Approx. 5 g of lignin was sampled and analysed (130°C, auto-stabilization method) in triplicate. The amounts of aromatic and aliphatic groups present were analysing by means of a ^{13}C-NMR (Varian NMR spectrometer). Approx. 0.2 g lignin was dissolved in 1000 µL DMSO-d_6 and used to perform a duplicate analysis using Varian

NMR-spectrometer (9.4 Tesla) with ^{13}C-detection. The spectra obtained were processed with an exponential line broadening (10 Hz), signal phasing and baseline correction.

3.4.2. Analysis of the aqueous phase

Figure 3.2 presents a block diagram showing the various steps of the analytical methods applied to the liquid products. The Total Carbon (TC) and Total Organic Carbon (TOC) of the aqueous phase samples obtained after centrifugation were measured at SP (Borås, Sweden) according to the SS-EN 1484 method. The relative uncertainty (95% confidence interval) of the TOC measurement is 8%. In addition, detailed identification of the water-soluble organics present in the aqueous phase was carried out by means of Gas Chromatography (GC) coupled with Mass Spectrometry (MS), according to the procedure described below.

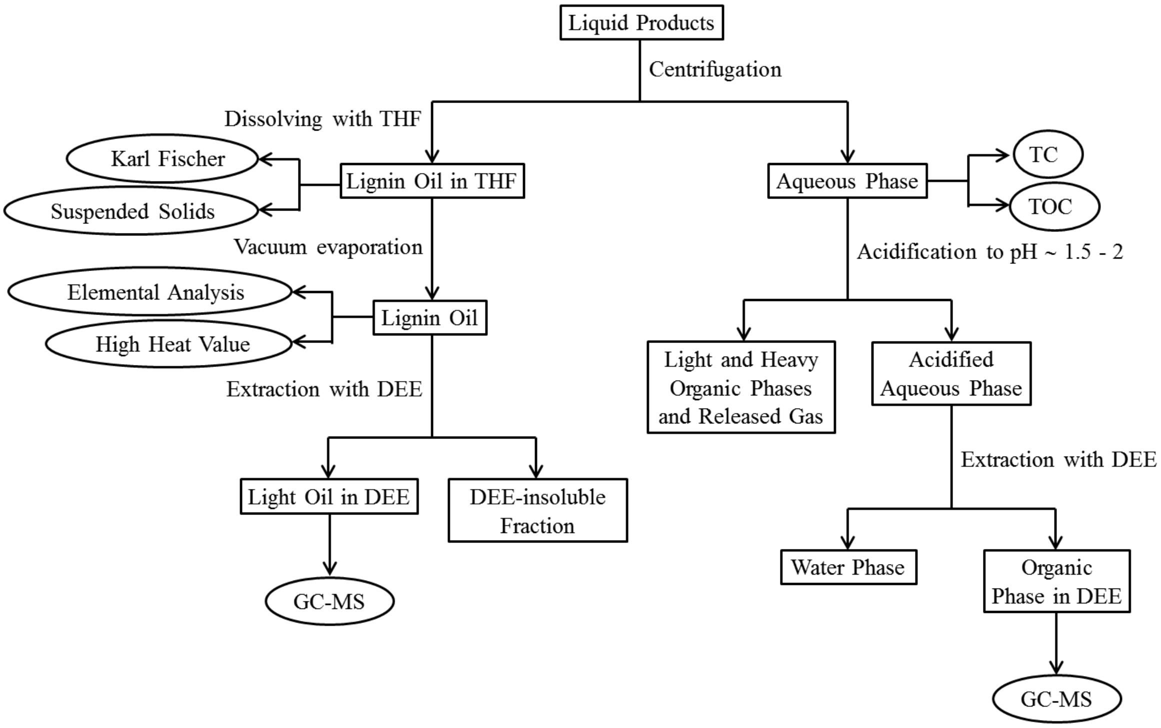


Figure 3.2 Block diagram of the analytical methods for the liquid products.

Approx. 50 g of the aqueous phase was withdrawn and acidified to pH 1.5–2 by adding HCl. In the runs with lignin in the feed, it was observed that acidification led to further clarification of the aqueous phase: a very small amount of additional phases also appeared, however, in the form of some heavier black drops at the bottom and a lighter yellowish phase at the top. These phases were not analysed because their amounts were very small. The gas that was released from the solution during acidification, on the other hand, was quantified gravimetrically. Identification and quantitation of the water-soluble organics were carried out as follows: approx. 10 g of the acidified aqueous phase was withdrawn, filtered through a 0.45 μm syringe filter, mixed with a known amount of internal standard and then extracted with DEE in a separating funnel with a solvent-to-feed ratio (S/F) equal to 1. Only a negligible amount of syringol is present in softwood lignin (see **Figure 4.1**) so it is not produced in the reaction but, since its structure is similar to the reaction products, it was selected for use as an internal standard (IST). The organic extracts were analysed using a gas chromatograph (Agilent 7890A) connected to a mass spectrometer (Agilent 5975C) operating in an electron ionization mode. The analytes were separated in a chromatographic column HP-5MS (length: 30 m; internal diameter: 0.25 mm; thickness of stationary phase: 0.25 μm) by injecting 1 μL of sample via an autosampler (Agilent 7693A), using helium at 1 mL/min as the carrier gas. The injector temperature is set at 300 °C and the temperature programme of the GC oven is 45 °C for 2.25 min, 2 °C/min up to 300 °C and 300 °C for 10 min. The MS source and quadruple temperatures are set at 250 °C and 150 °C, respectively. Spectral interpretation is carried out using the NIST MS Search programme (version 2.0) operating on the NIST/EPA/NIH Mass Spectral Database 2011 (NIST 11). An approximate quantitation of the water-soluble reaction products in the acidified aqueous phase is carried out assuming the following relationship:

$$w_i = w_{IST} \cdot \frac{A_i}{A_{IST}}$$

where w and A indicate the mass fraction in the acidified aqueous phase and chromatographic peak area, respectively, i is the generic analyte and IST is the internal standard. The average values of A_i and A_{IST} were calculated from the results of three injections of each sample. The average value of the Relative Standard Deviation (RSD) of the peak area was found to be 7.1%.

3.4.3. Analysis of the lignin-oil

The lignin-oil produced in the process was soluble in THF. The water content of the lignin-oil samples obtained after centrifugation prior to THF removal was measured through Karl Fischer volumetric titration, whereby approx. 1 g of oil was withdrawn, dissolved in

THF (about 20 g) and filtered under vacuum using a Büchner funnel equipped with Duran glass filters P2 (nominal maximum pore size 40–100 μm). This filtration step was carried out in order to prevent an accumulation of solid particles in the titrator. A loss of volatiles in the range of 1–7% (with respect to the mass of diluted oil) was observed during vacuum filtration and assumed to be composed of pure THF (i.e. not water); the oil/THF ratio was then recalculated accordingly. Both the diluted oil and THF used for dilution were titrated in triplicate. The titration of THF was performed to take into account the water derived from the solvent used for dilution. The SD of the water mass fraction, measured in triplicate titrations, was always below 0.4%. The accuracy of the titration was checked on solutions of water in THF, at a water mass fraction of approx. 1%. The Average Absolute Deviation (AAD) on a set of 10 measurements was found to be 0.025%.

THF-insoluble Suspended Solids (SS) in lignin-oil obtained after centrifugation but prior to the removal of THF were measured as follows: approx. 2 g of oil was withdrawn, dissolved in about 40 g of THF and filtered under vacuum through Büchner funnels by means of a two-step process. In the first of these, the diluted oil was filtered on Duran glass filters P2 (nominal maximum pore size 40–100 μm); the pre-filtered oil was filtered again through Duran glass filters P4 (nominal maximum pore size 10–16 μm). Prior to filtration, the glass filters were dried in an oven for 1 h at 105 ^{o}C, cooled in a desiccator and weighed. After each filtration step, the filters were washed with THF until the filtrates were clear. They were subsequently dried for 1 h at 105 ^{o}C, cooled in the desiccator and weighed again. The difference between the two weights is the mass of the retained solids. The amount of retained solids and a rough indication of their size distribution could be also determined. The reproducibility of this method was checked measuring the mass fraction of SS on three oil samples from Run C, and an RSD equal to 5.0% was obtained.

The elemental composition, ash content and heat value of the solvent-free lignin-oil obtained after THF removal were analysed at SP (Borås, Sweden). The carbon, hydrogen and nitrogen contents were measured according to the method SP 0528, whereas the sulphur content was measured according to the method ASTM D 1552. The ash content and heat value were determined according to the methods SS-EN 6245 and ASTM D 4809, respectively.

Furthermore, the DEE-soluble fraction of the lignin-oil sample obtained after THF removal was analysed using GC-MS, whereby approx. 1 g of oil was withdrawn, extracted with DEE (S/F approx. 40/1) and mixed with a known amount of IST. The oil was partly soluble in DEE and the resulting mixture contained black undissolved drops and solid particles. This mixture was filtered through a 0.45 μm syringe filter and a light-yellow clear DEE-rich phase was obtained. This phase was analysed by means of GC-MS and the main compounds were identified and quantitated according to the same procedure reported in Section 3.4.2. In this case, the average value of the RSD of the peak areas was found to be 8.8%.

3.4.4. Quantitation of char

The reactor was cooled down and disassembled after each run and the catalyst particles were recovered. A portion of the catalyst was sampled, washed with water, dried in oven at 105 °C for 24 h, cooled down and then weighed. The catalyst pellets were then regenerated by burning off char at 500 °C for 12 h before being cooled down and reweighed. In this way, the mass fraction of char on dry catalyst can thus be determined. Knowledge of the total amount of dry catalyst charged in the reactor prior to a run allows that the total amount of char deposited on the catalyst in each experimental run to be calculated.

4. RESULTS AND DISCUSSION

4.1. Properties of the LignoBoost Kraft lignin used

The moisture content of the LignoBoost Kraft lignin used was found to be 32.6±0.4% based on a set of 13 measurements. In **Table 4.1**, the results from the elemental analysis and higher heat value results are reported on a dry lignin basis. These results are found to be in a good agreement with Tomani (2010). The ^{13}C-NMR spectrum is shown in **Figure 4.1**; the mass fractions of the aromatic and aliphatic groups were 78% and 22%, respectively. No measurable amount of syringyl groups was found: this is consistent with the origin of this lignin, which is softwood.

Table 4.1 Elemental composition (as mass fraction) and higher heat value (HHV) of LignoBoost Kraft lignin used as feed material. The data are reported on a dry lignin basis, together with available uncertainties (95% confidence interval), relative (rel.) or absolute (abs.). Oxygen is calculated by difference.

Elemental composition (%)		Uncertainty
C	65.6	2% (rel.)
H	5.7	6% (rel.)
N	0.09	0.02 (abs.)
S	1.85	10% (rel.)
Cl	0.01	0.02 (abs.)
Ash	0.8	0.3 (abs.)
O	26	-
Na	0.23	-
K	0.07	-
HHV (MJ/kg)	27.67	0.39 (abs.)

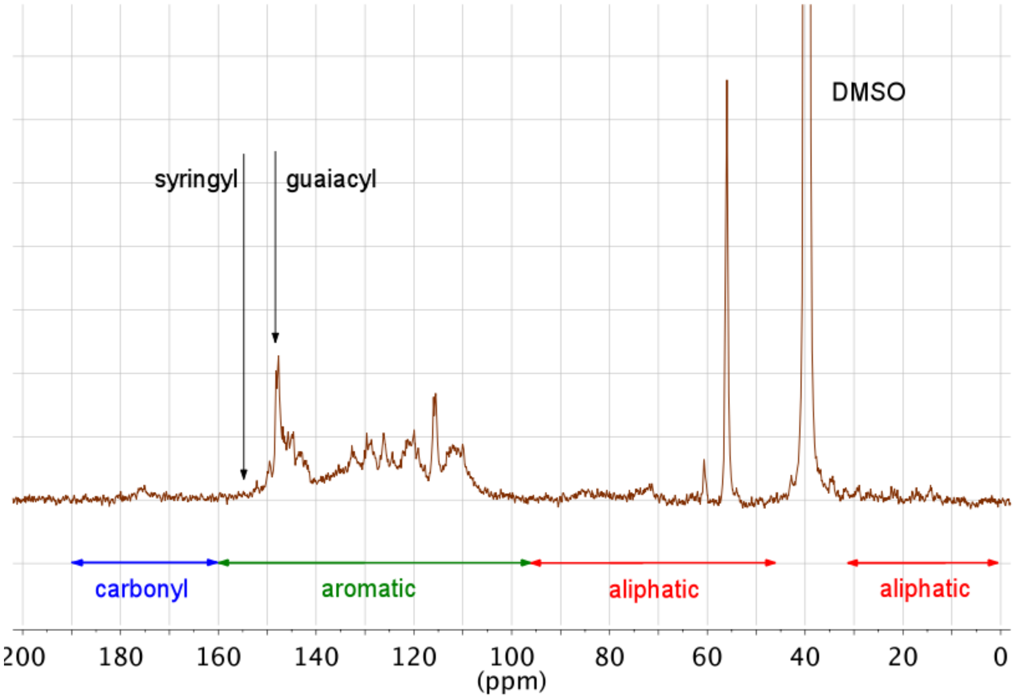


Figure 4.1 ^{13}C-NMR spectrum of the LignoBoost Kraft lignin used in the feed.

4.2. Nature of the liquid products after centrifugation

The physical appearance of liquid products is shown in **Figure 4.2**. The liquid products are composed of oil and an aqueous phase in all of the runs with the exception of Run E: being the reference run without lignin in the feed, it therefore had only a homogeneous aqueous phase. The visual appearance of the aqueous phase in Runs A – D ranged from yellowish to dark green as the mass fraction of K_2CO_3 in the feed increased; in Runs F – I, it was the same as in Run C due to the mass fraction of K_2CO_3 being the same. In **Table 4.2**, the steady-state oil fraction and pH, TC and TOC of the aqueous phase are reported. As can be seen, the oil fraction is between 4.9 and 6.6% of the total output flow rate. Comparing the pH values in **Table 3.1** (feed value) with **Table 4.2** (output value), it is obvious that the pH decreases, thus showing that the reactions involve the consumption of (OH^-) ions. Also, the pH of the aqueous phase after centrifugation increases from 7.1 to 8.2 as the mass fraction of K_2CO_3 in the feed increasesfrom 0.4 to 2.2%, which means that the base content in the aqueous phase increases as the base content in the feed increases. However, the pH of the aqueous phase decreases from 8.5 to 7.9 as the reaction temperature increases from 290 to 370 ^oC. So it is the higher reaction temperature that causes the larger consumption of (OH^-) ions. In the case of Run E (no lignin in the feed), on the other hand, the pH of the product is the same as the pH of the feed, providing that no reaction involving (OH^-) ions occurs. The concentration of organic carbon in the aqueous phase is between 25 and 27 g/L. Since the density of the aqueous phase is approx. 1000 kg/m^3, this also means that the mass fraction of organic carbon in the aqueous phase is in the range of 2.5–2.7%. The TC values are slightly higher than the TOC.

Figure 4.2 Typical appearance of the aqueous (left) and oil phases (right) after centrifugation.

Table 4.2 Steady-state output data of the experiments in Runs A – I. Oil/Total is the ratio between the mass flow rate of the output oil and the total mass flow rate at steady-state. pH$_a$, TC$_a$ and TOC$_a$ are pH, total carbon and total organic carbon of the aqueous phase after centrifugation.

Steady-state output data	K_2CO_3 mass fraction series					Reaction temperature series			
	A	B	C	D	E	F	G	H	I
Oil/Total (%)	5.2	5.1	5.3	5.6	0	6.6	6.0	5.8	4.9
pH$_a$	7.1	7.4	8.0	8.2	9.6	8.5	8.2	8.2	7.9
TC$_a$ (g/L)	28	27	29	30	-	27	28	27	28
TOC$_a$ (g/L)	27	26	27	27	-	25	26	25	26

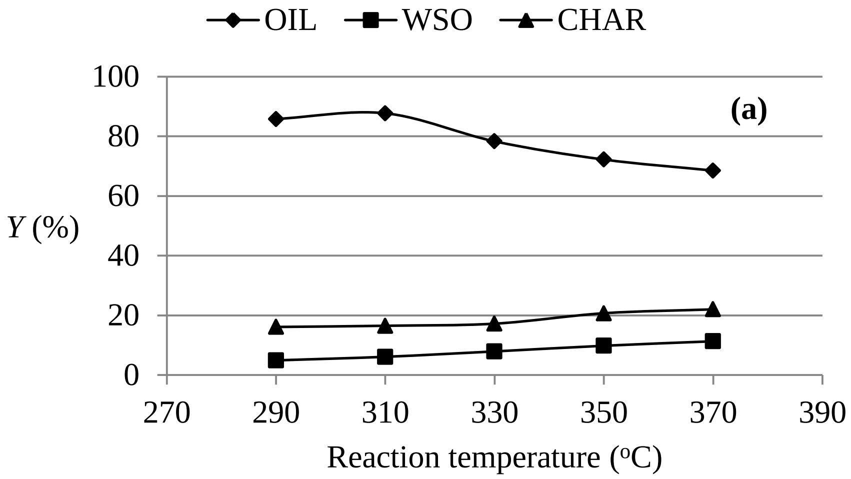
4.3. Carbon balances and product yields

The total carbon balance was calculated, i.e. including phenol and inorganic carbon. In these calculations the carbon content of char was assumed to be the same as that of dry lignin. It was found that the sum of the output and the accumulated carbon accounts from 95 to 103% of the carbon input. Overall, these results show that a very reliable carbon balance is obtained in all runs, indicating that the loss during the analytical procedure is very small. Elemental analysis of oil samples was used to calculate the ratio of potassium ending up in the wet oil to that entering the system. It was found that this value decreases from 9.1 to 7.0% as mass fraction of K_2CO_3 increases from 0.4 to 2.2%. This indicates that some potassium salts may precipitate or that potassium ions may act as counter ions, bonding with some organic acids in the lignin-oil during the process. This aspect should be investigated further in the development of the downstream processing of the lignin-oil. Furthermore, in the reaction temperature series used, this value was in the range of 6.5–9.2%, with no clear trend being discernable. This range coincides approx. to that found when the reactor was operated at 350 °C. In the ranges of the operating variables tested, it can be summarised that the amount of potassium found in the oil was quite constant, with values in the range of approx. 7–9%.

The product yields are reported in **Table 4.3**. These are calculated taking three different products into consideration: dry lignin-oil (OIL), water-soluble organics in the acidified aqueous phase (WSO) and char (CHAR). The corresponding yields (*Y*) are defined here as the mass of phenol-free products relative to the mass of dry lignin fed into the system. The calculations are made assuming that the average rate of char formation during the entire run (i.e. start-up, steady-state and cooling down) is equal to the rate of formation at steady-state. **Figure 4.3** shows the product yields as functions of K_2CO_3 mass fraction and reaction temperature. The yield of dry lignin-oil is approx. constant around 70% at a reaction temperature of 350 ^{o}C. In the temperature series, however, this value is around 85–88% at the two lower reaction temperatures (290 and 310 ^{o}C), decreasing to 69% as the reaction temperature increases to 370 ^{o}C. This means the oil yield is improved as reaction temperature decreases but, on the other hand, the amount of water-soluble organics found in the acidified aqueous phase increases slightly, from 9 to 11% of dry lignin, as the mass fraction of K_2CO_3 increases from 0.4 to 2.2%, and increases from 5 to 11% as the reaction temperature increases from 290 to 370 ^{o}C. As far as the amount of char deposited on the catalyst is concerned, this fraction is about 20% of the dry lignin at a reaction temperature of 350 ^{o}C. This value increases from 16 to 22% as the reaction temperature increases from 290 to 370 ^{o}C. Consequently, the reaction temperature has the different effects on the yields of both the lignin-oil and the char.

Table 4.3 Yields (%) of lignin-oil (Y_{OIL}), water-soluble organics in the acidified aqueous phase (Y_{WSO}) and char (Y_{CHAR}) calculated on phenol-free products on a dry lignin basis.

	K_2CO_3 mass fraction series				Reaction temperature series			
	A	B	C	D	F	G	H	I
Y_{OIL}	70.2	69.4	72.2	70.9	85.8	87.7	78.3	68.5
Y_{WSO}	8.7	8.9	9.8	10.8	4.9	6.1	7.9	11.3
Y_{CHAR}	20.6	17.8	20.7	17.2	16.1	16.5	17.2	22.0



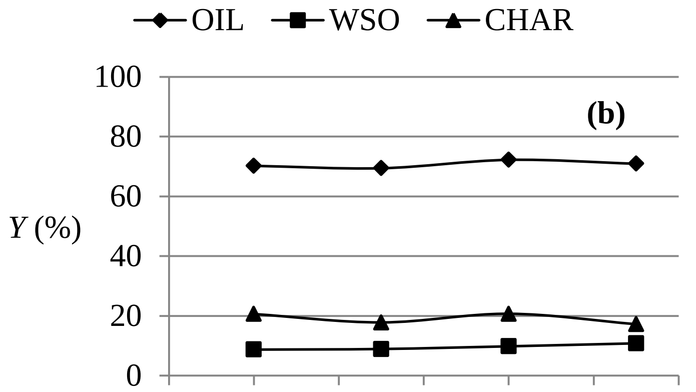


Figure 4.3 Yields (Y) of oil (OIL), water-soluble organics in the acidified aqueous phase (WSO) and char (CHAR) as a function of a) the reaction temperature (at K_2CO_3 mass fraction of 1.6%) and b) K_2CO_3 mass fraction (at the reaction temperature of 350 °C). Yields are defined on phenol-free dry reaction products on a dry lignin basis.

4.4. Effect of K_2CO_3 concentration

4.4.1. Aqueous phase

The mass of gas released during the acidification of the aqueous phase samples increases from 0.1 to 1.0% (on the basis of the sample's initial mass) from Run A to D, i.e. as the mass fraction of K_2CO_3 increases from 0.4 to 2.2%. In Runs A – C the mass of gas released is approx. equal to the mass of carbon dioxide expected from carbonates: the gas released in the sample from Run D, however, exceeds this expected value, which means that additional carbon dioxide and/or other gases must be released in the acidification process. Using the steady state data of Run D, this excess is found to be approx. 5% on the basis of the lignin fed into the reactor.

The GC-MS analysis of the aqueous phase produced in Run E (the reference run without lignin) shows that, with the exception of trace amounts of other compounds such as alkylphenols, phenol is the only solute in the aqueous phase: this is consistent with the profile of the impurities present in the reagent grade of the phenol used in the experiments.

Figure 4.4 shows a typical GC-MS total ion chromatogram (TIC) of the DEE extracts of the acidified aqueous sample obtained when lignin was fed into the system; the structure of the compounds identified is reported, along with number labels. When different isomers are compatible with a peak, the structure reported is one of the possible isomers. The mass fraction of the compounds identified by GC-MS in the acidified aqueous phase together with total values including, and excluding, phenol is reported in **Table 4.4**. The method used for determining mass fractions can be considered as being semi-quantitative, since it is assumed that the response factors of the MS detector and extraction yields from the acidified aqueous phase are the same for each compound. Besides phenol, which is used in the feed, the main compounds detected are alkylphenols (e.g. cresols), guaiacols (i.e. guaiacol and alkylguaiacols) and catechols (i.e. catechol and alkylcatechols). Alkyl side groups of aromatic rings are of a methyl or ethyl type only. Moreover, two non-phenolic aromatic compounds are also found (i.e. anisole and hydrocoumarin) along with small amounts of methanol, acetic acid, 2-butanone, propanoic acid, 3-methoxycatechol, salicylic acid, 4-hydroxybenzaldehyde, dimethylbenzenediol and three phenolic dimers of the type C6-C1-C6 (see **Figure 4.4**). The same set of compounds is found in Runs A – D (i.e. at different mass fractions of K_2CO_3). Since these are not found in Run E, it can be concluded that the compounds found in the aqueous phase of the runs with lignin in the feed derive from the chemical conversion of lignin. In **Table 4.5**, the mass fraction of the main classes of the compounds in the acidified aqueous phase for each run with lignin in the feed can be seen. The various main classes of the compounds show different trends as the mass fraction of K_2CO_3 increases from 0.4 to 2.2%. In particular, an increase in the mass fraction of catechols (from 0.22 to 0.30%) and alkylphenols (from 0.17 to 0.21%), together with a decrease in the mass fraction of guaiacols (from 0.10 to 0.04%) are observed. These results are in accordance with previous results reported in the literature (Karagöz, 2006; Bhaskar, 2008). The total mass fraction of organic compounds (excluding phenol) also increases (from 0.52 to 0.63%) with increasing K_2CO_3.

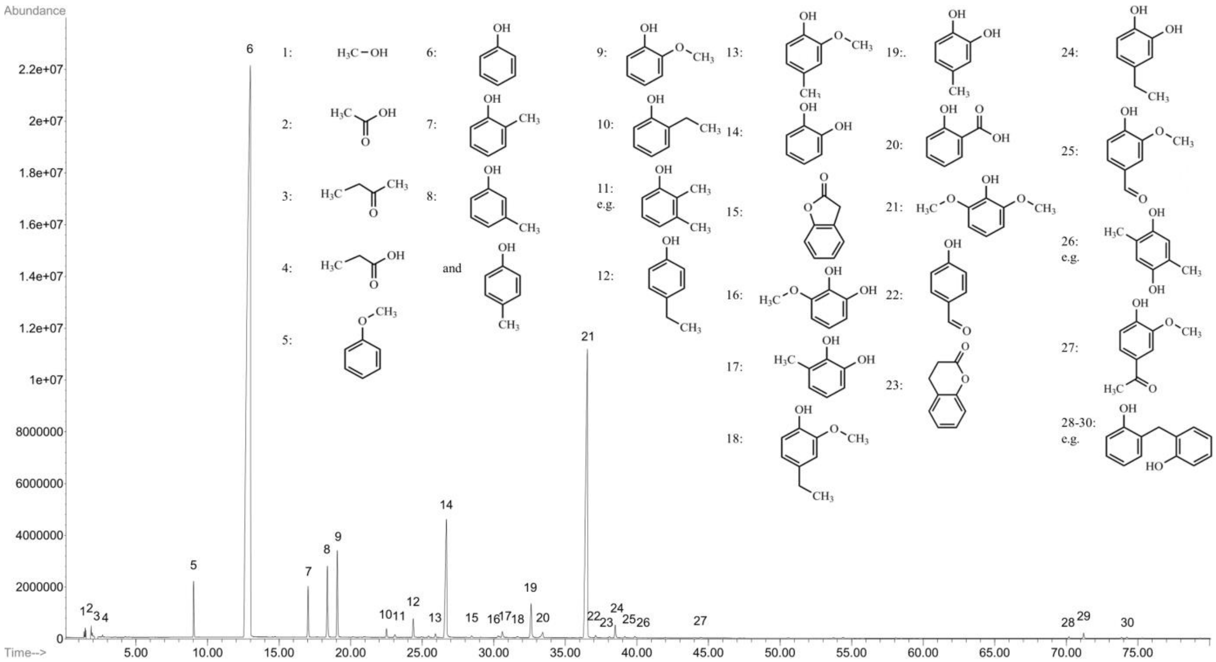


Figure 4.4 Typical GC-MS TIC of the DEE extracts of the acidified aqueous phase (sample from Run H). Peak 21 is the internal standard (syringol).

Table 4.4 Mass fraction (%) of the compounds identified by GC-MS in the acidified aqueous phase for each runs with lignin in the feed. LOD indicates the limit of detection.

	Compound	A	B	C	D
1	Methanol	0.004	0.004	0.004	0.002
2	Acetic acid	0.004	0.005	0.006	0.006
3	2-Butanone	0.004	0.004	0.004	0.003

4	Propanoic acid	0.002	0.002	0.002	0.002
5	Anisole	0.001	0.001	0.001	0.034
6	Phenol	2.183	2.078	1.964	1.648
7	*o*-Cresol	0.061	0.064	0.067	0.073
8	*m/p*-Cresol[1]	0.069	0.088	0.099	0.103
9	Guaiacol	0.094	0.067	0.054	0.038
10	2-Ethylphenol	0.013	0.011	0.010	0.010
11	Dimethylphenol	0.003	0.004	0.005	0.007
12	4-Ethylphenol	0.020	0.020	0.020	0.020
13	4-Methylguaiacol	0.006	0.004	0.003	0.002
14	Catechol	0.144	0.166	0.193	0.196
16	3-Methoxycatechol	0.005	0.005	0.006	0.002
17	3-Methylcatechol	0.009	0.010	0.013	0.018
18	4-Ethylguaiacol	0.004	0.001	<LOD	0.000
19	4-Methylcatechol	0.044	0.038	0.051	0.070
20	Salicylic acid	<LOD	<LOD	0.002	0.010
21	Syringol[2]	-	-	-	-
22	4-Hydroxybenzaldehyde	<LOD	<LOD	0.001	0.003
23	Hydrocoumarin	0.001	0.002	0.003	0.002
24	4-Ethylcatechol	0.019	0.013	0.016	0.019
26	Dimethylbenzenediol	0.002	0.002	0.002	0.003
28 – 30	Phenolic dimers (C6-C1-C6)	0.007	0.006	0.006	0.005
Total mass fraction including phenol		2.699	2.595	2.532	2.276
Total mass fraction excluding phenol		0.516	0.517	0.568	0.628

[1] *p*-Cresol and *m*-Cresol elute together

[2] Internal standard

Table 4.5 Mass fraction (%) of the main classes of the compounds in the acidified aqueous phase for each runs with lignin in the feed.

Class	A	B	C	D
Phenol	2.18	2.08	1.96	1.65
Alkylphenols	0.17	0.19	0.20	0.21
Guaiacols	0.10	0.07	0.06	0.04
Catechols	0.22	0.23	0.27	0.30
Phenolic dimers	0.01	0.01	0.01	0.01

4.4.2. Lignin-oil

Table 4.6 shows the water content of the oil separated from the aqueous phase both before and after vacuum evaporation (35 °C) together with the THF-insoluble SS. As can be seen, a large reduction in the water content (86–91%) is achieved during the removal of the solvent due to the manual separation of the oil from the aqueous phase after centrifugation. This situation can be eliminated by using the centrifugation or gravimetrical separator that is installed in the output pipe where the samples are collected in the pilot unit. The SS values are reported as a mass fraction on a dry lignin-oil basis (i.e. a THF-free and water-free basis), referring to the mass of retained solids on the filters P2 and P4, respectively. The total mass of retained solids (P2 and P4) is also given. It can be seen that the THF-insoluble SS are quite low in Runs A and B (with lower mass fraction of K_2CO_3) whereas they increase remarkably with higher K_2CO_3. In **Table 4.7**, elemental analysis, ash content and higher heat value measured on the oil samples obtained after evaporation are reported on a dry lignin-oil basis. It can be observed that the oil has been partially deoxygenated and that its carbon content is higher than that of lignin. The lower oxygen content of the oil renders it more chemically stable than the bio crude oil obtained by fast pyrolysis. A consistent increase in the heat value is also observed (+15% on average). Furthermore, the sulphur content is reduced, on average, from 1.85 to 0.36%; the ash content in the dry lignin-oil increases from 1.0 to 3.5% as the mass fraction of K_2CO_3 increases from 0.4 to 2.2% due to the increase in the amount of potassium ion.

Table 4.6 Water content and THF-insoluble suspended solids in the lignin-oil. Water mass fraction (%) in lignin-oil is given before and after vacuum evaporation to remove the THF. The suspended solids are given as mass fraction (%) on a dry lignin-oil basis (i.e. THF-free and water-free basis).

	A	B	C	D
Water content before evaporation	12.7	12.4	14.1	18.4
Water content after evaporation	1.2	1.1	2.0	1.8
Suspended solids on P2	0.0	0.1	0.6	2.4
Suspended solids on P4	0.1	1.8	22.2	20.5
Suspended solids	0.1	1.9	22.8	22.9

Table 4.7 Elemental composition (as mass fraction) and HHV of the lignin-oil obtained by hydrothermal depolymerisation and conversion of LignoBoost Kraft lignin. The data are reported on a dry lignin-oil basis, together with available uncertainties (95% confidence interval), absolute (abs.) for HHV or relative (rel.) for the others. Oxygen is calculated by difference.

Elemental composition (%)	A	B	C	D	Uncertainty
C	74.6	74.2	74.9	74.8	1.1
H	6.9	6.9	6.6	6.5	4
N	<0.1	<0.1	<0.1	-	20
S	0.37	0.38	0.38	0.29	16
Cl	<0.01	<0.01	<0.01	<0.01	-
Ash	1.0	2.1	2.8	3.5	-
O	17	16	15	15	-
Na	<0.01	<0.01	0.01	<0.01	-
K	0.5	1.0	1.6	1.9	-
HHV (MJ/kg)	31.93	31.83	31.90	31.86	0.16

A typical GC-MS TIC of the DEE-soluble fraction in the lignin-oil samples obtained in the runs containing lignin in the feed is shown in **Figure 4.5**. The structure of the compounds identified is also reported; along with number labels referring to **Table 4.8** in which the mass fractions of these compounds, along with total values including, and excluding, phenol are shown. When different isomers are compatible with a peak, the structure reported in **Figure 4.5** is one of the possible isomers. The DEE-soluble fraction of lignin-oil identified by GC-MS is in the range of 27–40% of the original weight of oil, and contains a large amount of 1-ring aromatic compounds. Besides phenol (from 13 to 16%), the compounds with high mass fractions are anisoles, alkylphenols, guaiacols and catechols. Some 2-ring phenolic compounds (phenolic dimers), with a C6-C1-C6 or C6-C2-C6 structure, are also found. Most of the compounds in the DEE-soluble fraction of lignin-oil are the same as in the aqueous phase, but the relative concentration differs depending on their hydrophilic or hydrophobic nature. For example, catechol with two hydroxyl (-OH) groups bonding to the aromatic ring exhibits a hydrophilic nature and is therefore relatively more abundant in the aqueous phase, whereas anisole with one methoxy (-OCH_3) group on the aromatic ring exhibits a hydrophobic nature and is concentrated in the oil. Also, some compounds not found in the aqueous phase are identified in the DEE-soluble fraction of lignin-oil, as in the case for alkylanisoles, 1-ring phenolic compounds with propyl side groups, ethylcresols, 2-acetylphenol and two 3-ring compounds (see **Figure 4.5**). In **Table 4.9**, the mass fraction of the main classes of DEE-soluble compounds in lignin-oil for each run with lignin in the feed is reported. The total mass fraction of these specific classes shows the same trends as with the water-soluble compounds in the aqueous phase.

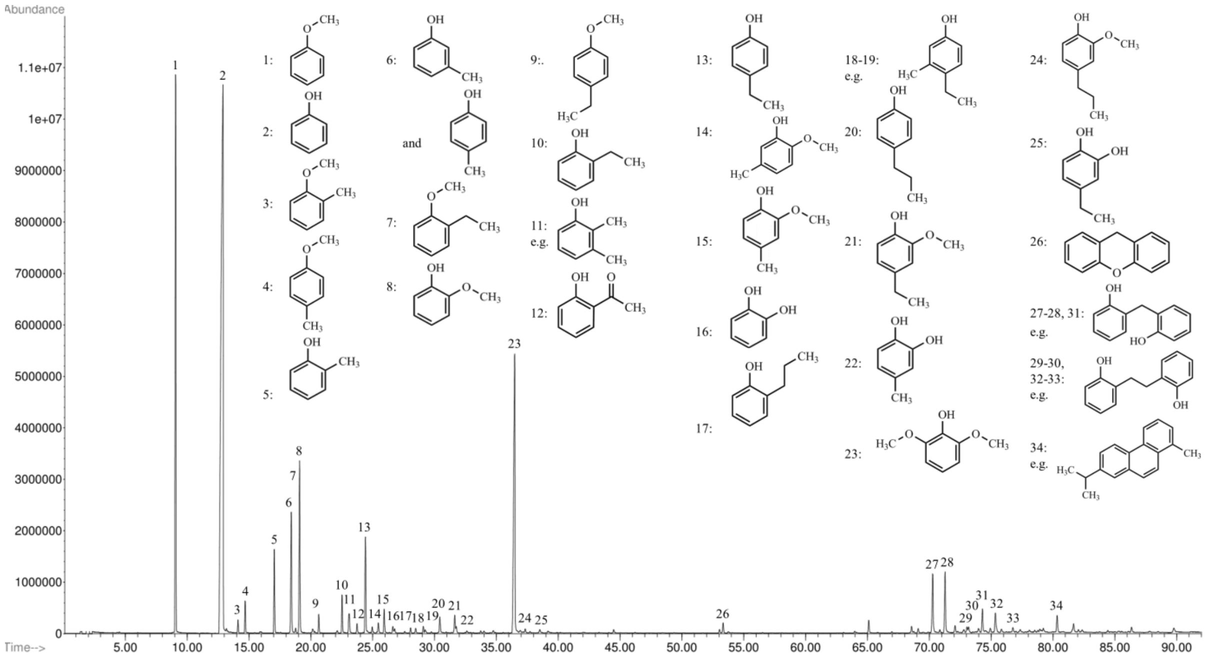


Figure 4.5 Typical GC-MS TIC of the DEE-soluble fraction of lignin-oil (sample from Run H). Peak 23 is the internal standard (syringol).

Table 4.8 Mass fraction (%) of the compounds identified by GC-MS in the DEE-soluble fraction of the lignin-oil. Mass fraction, based on a dry lignin-oil, is reported for each runs with lignin in the feed.

	Compound	A	B	C	D
1	Anisole	2.103	4.412	4.414	8.170
2	Phenol	13.428	14.559	12.797	16.220
3	2-Methylanisole	0.064	0.147	0.173	0.270
4	4-Methylanisole	0.133	0.330	0.409	0.652
5	*o*-Cresol	0.936	1.155	1.158	1.306
6	*m/p*-Cresol[1]	1.202	1.809	1.923	2.257
7	2-Ethylanisole	0.042	0.075	0.094	0.114
8	Guaiacol	1.969	1.729	1.344	1.818
9	4-Ethylanisole	0.087	0.189	0.238	0.323
10	2-Ethylphenol	0.538	0.563	0.511	0.541
11	Dimethylphenol	0.251	0.361	0.402	0.507
12	2-Acetylphenol	0.102	0.153	0.156	0.238
13	4-Ethylphenol	1.006	1.241	1.200	1.363
14	5-Methylguaiacol	0.125	0.155	0.146	0.188
15	4-Methylguaiacol	0.389	0.313	0.253	0.340
16	Catechol	0.182	0.206	0.181	0.275
17	2-Propylphenol	0.087	0.095	0.088	0.091
18 – 19	Ethylcresols	0.183	0.239	0.259	0.292
20	4-Propylphenol	0.231	0.281	0.288	0.301
21	4-Ethylguaiacol	0.571	0.276	0.204	0.249
22	4-Methylcatechol	0.196	0.202	0.122	0.282
23	Syringol[2]	-	-	-	-
24	4-Propylguaiacol	0.156	0.069	0.050	0.061
25	4-Ethylcatechol	0.213	0.167	0.113	0.245
26	9H-Xanthene	0.232	0.169	0.100	0.449
27 – 28, 31	Phenolic dimers (C6-C1-C6)	1.530	1.634	1.357	2.087

29 – 30, 32 – 33	Phenolic dimers (C6-C2-C6)	0.375	0.488	0.485	0.670
34	Isopropyl-methyl-phenanthrene	0.367	0.322	0.242	0.212
Total mass fraction including phenol		26.70	31.34	28.71	39.52
Total mass fraction excluding phenol		13.27	16.78	15.91	23.30

[1] *p*-Cresol and *m*-Cresol elute together

[2] Internal standard

Table 4.9 Mass fraction (%) of the main classes of compounds of the DEE-soluble fraction in the lignin-oil. Mass fraction, based on dry lignin-oil, is reported for each runs with lignin in the feed.

Class	A	B	C	D
Anisoles	2.39	5.08	5.23	9.42
Phenol	13.43	14.56	12.80	16.22
Alkylphenols	4.26	5.54	5.83	6.44
Guaiacols	3.21	2.54	2.00	2.66
Catechols	0.59	0.58	0.42	0.80
Phenolic dimers	1.79	2.02	1.84	2.61

4.4.3. Overall yields of 1-ring aromatic compounds

Table 4.10 shows the yields of different classes of 1-ring aromatic compounds, taking into account the quantities found in both the aqueous phase and the DEE-fraction in the oil phase on a dry lignin basis. As can be seen, the overall yield increases remarkably from approx. 17 to more than 27% as the mass fraction of K_2CO_3 increases from 0.4 to 2.2%. The larger relative increase is found for anisoles in particular (from 20 to 86 g/kg), while alkylphenols and catechols increase moderately; the maximum yield of guaiacols is to be found at the lowest mass fraction of K_2CO_3.

Table 4.10 Yields (%) of different classes of aromatic compounds (in the aqueous phase and DEE-soluble lignin-oil) produced in the depolymerisation and conversion of lignin, calculated on a dry lignin basis.

Class	A	B	C	D
Anisoles	2.0	4.1	4.4	8.6
Alkylphenols	6.3	7.7	8.3	9.2
Guaiacols	4.4	3.3	2.6	2.9
Catechols	4.1	4.4	5.0	6.0
Phenolic dimers	1.6	1.7	1.5	2.3
Total 1-ring aromatic compounds*	16.9	19.8	20.8	27.1

*These include 2-acetylphenol, 3-methoxycatechol, salicylic acid, 4-hydrobenzaldehyde, hydrocoumarin and dimethylbenzenediol.

4.5. Effect of reaction temperature

4.5.1. Aqueous phase

In this series of experimental runs (i.e. the reaction temperature was varied), the mass of gas released is approx. equal to the mass of carbon dioxide expected from the carbonates. In **Table 4.11**, the mass fraction of the compounds identified by GC-MS in the acidified aqueous phase is reported, together with total values including, and excluding, phenol. The main compounds detected besides phenol, which is used in the feed, are alkylphenols, guaiacols and catechols. Other phenolic compounds detected are 3-methoxycatechol, salicylic acid, 4-hydroxybenzaldehyde, dimethylbenzenediol, vanillin, acetovanillone and three phenolic dimers with the structure C6-C1-C6. Alkyl side groups of aromatic rings are of methyl or ethyl type only. Furthermore, three non-phenolic aromatic compounds are found (i.e. anisole, 2-coumaranone and hydrocoumarin), together with small amounts of methanol, acetic acid, 2-butanone and propanoic acid.

Table 4.11 Mass fraction (%) of the compounds identified by GC-MS in the acidified aqueous phase for each runs with lignin in the feed. LOD indicates the limit of detection.

	Compound	F	G	H	C	I
1	Methanol	0.002	0.003	0.003	0.004	0.003
2	Acetic acid	0.005	0.005	0.006	0.006	0.007

3	2-Butanone	0.004	0.007	0.006	0.004	0.006
4	Propanoic acid	0.002	0.002	0.002	0.002	0.003
5	Anisole	0.014	0.021	0.031	0.001	0.030
6	Phenol	1.806	1.714	1.639	1.964	1.702
7	*o*-Cresol	0.006	0.016	0.037	0.067	0.109
8	*m/p*-Cresol[1]	0.010	0.026	0.057	0.099	0.134
9	Guaiacol	0.123	0.104	0.068	0.054	0.022
10	2-Ethylphenol	0.002	0.004	0.007	0.010	0.013
11	Dimethylphenol	0.001	0.001	0.003	0.005	0.010
12	4-Ethylphenol	0.006	0.010	0.014	0.020	0.023
13	4-Methylguaiacol	0.002	0.003	0.003	0.003	0.001
14	Catechol	0.065	0.101	0.148	0.193	0.191
15	2-Coumaranone	0.004	0.003	0.002	<LOD	0.001
16	3-Methoxycatechol	0.003	0.002	0.002	0.006	0.001
17	3-Methylcatechol	0.001	0.002	0.006	0.013	0.019
18	4-Ethylguaiacol	0.001	0.001	0.001	<LOD	0.001
19	4-Methylcatechol	0.004	0.014	0.035	0.051	0.054
20	Salicylic acid	0.004	0.006	0.008	0.002	0.004
21	Syringol[2]	-	-	-	-	-
22	4-Hydroxybenzaldehyde	0.003	0.002	0.002	0.001	0.002
23	Hydrocoumarin	0.001	0.001	0.001	0.003	0.002
24	4-Ethylcatechol	0.002	0.005	0.011	0.016	0.014
25	Vanillin	0.004	0.002	0.001	<LOD	<LOD
26	Dimethylbenzenediol	<LOD	0.001	0.002	0.002	0.002
27	Acetovanillone	0.002	0.001	0.001	<LOD	<LOD
28 – 30	Phenolic dimers (C6-C1-C6)	0.016	0.015	0.007	0.006	0.001
Total mass fraction including phenol		2.093	2.072	2.103	2.532	2.355
Total mass fraction excluding phenol		0.287	0.358	0.464	0.568	0.653

[1] *p*-Cresol and *m*-Cresol elute together

[2] Internal standard

Table 4.12 Mass fraction (%) of the main classes of the compounds in the acidified aqueous phase for each runs with lignin in the feed.

Class	F	G	H	C	I
Phenol	1.81	1.71	1.64	1.96	1.70
Alkylphenols	0.03	0.06	0.12	0.20	0.29
Guaiacols	0.13	0.11	0.07	0.06	0.02
Catechols	0.07	0.12	0.20	0.27	0.28
Phenolic dimers	0.02	0.02	0.01	0.01	0.00

Table 4.12 gives the mass fraction of the main classes of the compounds in the acidified aqueous phase for each run with lignin in the feed. Here, the mass fractions of catechols and alkylphenols are seen to increase with an increase in reaction temperature, whereas those of guaiacols and phenolic dimers decrease. More specifically, the mass fraction of alkylphenols increases from 0.03 to 0.29%, catechols increases from 0.07 to 0.28% and guaiacols decreases from 0.13 to 0.02%. The mass fractions of both vanillin and acetovanillone also decrease with reaction temperature even though the amounts detected are small; these two compounds are not detected in the two runs at the higher temperatures (350 and 370 ^{o}C) (see **Table 4.11**). These results are consistent with those of Lavoie et al. (2011), Beauchet et al. (2012) and Pińkowska et al. (2012). It may be summarised that the total mass fraction of water-soluble organic compounds (excluding phenol) in the aqueous phase clearly increases as the reaction temperature increases (see **Table 4.11**).

4.5.2. Lignin-oil

Table 4.13 shows the water content of the oil separated from the aqueous phase both before and after vacuum evaporation (35 °C), along with the THF-insoluble SS. As can be seen, a large reduction in the water content (approx. 80%) is also achieved during the removal of the solvent. The SS values are reported as mass fraction on a dry lignin-oil basis (i.e. a THF-free and water-free basis), referring to the mass of solids retained on the filters P2 and P4, respectively; the total mass of these solids is also given. Although there is no clear trend visible of the total amount of SS present in Runs F – I, the data clearly show whereas the fraction of SS with larger size (i.e. retained on filter P2) is high at lower temperatures (290 and 310 °C), it is quite low at higher temperatures (from 330 °C upwards), when fine particles predominate. A minimum value of SS was obtained at 330 °C (8.6%), the reason for which is not known.

Table 4.13 Water content and THF-insoluble suspended solids in the lignin-oil. Water mass fraction (%) in lignin-oil is given before and after vacuum evaporation to remove the THF. The suspended solids are given as mass fraction (%) on a dry lignin-oil basis (i.e. THF-free and water-free basis).

	F	G	H	C	I
Water content before evaporation	19.2	10.9	15.2	14.1	13.3
Water content after evaporation	9.8	1.3	2.4	2.0	2.1
Suspended solids on P2	21.2	14.0	0.3	0.6	1.9
Suspended solids on P4	2.6	11.4	8.3	22.2	11.3
Suspended solids	23.8	25.4	8.6	22.8	13.2

Elemental analysis, ash content and higher heat value measured on the oil samples obtained after evaporation are reported on a dry lignin-oil basis in **Table 4.14**. It shows that the oil has been partially deoxygenated and that the carbon content is higher than in lignin. A consistent increase in the heat value is also observed (+14% on average). Furthermore, the sulphur content is reduced, on average, from 1.85 to 0.42% and the ash content is increased, on average, from 1.0 to 2.3%.

Table 4.14 Elemental composition (as mass fraction) and HHV of the lignin-oil obtained by hydrothermal depolymerisation and conversion of LignoBoost Kraft lignin. The data are reported on a dry lignin-oil basis, together with available uncertainties (95% confidence interval), absolute (abs.) for HHV or relative (rel.) for the others. Oxygen is calculated by difference.

Elemental composition (%)	F	G	H	C	I	Uncertainty
C	70.0	72.6	73.9	74.9	76.0	1.1
H	6.5	6.4	6.1	6.6	6.8	4
N	-	<0.1	<0.1	<0.1	<0.1	20
S	0.41	0.51	0.56	0.38	0.25	16

Cl	<0.01	<0.01	<0.01	<0.01	<0.01	-
Ash	2.4	2.0	2.4	2.8	1.8	-
O	21	18	17	15	15	-
Na	0.01	0.01	0.01	0.01	0.01	-
K	1.5	1.4	1.7	1.6	1.4	-
HHV (MJ/kg)	31.66	31.12	31.03	31.90	32.73	0.16

Table 4.15 shows the mass fraction (based on a dry lignin-oil) of compounds identified by GC-MS in the DEE-soluble fraction of the lignin-oil. The DEE-soluble fraction of lignin-oil that is identified in GC-MS is in the range of 21–29% of the original weight of the oil and contains a large amount of 1-ring aromatic compounds. Apart from phenol (from 10 to 13%), the 1-ring aromatic compounds with relatively high mass fractions at the temperature investigated, based on dry lignin-oil, are anisoles (increasing with the temperature from 2 to 6%), alkylphenols (increasing from 1 to 8%), guaiacols (decreasing from 3 to 1%), and a small amount of catechols (increasing from 0.1 to 0.6%). A large amount of phenolic dimers are also found (decreasing from 5 to 1%), with a C6-C1-C6 or C6-C2-C6 structure. Most of the compounds in the DEE-soluble fraction of lignin-oil are the same as in the aqueous phase, with distribution coefficients that depend on whether they are hydrophilic or hydrophobic nature. In addition, some compounds not found in the aqueous phase are identified in the DEE-soluble fraction of lignin-oil, such as alkylanisoles, 1-ring phenolic compounds with propyl side groups, ethylcresols, acetylphenol and two 3-ring compounds (see **Figure 4.5**). The total mass fraction of DEE-soluble compounds in lignin-oil increases with increasing the reaction temperature; with regard to specific classes of compounds, the amount of anisoles, alkylphenols and catechols increases whilst that of phenolic dimers and guaiacols decreases (see **Table 4.16**). These trends are also found for the water-soluble compounds in the aqueous phase.

Table 4.15 Mass fraction (%) of the compounds identified by GC-MS in the DEE-soluble fraction of the lignin-oil. Mass fraction, based on a dry lignin-oil, is reported for each runs with lignin in the feed.

	Compound	F	G	H	C	I
1	Anisole	1.964	2.897	4.173	4.414	4.966
2	Phenol	11.505	9.772	12.436	12.797	11.351
3	2-Methylanisole	0.011	0.032	0.098	0.173	0.273

4	4-Methylanisole	0.023	0.074	0.242	0.409	0.570
5	*o*-Cresol	0.101	0.222	0.662	1.158	1.823
6	*m/p*-Cresol[1]	0.187	0.413	1.167	1.923	2.533
7	2-Ethylanisole	0.007	0.018	0.047	0.094	0.128
8	Guaiacol	2.226	1.820	1.586	1.344	0.611
9	4-Ethylanisole	0.031	0.066	0.156	0.238	0.232
10	2-Ethylphenol	0.100	0.163	0.321	0.511	0.637
11	Dimethylphenol	0.137	0.165	0.253	0.402	0.605
12	2-Acetylphenol	0.080	0.093	0.104	0.156	0.114
13	4-Ethylphenol	0.315	0.473	0.848	1.200	1.278
14	5-Methylguaiacol	0.018	0.047	0.105	0.146	0.103
15	4-Methylguaiacol	0.118	0.167	0.230	0.253	0.145
16	Catechol	0.096	0.115	0.097	0.181	0.212
17	2-Propylphenol	0.014	0.024	0.049	0.088	0.126
18 – 19	Ethylcresols	0.022	0.045	0.119	0.259	0.409
20	4-Propylphenol	0.077	0.109	0.181	0.288	0.341
21	4-Ethylguaiacol	0.155	0.180	0.193	0.204	0.120
22	4-Methylcatechol	0.017	0.059	0.039	0.122	0.219
23	Syringol[2]	-	-	-	-	-
24	4-Propylguaiacol	0.031	0.041	0.048	0.050	0.038
25	4-Ethylcatechol	0.026	0.078	0.051	0.113	0.191
26	9H-Xanthene	0.129	0.195	0.103	0.100	0.346
27 – 28, 31	Phenolic dimers (C6-C1-C6)	3.973	3.254	1.760	1.357	0.665
29 – 30, 32 – 33	Phenolic dimers (C6-C2-C6)	1.104	0.822	0.513	0.485	0.366
34	Isopropyl-methyl-phenanthrene	0.073	0.127	0.182	0.242	0.264
Total mass fraction including phenol		22.54	21.47	25.76	28.71	28.67
Total mass fraction excluding phenol		11.04	11.70	13.33	15.91	17.32

[1] *p*-Cresol and *m*-Cresol elute together

[2] Internal standard

Table 4.16 Mass fraction (%) of the main classes of compounds of the DEE-soluble fraction in the lignin-oil. Mass fraction, based on dry lignin-oil, is reported for each runs with lignin in the feed.

Class	F	G	H	C	I
Anisoles	2.04	3.09	4.72	5.23	6.17
Phenol	11.51	9.77	12.44	12.80	11.35
Alkylphenols	0.95	1.61	3.60	5.83	7.75
Guaiacols	2.55	2.26	2.16	2.00	1.02
Catechols	0.14	0.25	0.19	0.42	0.62
Phenolic dimers	5.08	4.08	2.27	1.84	1.03

4.5.3. Overall yields of 1-ring aromatic compounds

Table 4.17 gives the overall yields of specific classes of 1-ring aromatic compounds and phenolic dimers, taking into account the quantities found in both the aqueous phase and the oil phase. The overall yield increases remarkably from 10 to 23% with increasing reaction temperature, which varies from 290 to 370 ^{o}C. In particular, the larger relative increase is found for alkylphenols (from 14 to 110 g/kg), anisoles and catechols increase moderately and the maximum yield of guaiacols is found at the lowest reaction temperature (290 ^{o}C).

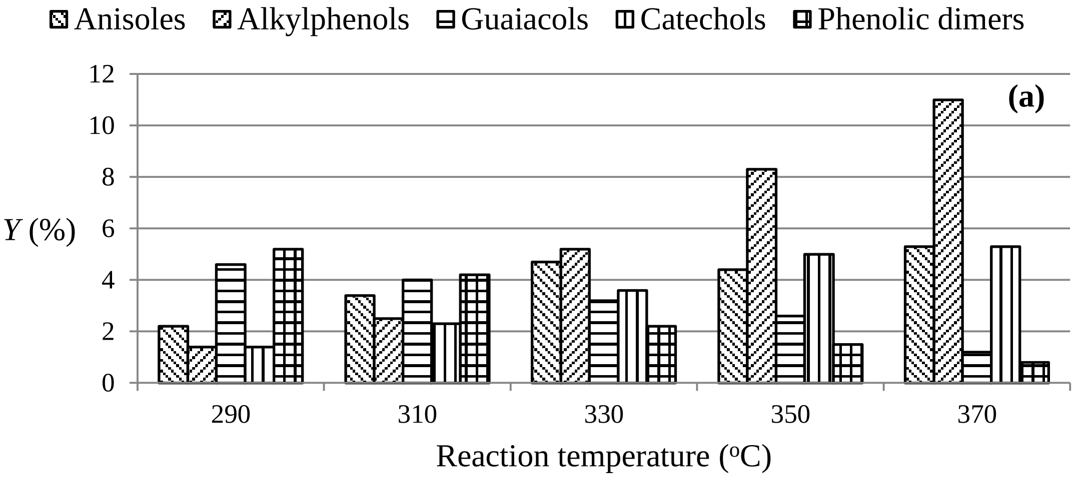
Table 4.17 Yields (%) of different classes of aromatic compounds (in the aqueous phase and DEE-soluble lignin-oil) produced in the depolymerisation and conversion of lignin, calculated on a dry lignin basis.

Class	F	G	H	C	I
Anisoles	2.2	3.4	4.7	4.4	5.3
Alkylphenols	1.4	2.5	5.2	8.3	11.0
Guaiacols	4.6	4.0	3.2	2.6	1.2
Catechols	1.4	2.3	3.6	5.0	5.3
Phenolic dimers	5.2	4.2	2.2	1.5	0.8
Total 1-ring aromatic compounds*	10.0	12.7	17.2	20.8	23.1

*These include 2-acetylphenol, 2-coumaranone, 3-methoxycatechol, salicylic acid, 4-hydrobenzaldehyde, hydrocoumarin, vanillin, dimethylbenzenediol and acetovanillone.

4.6. Comparison of the effect of K_2CO_3 concentration and reaction temperature

The comparison the yields obtained when varying the mass fraction of K_2CO_3 and the reaction temperature (see **Figure 4.6**) shows some interesting features. An increase in both the K_2CO_3 mass fraction and the reaction temperature has the same effects on the yields of all the product fractions (anisoles, alkylphenols and catechols increase but guaiacols decrease) but not on the phenolic dimers. Their yield increases with the mass fraction of K_2CO_3, but decreases with increasing reaction temperature. It can also be observed that the reaction temperature has a relatively large effect on alkylphenols, whereas K_2CO_3 has a relatively large effect on anisoles. The K_2CO_3 concentraion and reaction temperature therefore exert different effects on liquid products. The largest concentration of anisoles is obtained at the highest K_2CO_3 mass fraction (2.2%), where it accounts for 8.6% of dry lignin. The greatest concentration of alkylphenols (11%) and the lowest concentration of phenolic dimers (0.8%), on the other hand, are obtained at the highest temperature (370 ^oC). The lowest concentration of guaiacols and the highest concentration of catechols, however, are obtained not only at the highest K_2CO_3 mass fraction but also the highest temperature.



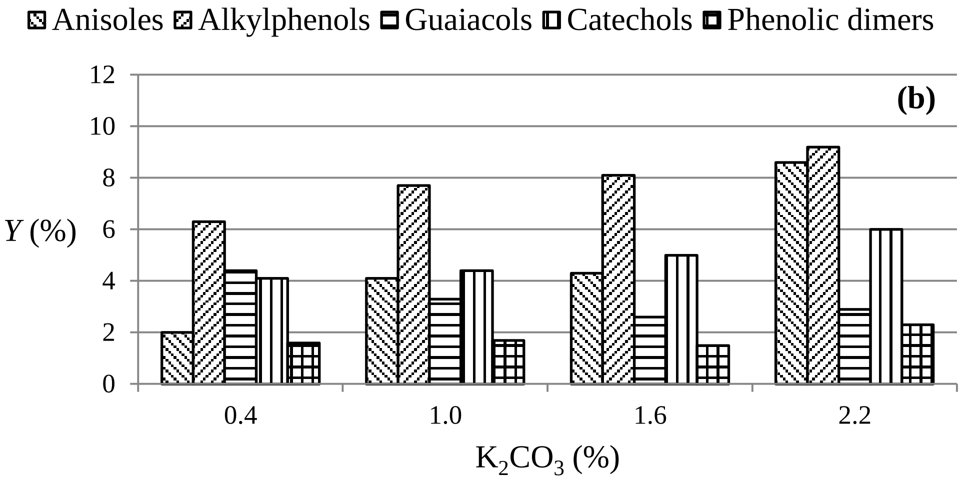


Figure 4.6 Yields (Y) of different classes of aromatic compounds (in water-soluble organics and DEE-soluble lignin-oil) as a function of a) the reaction temperature (at K_2CO_3 mass fraction of 1.6%) and b) K_2CO_3 mass fraction (at the reaction temperature of 350 ^oC). Yields are based on a dry lignin basis.

5. CONCLUSIONS

- It has been demonstrated that it is feasible to use a catalytic process in near-critical water to convert solid LignoBoost Kraft lignin into lignin-oil (OIL) that is partly soluble in water (water soluble organics, WSO).
- The analytic procedure for the determination of the reaction products has been developed.
- The yields (on dry lignin basis) of the OIL and the char do not change as K_2CO_3 mass fraction increases, although the WSO increases slightly. As the reaction temperature increases, however, the OIL decreases whereas the WSO and char both increase.
- The main WSO are cresols, guaiacols and catechols, with methyl and ethyl side groups only.
- The OIL, being partially deoxygenated, has a higher content of carbon and a higher HHV than lignin but a lower content of sulphur. The DEE-soluble OIL contains the same compounds as the WSO but with the addition of alkylanisoles, alkylphenols with propyl side groups and 3-ring compounds.
- The overall yield of 1-ring aromatic compounds (in the WSO and DEE-soluble OIL) increases remarkably as the K_2CO_3 mass fraction or reaction temperature increases. More specifically, anisoles, alkylphenols and catechols increase whereas guaiacols decrease.
- The yield of phenolic dimers increases with an increase in the mass fraction of K_2CO_3 but decreases with increasing reaction temperature, which is interesting. Furthermore, there is a remarkable increase in anisoles with increasing K_2CO_3 mass fraction and a remarkable increase in alkylphenols with increasing the reaction temperature.

6. FUTURE WORKS

- Lignin needs to be characterised using different methods. The heavy fraction in the lignin-oil that is insoluble in DEE but soluble in THF needs to be analysed in order to understand the mechanism of the catalytic process.
- Phenol acts as a co-solvent in the catalytic conversion of lignin. Phenol is added to this process because of the positive effect it has in preventing the formation of char. A study of the effect of the mass fraction of phenol in this conversion of lignin is thus of interest.
- The conversion of some specific models of lignin should be studied in the same process. Finding some simple models of lignin that could be applied and analysed would therefore be a good way of improving knowledge and understanding of the kinetics and conversion pathways of cracking lignin.

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