THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

Hydrothermal Liquefaction of Lignin into Bio-Oil

Influence of the Reaction Conditions and Stability of the Bio-Oil Produced

HUYEN NGUYEN LYCKESKOG

Department of Chemistry and Chemical Engineering
CHALMERS UNIVERSITY OF TECHNOLOGY
Gothenburg, Sweden 2016

Hydrothermal Liquefaction of Lignin into Bio-Oil

Influence of the Reaction Conditions and Stability of the Bio-Oil Produced

HUYEN NGUYEN LYCKESKOG

ISBN 978-91-7597-503-0

Doktorsavhandlingar vid Chalmers tekniska högskola

Ny series nr 4184

ISSN 0346-718X

Department of Chemistry and Chemical Engineering

Chalmers University of Technology

SE-412 96 Gothenburg

Sweden

Telephone +46 (0)31 772 1000

Cover: Hydrothermal liquefaction of LignoBoost^{TM} Kraft lignin for the high value-added products

Printed by Chalmers Reproservice

Gothenburg, Sweden 2016

Hydrothermal Liquefaction of lignin into Bio-Oil

Influence of the Reaction Conditions and Stability of the Bio-Oil Produced

HUYEN NGUYEN LYCKESKOG

Forest Products and Chemical Engineering

Department of Chemistry and Chemical Engineering

Chalmers University of Technology

ABSTRACT

Lignin, one of the three main components of lignocellulosic biomass, is the second most abundant organic polymer found on Earth. Nowadays, most of the lignin (almost 99%) produced in the Kraft pulping process is used as internal fuel. However, modern Kraft mills have an energy surplus, which provides an opportunity for extracting lignin that can be used as a new source of specialty chemicals as well as transportation fuel. Furthermore, a new process, called "LignoBoost™", has been developed recently to extract a large quantity of pure lignin and has gained commercial status.

In this work, hydrothermal liquefaction (HTL) was used to produce bio-oil from LignoBoost™ Kraft lignin in subcritical water, using ZrO_2/K_2CO_3/KOH as the catalytic system and phenol as the capping agent, in a small pilot unit (in continuous mode) developed and located at Chalmers University of Technology in Gothenburg, Sweden. An analytical procedure for the reaction products was developed in order to analyse the liquid products. In addition, the influence of the concentration of K_2CO_3 and the reaction temperature was investigated to optimise the yields and quality of the resulting liquid products. The stability of bio-oil is a significant factor to study since it influences the further upgrading of bio-oil into fuel to be used in industry: high stability makes it more versatile and thus suitable for wider range of applications. The stability of the resulting bio-oil was, therefore, studied under natural (room temperature, 2 years) and accelerated aging (up to 80°C, up to 1 month); the accelerated aging of bio-oil fractions was also studied to obtain a deeper understanding of the aging mechanism.

The results show that these two variables, *i.e.* the concentration of K_2CO_3 and the reaction temperature, affect the products obtained differently: these products consist of bio-oil (69–88%), water-soluble organics (5–11%) and char (16–22%). The main monomers are anisoles, alkyl phenols, guaiacols and catechols, the relative amounts of which varied with the reaction conditions. Being partially deoxygenated, lignin HTL bio-oil has low contents of water and ash, which is beneficial for achieving bio-oil of high quality. This bio-oil was found to be remarkably stable at both room temperature and elevated temperature. Furthermore, its stability was found to be enhanced by the removal of insoluble high Mw molecules.

Keywords: lignin, hydrothermal conversion, bio-oil, subcritical water, stability, aging.

List of Publications

This thesis is based on the work contained in the following papers, which are appended at the end of this 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 and Sven-Ingvar Andersson

Journal of Supercritical Fluids 86 (2014) 67–75

II. The 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 and Hans Theliander

Bioresource Technology 170 (2014) 196–203

III. Kraft lignin depolymerization in near-critical water: effect of changing co-solvent

Tallal Belkheiri, Lennart Vamling, Thi Dieu Huyen Nguyen, Marco Maschietti, Lars Olausson, Sven-Ingvar Andersson, Lars-Erik Åmand and Hans Theliander

Cellulose Chemistry and Technology 48 (9–10), 813–818 (2014)

IV. Storage stability of bio-oils derived from the catalytic conversion of softwood Kraft lignin in subcritical water

Huyen Nguyen Lyckeskog, Cecilia Mattsson, Lars-Erik Åmand, Lars Olausson, Sven-Ingvar Andersson, Lennart Vamling and Hans Theliander

Energy and Fuels 2016, 30, 3097−3106

V. Thermal stability of low and high Mw fractions of bio-oil derived from lignin conversion in subcritical water

Huyen Nguyen Lyckeskog, Cecilia Mattsson, Lars Olausson, Sven-Ingvar Andersson, Lennart Vamling and Hans Theliander

Submitted to Biomass Conversion and Biorefinery

VI. Accelerated aging of bio-oil from lignin conversion in subcritical water

Huyen Nguyen Lyckeskog, Cecilia Mattsson, Lars Olausson, Sven-Ingvar Andersson, Lennart Vamling and Hans Theliander

Submitted to Tappi

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

i. 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 and Sven-Ingvar Andersson

   (Oral presentation)

   In: Conference proceedings. 21st European Biomass Conference and Exhibition, Copenhagen, Denmark, June 3–7, 2013, pp 485–493

ii. Catalytic conversion of Kraft lignin in near-critical water

   Marco Maschietti, Thi Dieu Huyen Nguyen, Lars-Erik Åmand, Hans Theliander, Lennart Vamling, Lars Olausson and 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

iii. Storage stability of bio-oils derived from the catalytic conversion of Kraft lignin in subcritical water

   Huyen Nguyen Lyckeskog, Cecilia Mattsson and Hans Theliander

   (Oral presentation)

   In: Conference proceedings. 24th European Biomass Conference and Exhibition, Amsterdam, The Netherlands, June 6–9, 2016, pp 1107–1110

iv. Thermal stability of bio-oil derived from the lignin conversion in subcritical water

   Huyen Nguyen Lyckeskog, Cecilia Mattsson, Lars Olausson, Sven-Ingvar Andersson, Lennart Vamling and Hans Theliander

   (Poster presentation)

   In: Book of abstracts, 6th Avancell conference–Creating Value from the Swedish Forest Resources, Gothenburg, Sweden, October 18–19, 2016

Contribution Report

The author of this thesis has made the following contributions to the papers:

I. Main author. Active in planning and performing all the experiments, analysing and evaluating the results and writing the papers with the supports of all co-authors.

II. Main author. Active in planning and performing all the experiments, analysing and evaluating the results and writing the papers with the supports of all co-authors.

III. Active in planning and performing the experiments, analysing and evaluating the results with the first author. Joint effort made in writing the papers.

IV. Main author. Active in planning and performing all the experiments, analysing and evaluating the results and writing the papers with the supports of all co-authors.

V. Main author. Active in planning and performing all the experiments, analysing and evaluating the results and writing the papers with the supports of all co-authors. Did not perform the pulse-sequence and the setup of 2D HSQC NMR instruments.

VI. Main author. Active in planning and performing all the experiments, analysing and evaluating the results and writing the papers with the supports of all co-authors. Did not perform the pulse-sequence and the setup of 2D HSQC NMR instruments.

List of abbreviations

aLO_ES: aged light oil_DEE solubles

aLO_EIS: aged light oil_DEE insolubles

aHO_TS: aged heavy oil_THF solubles

aHO_TIS: aged heavy oil_THF insolubles

aRO_LO: aged raw oil_light oil

aRO_HO: aged raw oil_heavy oil

aRO_TIS: aged raw oil_THF insolubles

C–C: carbon–carbon

DEE: diethyl ether

GC–MS: gas chromatography–mass spectroscopy

GPC: gel permeation chromatography

HHV: higher heat value

HO: heavy oil

HSQC: heteronuclear single quantum coherence

HTL: hydrothermal liquefaction

IST: internal standard

LO: light oil

Mw: molecular weight

MwD: molecular weight distribution

NMR: nuclear magnetic resonance

PAH: polycyclic aromatic hydrocarbon

RT: room temperature

TC: total carbon

THF: tetrahydrofuran

TICC: total ion current chromatogram

TIS: THF insolubles

TOC: total organic carbon

WSO: water-soluble organics

1 h: 1 hour

1 d: 1 day

1 w: 1 week

1 m: 1 month

Content

1. Introduction 1
1.1. Challenges in the area of research 1
1.2. Objectives 2
1.3. Outline of the thesis 2
2. Background 3
2.1. Lignin 3
2.1.1. General properties of lignin 3
2.1.2. Kraft lignin 4
2.2. Biorefinery 6
2.3. Conversion of lignin 7
2.3.1. Pyrolysis 7
2.3.2. Gasification 8
2.3.3. Oxidation 8
2.3.4. Hydrogenolysis 9
2.4. Depolymerisation of lignin in water at subcritical conditions 10
2.4.1. Subcritical water 10
2.4.2. Base catalyst and capping agent 10
2.4.3. Reaction mechanism 11
2.5. Stability of bio-oil 12
2.5.1. Physical properties 12
2.5.2. Chemical properties 13
2.5.3. Aging mechanism 14
3. Materials and Methods 15
3.1. Materials 15
3.2. Apparatus and procedure 15
3.3. Experimental 17
3.3.1. Reaction conditions of the lignin HTL process 17
3.3.2. Stability conditions of the lignin HTL bio-oil 18
3.4. Analytical methods 18
3.4.1. Characterisation of LignoBoost^{TM} Kraft lignin 18
3.4.2. Analytical methods applied to the liquid products 19

3.4.3. Quantitation of char 21
4. Results and Discussion 23
4.1. Outline of the results presented 23
4.2. LignoBoost^{TM} Kraft lignin 24
4.3. Influence of reaction conditions on the lignin HTL process 25
4.3.1. Carbon balances and product yields 25
4.3.2. Liquid products 27
4.3.3. A suggested reaction mechanism 35
4.4. Stability studies of lignin HTL bio-oil 37
4.4.1. Storage stability (RT, 2 years) 37
4.4.2. Thermal stability (80°C, 1 month) 39
4.4.3. A suggested accelerated aging mechanism 46
5. Conclusions 47
6. Acknowledgements 49
7. References 51

1. Introduction

1.1. Challenges in the area of research

In the context of the current over-consumption of fossil fuels, coupled with growing concerns related to environmental issues, the utilisation of biomass as an alternative sustainable resource for the production of renewable transportation fuel is of great significance in securing a supply of energy. Wood, which consists of approx. 40–50% cellulose, 20–30% hemicelluloses and 20–30% lignin on a mass basis, is the most common lignocellulosic biomass found on Earth. Modern Kraft mills, where paper pulp is produced from wood, have an energy surplus and, therefore, the potential of evolving into a large-scale biorefinery: one viable option is to extract lignin from black liquor, which then becomes a new source of specialty chemicals and fuel (**Lora**, 2008). Its aromatic nature and abundant availability have meant that the conversion of lignin into high-quality biofuel and high value-added chemicals has increased in interest (**Pandey** and **Kim**, 2011; **Vigneault** *et al*., 2007).

The development of fundamentally new approaches for the conversion of lignin and analytical methodology is, however, challenged by the complexity of lignin, which may be described as being a heterogeneous aromatic macromolecule: the issues that are faced include the structural determination of the material to be used and the characterisation of complex product mixtures. Lignin model compounds or organosolv lignin (a non-commercial lignin) have been used in most studies whereas only a few studies can be found using Kraft lignin (a commercial lignin). It has nevertheless been noted that the conversion of Kraft lignin is demanding (**Löfstedt** *et al.*, 2016). Both the origin of the lignin and the reaction conditions (*e.g.* base concentration and reaction temperature) influence the quantity and quality of the biofuels obtained: optimising these conditions to obtain an efficient conversion of lignin is the main challenge being faced in making this financially viable.

In order to be upgraded into transportation fuel and/or chemicals, lignin HTL bio-oil must be able to retain its original properties and quality when stored for a long period of time, and

especially so at higher temperatures. Even though this type of bio-oil is characterised by low contents of both oxygen (15–21%) and water (11–19%) and a high calorific value (31–33 MJ/kg), it has high concentrations of reactive organic functional groups (*i.e.* aromatic rings, hydroxyl and methoxyl groups and unsaturated bonds) and ash (1.0–3.5%). Their presence may cause changes in the physical and chemical properties of the bio-oil (*e.g.* reactions that form larger molecules) and, as a result, reduce storage stability (**Chen** *et al*., 2014; **Yang** *et al*., 2015). To the author's knowledge, no publication has focused on the stability of lignin HTL bio-oil yet.

1.2. Objectives

A small, high-pressure, pilot unit operating in continuous mode was developed at Chalmers University of Technology to convert LignoBoost™ Kraft lignin in subcritical water into a renewable fuel-intermediate bio-oil. ZrO_2/K_2CO_3/KOH was used as the catalytic system and phenol as the capping agent to increase the yield of the liquid product and decrease the yield of char.

The first objective of this work was to demonstrate the operability of the HTL equipment and the feasibility of converting lignin into a bio-oil product, and then develop an analytical procedure for the resulting products. The second was to investigate the effects of the K_2CO_3 concentration (a homogeneous base catalyst) and the reaction temperature on this conversion in order to optimise the yield and quality of the bio-oil obtained. Studying the stability of this bio-oil was the third objective: both for long-term storage at room temperature (RT) and short-term storage at elevated temperatures. The fourth, and final, objective was to study the thermal stability of the individual bio-oil fractions in order to improve understanding of the aging mechanisms that take place in this bio-oil during storage.

1.3. Outline of the thesis

This thesis is based on six research papers, all of which can be found at the end of this work. Chapter 2 provides a brief summary of lignin and its thermo-chemical conversion, and the stability of bio-oil. In Chapter 3, the materials, apparatus and procedure are described, together with the experimental conditions and analytical methods used. The main results obtained are presented and discussed in Chapter 4; the conclusions that were drawn are given in Chapter 5, which summarises the important findings of this work.

2. Background

2.1. Lignin

2.1.1. General properties of lignin

Lignin (derived from *lignum*, which is Latin for wood), one of the most abundant amorphous macromolecules found on Earth, has a very complex structure with a mixture of aromatic and aliphatic moieties. It is composed mainly of three monolignols (**Figure 2.1**), namely *p*-coumaryl alcohol (with no methoxyl group attached to the aromatic ring), coniferyl alcohol (with one methoxyl group) and sinapyl alcohol (with two methoxyl groups). These monomers are connected randomly by a number of different types of 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 species of trees (see **Table 2.1**): softwood has almost exclusively coniferyl alcohol, although a small amount of *p*-coumaryl alcohol is present; hardwood has both coniferyl and sinapyl alcohols, with an amount of sinapyl alcohol that is up to three times higher, and a small amount of *p*-coumaryl alcohol; grass has all three monolignols but its content of *p*-coumaryl alcohol is higher than for other types of lignin.

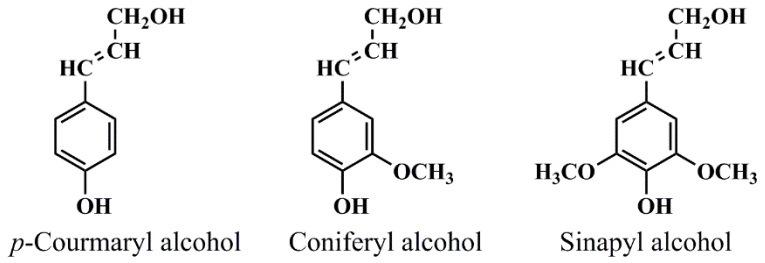


Figure 2.1 The monomers composing the lignin polymer (**Henriksson**, 2009).

The high molecular complexity of lignin means that many structural questions remain to be answered. More than two thirds of the units in native lignin are linked by ether bonds (approx. 70%) and the rest by C–C bonds. The latter, which are generally more stable than the former, 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' (**Table 2.2**). The *β*–O–4'bond is the most common found in lignin, accounting for about 50% in softwood and 60% in hardwood. The characteristic functional groups in lignin are phenolic hydroxyl groups (Ar–OH), methoxyl groups (Ar–OCH_3) and some terminal aldehyde groups (Ar–CHO) (**Figure 2.2)**, which are important for its reactivity. Phenolic hydroxyl groups (*i.e.* free phenolic groups with the oxygen in the 4-position does not form an ether bond) compose 10–13% of the aromatic rings in native lignin (**Henriksson**, 2009). In addition, some alcoholic hydroxyl and carbonyl groups are also present in the lignin macromolecule.

Table 2.1 The composition (%) of monolignols in various 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

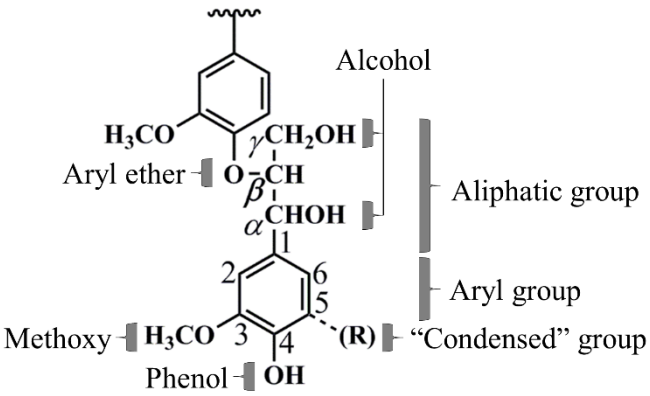
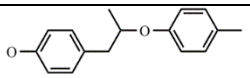
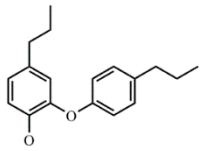
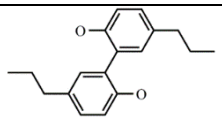
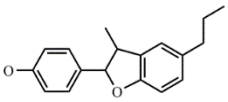
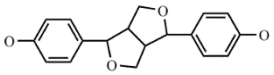
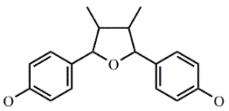
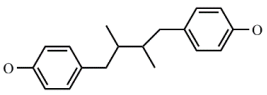
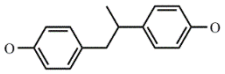
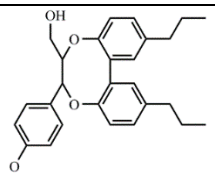
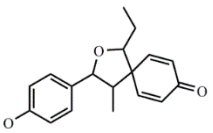
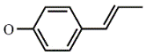
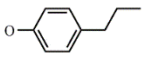
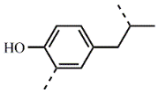


Figure 2.2 Functional groups in lignin (**Dimmel**, 2010).

2.1.2. Kraft lignin

Today, Kraft pulping is the dominant process employed for making chemical paper pulp since it is an effective process that gives strong fibres. The Kraft cooking process uses hydroxide (OH^-) and hydrosulphide (HS^-) ions as the active chemicals to dissolve lignin and thereby 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 the *β*–O–4' structures but also the lignin-carbohydrate linkages at the C*α*-position (*i.e.* benzyl ether and benzyl ester linkages) are hydrolysed, and the resulting lignin fragments dissolve in the alkaline solution (*i.e.* black liquor). After pulping, the black liquor leaves the digester as an aqueous stream with a solid content of about 15% (*i.e.* weak black liquor).

Table 2.2 The important bonds (as % of the total bonds) in softwood and hardwood (**Gellerstedt**, 2009a, 2009b). Only the "carbon skeleton" is shown in the structures.

Name	Bonds	Structures	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' (*β*–5'*α*–O–4')		11–12	4–9
Pinoresinol	*β*–*β'* (*α*–O–*γ'β*–*β'γ*–O–*α'*)		2–3	3–4
-	*β*–*β'* (*α*–O–*α'β*–*β'*)		<1	None
Secoisolariciresinol	*β*–*β'*		1–2	None
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
End group			1–6	Trace–6
Dihydroconiferyl alcohol			2	None
Free phenol			11	9

The fragmentation reaction of phenolic *β*–O–4' structures leads to the formation of Kraft lignin with a relatively low content of sulphur, high content of free phenolic groups and low molecular weight (Mw), all of which enhance its solubility. The competing reactions in Kraft pulping (*i.e.* elimination, reduction and condensation reactions from the quinone methide intermediate) are

much slower than the reactions between quinone methide and HS^-, which would explain why lower contents of condensation and stable enol ether structures are observed in Kraft lignin than in soda lignin (**Gellerstedt**, 2009a, 2009b; **Lora**, 2008).

2.2. Biorefinery

Nowadays, a modern Kraft mill (**Figure 2.3**) has the potential of being a large-scale biorefinery that not only produces market pulp and green electricity but also uses black liquor as the raw material for the production of specialty chemicals and transportation biofuels.

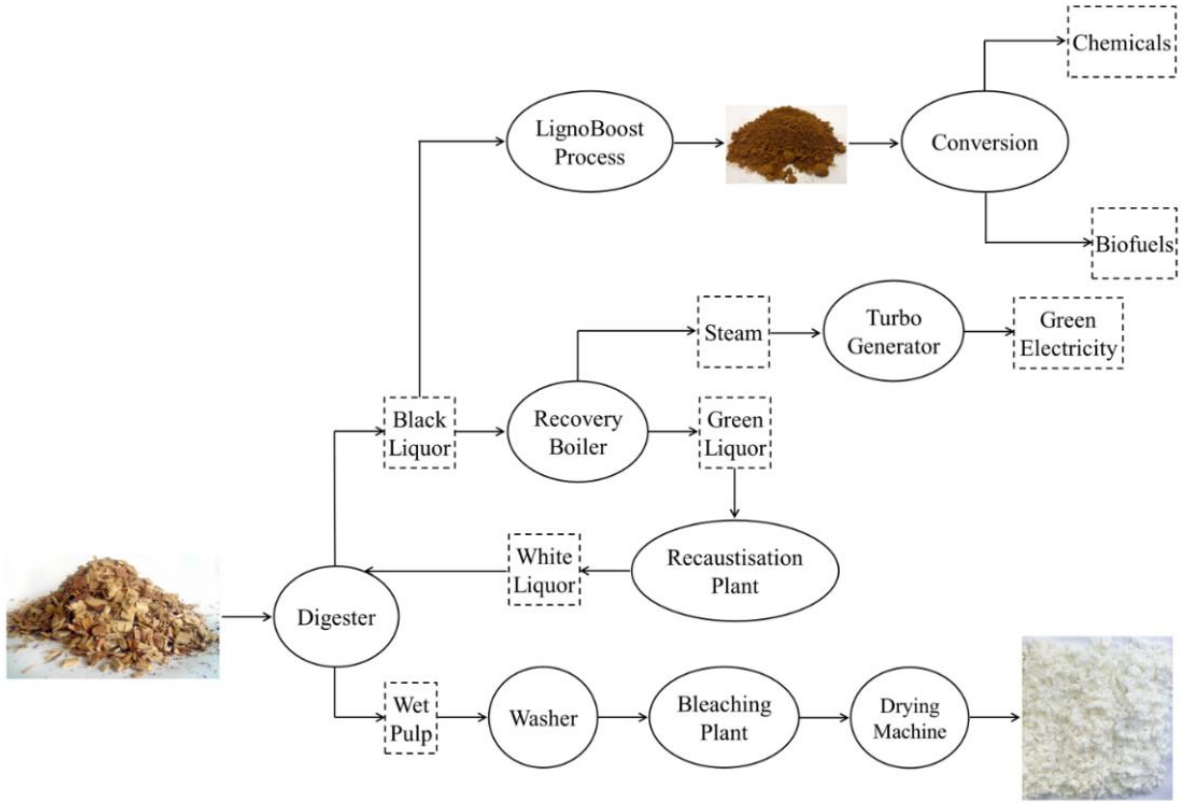


Figure 2.3 Schematic diagram of a modern Kraft mill.

The efficient removal of lignin from black liquor can exploit the energy surplus of a Kraft mill and produce a bulk raw material for either generating energy or 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 the conventional process, a filter

cake is washed directly after dewatering, resulting in a Kraft lignin with a relatively low content of dry solid, high content of ash (and sodium) and poor dewatering properties.

The LignoBoost™ process has been developed by researchers at Chalmers University of Technology and Innventia, a 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 and, thereafter, dewatered and washed in a second step. The resulting lignin, known as LignoBoost™ Kraft lignin, has a high level of purity and improved dewatering properties. Moreover, the yield is higher in this process than in a conventional one (**Öhman** *et al*., 2007; **Tomani**, 2010). The first commercial-scale LignoBoost™ plant was started in 2013 at a pulp mill in Plymouth, USA, with an annual capacity of 25000 tonnes; a second commercial-scale plant was started up in 2015 at Stora Enso's Sunila mill in Finland with twice this capacity.

2.3. Conversion of lignin

2.3.1. Pyrolysis

There are many ways of breaking down lignin into small molecules (**Figure 2.4**). One is by pyrolysis, subjected it to thermal treatment with or without a catalyst and in the absence of oxygen. At these conditions, the organic substances in the lignin are disintegrated into smaller units without any further conversion into carbon dioxide (CO_2). The pyrolysis of lignin is highly complex in terms of the distribution of the products and the composition of the bio-oil. Conversion occurs over a wide range of temperatures (160–900°C) and is affected by several factors, such as the type of feedstock, the severity of the treatment and the catalyst used.

Lignin degradation begins by the weaker bonds being cleaved at lower (160–300°C), and the stronger bonds at higher, temperatures and proceeds thereafter to crack or repolymerise the aromatic rings at significantly high temperatures (>500°C). The bio-oil (pyrolytic bio-oil) obtained is a complex mixture of volatile liquids (methanol, acetone and acetaldehyde), monolignols, phenolic aromatics (phenol, guaiacol, syringol and catechol) and other poly-substituted phenols. The bio-oil has a high content of oxygen 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 temperature of the pyrolysis process (**Pandey** and **Kim**, 2011; **Azadi** *et al*., 2013).

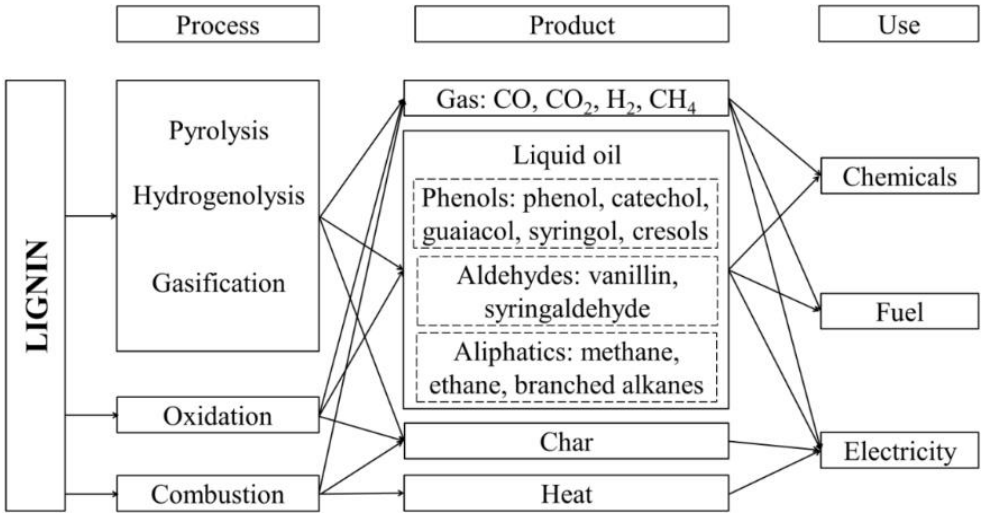


Figure 2.4 The major thermo-chemical conversion processes used for lignin, and their resulting products (**Pandey** and **Kim**, 2011).

2.3.2. Gasification

Gasification is a thermal treatment method for converting lignin into a mixture of small 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 already in the generation of electricity, pure hydrogen and synthetic liquid fuels and chemicals.

Lignin gasification can be achieved by conventional gasification in the presence/absence of active agents (*i.e.* oxygen and/or steam) at high temperatures (around 700°C) and near atmospheric pressure or hydrothermal gasification at moderate temperatures (350°C) and high pressures (15–27.5 MPa). Hydrothermal gasification (supercritical water gasification) is promising technology for producing H_2 and CH_4 from feedstock with a high content of water because 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).

2.3.3. Oxidation

Oxidation, which is thermal treatment in the presence of oxygen, is primarily employed for converting lignin into aromatic aldehydes, *e.g.* vanillin, syringaldehyde and *p*–hydroxybenzaldehyde. The reaction temperatures range from 100°C to 320°C and pressures

from 0.5 to 20 MPa (**Kang** *et al*., 2013). In fact, of the products named above, vanillin is one of the low Mw chemicals that is currently produced industrially in large quantities from technical lignin by alkaline oxidation in air (**Silva** *et al*., 2009).

The oxidation of lignin involves cleaving the aromatic rings, aryl ether bonds or other linkages; nitrobenzene, metal oxides and hydrogen peroxide are the oxidants most commonly used for this purpose. The yield and composition of the degradation products vary, depending on the severity of the reaction conditions, although **Villar** *et al*., (2001) have 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 thanks to their low cost (**Kang** *et al*., 2013).

2.3.4. Hydrogenolysis

Hydrogenolysis is pyrolysis in the presence of hydrogen. Hydrogenolysis is carried out at significantly lower temperatures (250–450°C) than normal pyrolysis: it favours a higher net conversion, gives higher yields of liquid products (including monomeric phenols) and less char is formed. Moreover, it has the advantage that pre-drying the feedstock is unnecessary, which is an energy-demanding process (**Kang** *et al*., 2013). Furthermore, the employment of both a suitable solvent and catalyst can improve the conversion and yields of products. Hydrogenolysis is therefore probably the most promising method for producing phenols from lignin.

Lignin is degraded in this process via many chemical reactions, such as the cleavage of 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 in the hydrogenolysis can be a pressurised hydrogen gas or hydrogen-donor solvent, *e.g.* tetralin (**Davoudzadeh** *et al*., 1985; **Jegers** and **Klein**, 1985; **Kudsy** *et al*., 1995; **Thring** *et al*., 1993) and formic acid with alcohol (**Gellerstedt** *et al*., 2008a, 2008b; **Kleinert** and **Barth**, 2008a, 2008b; **Kleinert** *et al*., 2009). Many authors (**Shabtai** *et al*., 1999a, 1999b, 2000; **Miller** *et al*., 1999; **Zmierczak** and **Miller**, 2006) have used a hydrogen-donor solvent at supercritical conditions (such as methanol/ethanol plus water), which resulted in a high liquid yield: these works used base-catalysed depolymerisation (BCD) followed by hydrodeoxygenation (HDO) and/or hydrocracking.

2.4. Depolymerisation of lignin in water at subcritical conditions

2.4.1. Subcritical water

One of the most effective hydrogenolysis processes used to break down lignin is depolymerisation in water at sub/supercritical conditions, which is a hydrothermal liquefaction (HTL) process. An advantage of this process is that no drying step is needed for the raw material, which decreases the energy demand.

Water at sub/supercritical conditions (T_c = 374.1°C and P_c = 22.1 MPa) has a lower dielectric constant and ionic product compared to ambient temperature (**Carr** *et al*., 2011; **Möller** *et al*., 2011; **Pandey** and **Kim**, 2011; **Toor** *et al*., 2011; 2012): it has been suggested that such water has positive effects on the degradation of lignin and the subsequent formation of phenolic compounds. Another advantage of using hydrogenolysis in water at subcritical conditions is that the inorganic components of the feedstock can be separated from the bio-oil because these salts end up in the water phase (**Hammerschmidt** *et al.*, 2011). There is also the potential of producing an oil with a low content of oxygen, since part of the oxygen present in lignin is hydrolysed into small organic compounds that are dissolved in the water phase (**Kang** *et al*., 2013). The main phenolic compounds recovered from this conversion are phenol, *o*-cresol and catechol (**Kang** *et al*., 2013). It has been demonstrated recently (**Fang** *et al*., 2008; **Kang** *et al*., 2013; **Okuda** *et al*., 2004; **Saisu** *et al*., 2003) that it is possible to convert lignin without using a catalyst in supercritical water (from 400 to 600°C), although the yield of phenolic compounds that was reported low.

2.4.2. Base catalyst and capping agent

Several authors (**Lavoie** *et al*., 2011; **Miller** *et al*., 2002; **Schmiedl** *et al*., 2009; **Unkelbach** *et al*., 2010) who studied the conversion of lignin in subcritical water, using strong bases as the catalyst, obtained high yields of an oil with a high Mw and char. These lignin conversion systems give low yields of liquid products and high amounts of oligomeric residues, due to the ease of formation of a more condensed structure through repolymerisation reactions of reactive, decomposed fragments of lignin (**Azadi** *et al*., 2013; **Roberts** *et al*., 2011). **Karagöz** *et al.* (2005) showed that the catalytic activity follows the order: K_2CO_3 > KOH > Na_2CO_3 > NaOH, based on the conversion and the yield of liquid products from wood biomass in subcritical water. They concluded that K_2CO_3 is an effective base catalyst for decomposing biomass material. It has been shown that the use of an organic solvent inhibits the formation of char in

the lignin conversion process (**Okuda** *et al*., 2004; **Saisu** *et al*., 2003). The addition of phenol or alkyl phenols (such as *p*-cresol) in particular facilitates the production of phenolics from lignin, while the addition of formic acid or an alcohol is favoured for the production of lignin-derived oils with low content of oxygen (**Kang** *et al*., 2013).

2.4.3. Reaction mechanism

The reaction mechanism of lignin in subcritical water can follow at least two different paths, namely ionic (hydrolysis) and radical (pyrolysis) mechanisms (**Roberts** *et al*., 2010a, 2010b; **Yong** and **Matsumura**, 2013). According to these authors, however, the mechanism in the presence of a base (K_2CO_3 or K_2CO_3/ZrO_2) is mainly ionic (**Figure 2.5**) due to the following reasons: firstly, the presence of alkali carbonate (or an alkali cation) leads to the polarisation of the ether bond, thus shifting the reaction to the ionic cleavage of this bond. Secondly, the ion product of water and dielectric constant is higher at subcritical condition (100–370°C) than at supercritical (> 370°C): OH^- and H^+ ions are therefore present at higher levels of concentration and the stability of the salt is also higher, which promotes ionic reactions. Thirdly, the dispersion and accessibility of lignin in the medium is improved when ZrO_2 is used in combination with K_2CO_3: this can be explained by the increase in the amount of hydroxyl groups (which presumably cover the ZrO_2 surface) caused by the incorporation of the K^+ and Zr^{4+} ions due to their different electro negativity (*i.e.* K^+ about 13 and Zr^{4+} about 8) (**Hammerschmidt** *et al.*, 2011).

In the presence of a base (*e.g.* NaOH), the conversion of lignin in sub/supercritical water (base catalysed depolymerisation) has been proposed as following various different paths: one is the hydrolysis of C–O bonds (*i.e.* ether bonds) in lignin structures (**Schmiedl** *et al*., 2009; **Unkelbach** *et al*., 2010) and another is the dealkylation of C–C bonds in the propane chains of lignin at a longer reaction time (**Pińkowska** *et al*., 2012). When a higher reaction temperature is applied, the demethylation reaction takes place, which results in an increase in compounds with hydroxyl groups (phenols and catechols) and a decrease in those with methoxyl groups (guaiacols) (**Lavoie** *et al*., 2011, **Beauchet** *et al*., 2012).

In the presence of phenol, a plausible pathway for the decomposition of lignin in sub/supercritical water has been proposed (**Saisu** *et al*., 2003; **Okuda** *et al*., 2004; **Fang** *et al*., 2008): (a) the conversion of lignin to form lower Mw aromatic products; (b) the decomposition of aromatic products formed to monomeric products. The addition of phenol to this medium

causes it to react with the reactive fragments (formaldehyde, aldehyde, etc.) present in the reaction system, which results in the suppression of cross-linking/ repolymerisation reactions between reactive fragments to form compounds of higher Mw.

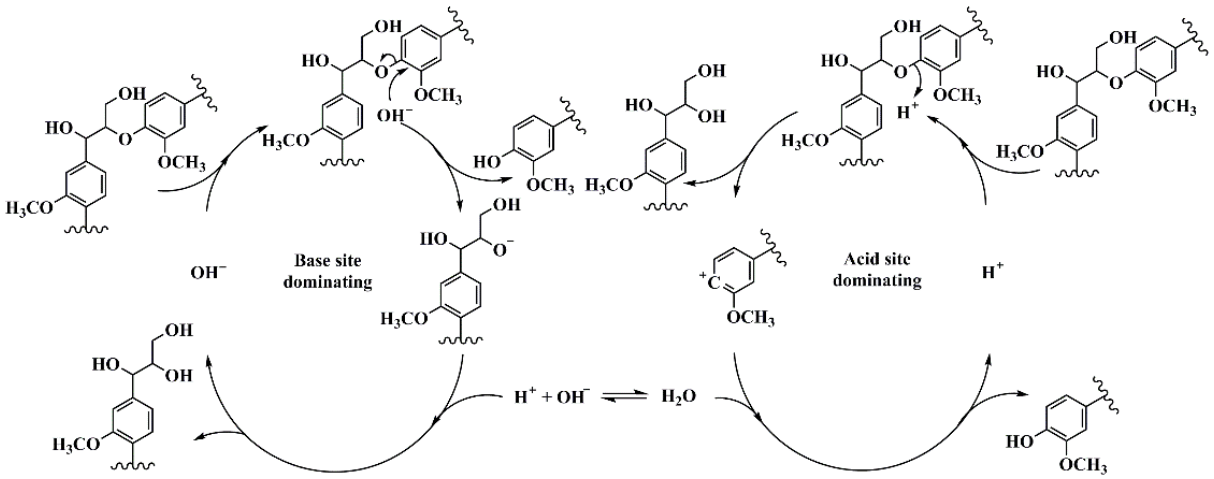


Figure 2.5 The ionic mechanism of lignin, showing possible products (modified from **Roberts** *et al.*, 2010b).

2.5. Stability of bio-oil

The stability of bio-oil can be investigated with respect to "storage time" and "storage temperature" (**Grioui** *et al*., 2014). The former refers to storage stability, defined as the ability of a bio-oil to maintain its original properties during storage at RT over an extended period of time. The latter refers to thermal stability, defined as the ability of the bio-oil to withstand relatively high temperatures for a short period of time without significant degradation occurring (**Yang** *et al*., 2015). The stability of a bio-oil can be evaluated by examining the changes that take place in its physical and chemical properties. It should be observed here that the majority of studies on stability have used biomass-pyrolysis bio-oil: studies on lignin HTL bio-oil have not been found in the literature. The changes in physical and chemical properties are therefore reported here for biomass-pyrolysis bio-oil.

2.5.1. Physical properties

The major factors that influences the stability of biomass-pyrolysis bio-oil are the contents of water, oxygen, solids and acids. The water content of the biomass-pyrolysis bio-oil, which has an initial value of 20–30%, increases during storage because the aging reactions (*e.g.* condensation and dehydration) release water (**Alsbou** and **Helleur**, 2014; **Chaala** *et al*., 2004; **Jiang** *et al*., 2011b). This increase in water content results in phase separation due to the

difference between the polarity and solubility of the compounds in the bio-oil (**Ba** *et al*., 2004). Moreover, an increase in water content causes a decrease in the heat value of the bio-oil (**Samanya** *et al*., 2011). Biomass-pyrolysis bio-oil has a high content of oxygen (45–65%), which stems from the water and oxygenated organic compounds in the bio-oil (**Yang** *et al*., 2015). The oxygen content of dry bio-oil decreases after aging due to the formation of water (**Meng** *et al*., 2015).

The viscosity of biomass-pyrolysis bio-oil tends to increase with both time and temperature during storage (**Oasmaa** *et al*., 2003; 2011; **Li** *et al*., 2015). **Meng** *et al*. (2015) suggested that the effect of the physical aggregation process, in which pyrolytic lignin (*i.e.* lignin obtained from the pyrolysis of biomass) slowly agglomerates to form larger aggregates, influences the viscosity of the bio-oil more after aging than if polymerisation should occur: this is especially true for bio-oil with a high content of pyrolytic lignin. The Mw of bio-oil has been found to increase during storage due to the polymerisation and formation of oligomers with a higher Mw (**Joseph** *et al*., 2016). **Joseph** *et al*. (2016) discovered that the formation of water-insoluble lignin fractions of low and high Mw is due to the oligomerisation/polymerisation reactions that occur during the aging process, thereby leading to the Mw of the bio-oil increasing.

The solids/ashes present in biomass-pyrolysis bio-oil are mainly alkali metals (potassium and sodium), which act as catalysts and accelerate the aging process (**Yang** *et al*., 2015). The solid content of bio-oil is often defined as the part that is insoluble in an organic solvent (such as ethanol, methanol or methylene chloride). **Joseph** *et al*. (2016) reported an increase in the solid (water-insoluble lignin fractions of low and high Mw) and a decrease in the mass fraction for extractives, polar aromatics and carbohydrates as the bio-oil aged. Biomass-pyrolysis bio-oil is acidic (pH ranging from 2 to 4) due to the carboxylic acids formed during the decomposition of biomass polymers. Such high levels of acidity make this bio-oil very corrosive which, in turn, affects the choice of materials that may be used for its transportation (**Yang** *et al*., 2015). Aging reactions, such as the decomposition of sugar, may produce organic acids (*e.g.* formic and acetic acid) and thus increase the acidity of the bio-oil (**Meng** *et al*., 2015).

2.5.2. Chemical properties

Oasmaa *et al*. (2003) found that the principal compositional changes that occur during aging include a decrease in carbonyl compounds (*i.e.* aldehydes and ketones) and an increase in the water-insoluble compounds (*i.e.* lignin fragments, extractives and solid residue). **Li** *et al*. (2015)

concluded that the solids not only interact with active molecules, which promotes condensation reactions, but also generate self-aggregation, resulting in the separation of phases in the bio-oil.

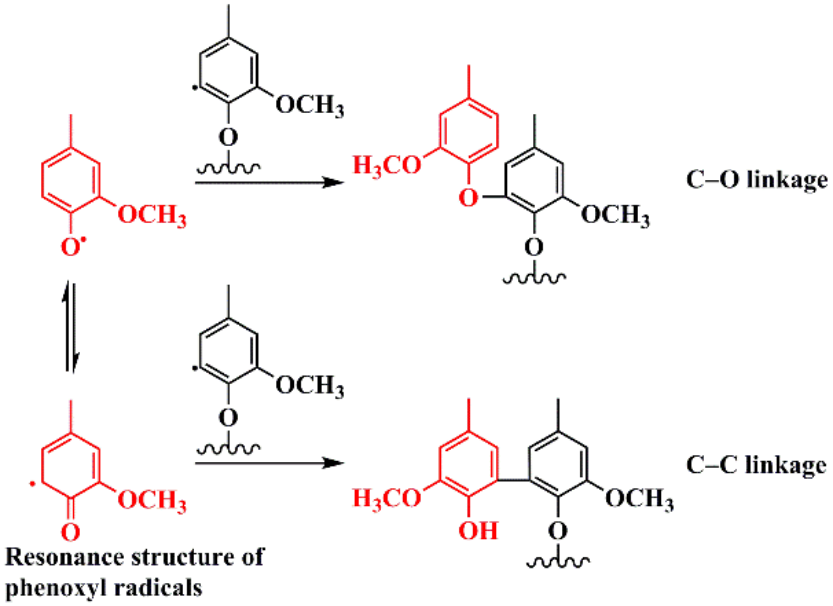


Figure 2.6 Condensation of free radicals in lignin fractions during the aging of bio-oil (**Meng** *et al*., 2014).

2.5.3. Aging mechanism

Alsbou and **Helleur** (2014), in a study, they conducted of the compositional changes that occur in pyrolysis bio-oil during aging, proposed that the aging mechanism was based on the fact that olefin, aldehyde and alcohol groups can undergo repolymerisation/ condensation reactions (*i.e.* esterification, etherification and olefinic condensation). Moreover, **Meng** *et al*. (2014) studied the aging mechanisms of bio-oil fractions (*i.e.* water solubles, ether insolubles and pyrolytic lignin) and demonstrated that repolymerisation/ condensation reactions take place not only through acid-catalysed reactions between the electron-rich aromatic ring and the cationic sites of benzyl alcohol and benzyl ether at the α-carbon position) but also through free radical reaction mechanisms. The absence of an acid catalyst means that this aromatic condensation is initiated primarily by the free radicals present (**Figure 2.6**).

3. Materials and Methods

3.1. Materials

The raw material used in this work was Kraft lignin originating from softwood; it was produced in the LignoBoost^{TM} demonstration plant at the Bäckhammar mill, Sweden. Zirconia (ZrO_2) pellets from Harshaw Chemie BV (length: 3 mm, diameter: 3 mm, BET surface area 48 m^2/g) were used as the heterogeneous catalyst in the reactor. The potassium carbonate (K_2CO_3, ≥ 99.5%) and potassium hydroxide (KOH, ≥ 85% of dry content) used as the homogeneous co-catalysts, along with the phenol (crystallized, ≥ 99.5%) used as the co-solvent, were all sourced from Scharlau. Hydrochloric acid (HCl, 1 mol/L), tetrahydrofuran (THF, ≥ 99.9%) and diethyl ether (DEE, ≥ 99.9%) from Scharlau were used in the analytical protocol. All the analytical standards for Gas Chromatography–Mass Spectroscopy (GC–MS), Gel Permeation Chromatography (GPC) and Nuclear Magnetic Resonance (NMR) analyses were from Sigma-Aldrich. The chemicals were all used as provided, without further purification.

3.2. Apparatus and procedure

The catalytic conversion (HTL) of lignin was performed in the pilot plant (**Figure 3.1)**. The lignin slurry was prepared by mixing the lignin, which had been crushed manually, with K_2CO_3 (with or without KOH) and deionised (DI) water using an Ultra Turrax disperser (IKA WERK T 45/N). The feed, *i.e.* a mixture of lignin slurry and phenol, was pumped continuously into the system during the run by a high-pressure diaphragm pump (Lewa) at a flow rate of 1–2 kg/h measured by a mass flow-meter (Endress and Hauser, Promass). Preceding every run, this system was heated up and pressurized to operating conditions, with a continuous flow of DI water being maintained. The feed solution was stored in a 10 L feed tank equipped with an impeller and kept at 40°C. The feed was heated to 80°C using an electric preheater prior to entering the reactor. The feed was mixed with a stream recirculated from the reactor: the recirculation pump was of a high-temperature and high-pressure type. The recycle-to-feed ratio

was kept at approx. 10 for all runs except for the highest reaction temperature (*i.e.* 370°C): the value for this run was set at 2 for operational reasons. The ratio was estimated by measuring temperatures before and after the mixing point and then applying an energy balance. Recirculation allowed the fresh feed to be heated rapidly and mixed before coming into contact with the heterogeneous catalyst in the reactor: there was a second electric heater installed prior to the inlet of the reactor. The reaction mixture came 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 was 294 cm^3. At reaction conditions (*i.e.* reaction temperature in the range 290–370°C and pressure 25 MPa), the reactor residence time (τ) was around 10–13 min. The reaction products were then cooled down and depressurised to ambient conditions. Two pressure control valves were used to control the system's pressure and to depressurise the reaction products. These valves were in parallel, allowing them to be switched over from one to the other if the valve in operation became congested.

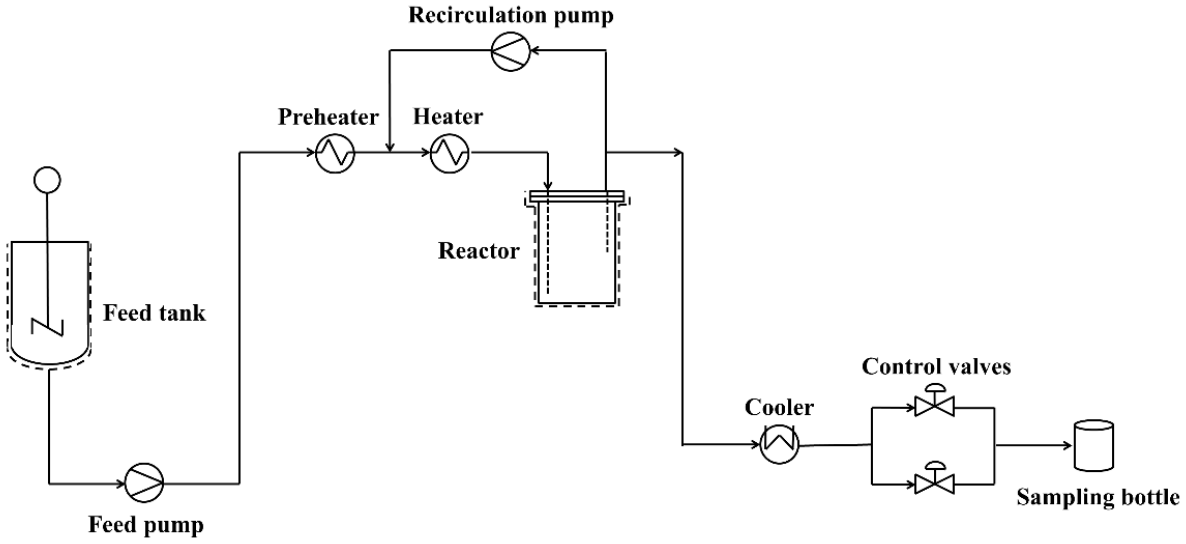


Figure 3.1 Schematic diagram of the pilot plant.

During the run, the liquid products were collected continuously in sampling bottles for analysis: each bottle was used to collect the liquid products corresponding to approx. 45 min of operation. Samples of gas were not taken during the runs that were carried out since no significant amount was collected in the gas sampling bag (Tedlar sample bag, SKC, USA) placed downstream, on the outlet line exiting the cap of the sampling bottle. Also, auxiliary lines for cleaning the apparatus in between the runs and safety systems were installed.

The observation was made that the visual appearance of the products in the sampling bottles changed progressively during the start-up period, showing a progressive darkening; the exception was a single run without lignin in the feed (Run E), the products in which consisted of a homogeneous liquid phase that showed a steady appearance right from the beginning. 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 after a period of approx. 2 h from the start. 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. The plant was cleaned after the end of each experimental run: the reactor was disassembled and the char deposited on the catalyst was measured.

Several samples of liquid products were taken during the steady-state operation. When lignin was fed into 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 gave a fairly transparent aqueous phase with a colour ranging from yellowish to dark green (depending on the concentration of K_2CO_3 in the feed) and a highly viscose black oil phase that was heavier than the aqueous phase. A large, single sample for use in the analytical procedures was obtained by taking all of the aqueous samples obtained during each steady-state operation and mixing them together; 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 partly because of its high viscosity and to facilitate the 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

3.3.1. Reaction conditions of the lignin HTL process

The effects of a co-catalyst and the reaction temperature on the process were evaluated in this work (**Table 3.1**). In Run E, the feed was prepared without lignin: the aim of this run was not only to study the HTL process without lignin being present in the system but also to demonstrate that the products obtaining in the other runs are, in fact, derived from lignin. In Run K, the feed

was prepared with methanol (4.1%) instead of phenol: the aim here was to study the process when phenol is not used as the capping agent.

Table 3.1 Feed data (mass fraction %) and reaction temperature (°C) of all of the runs.

Input data	Base concentration series				Reaction temperature series					Extra runs	
	A	**B**	**C**	**D**	**F**	**G**	**H**	**C**	**I**	**E**	**K[a]**
T (°C)	350	350	350	350	290	310	330	350	370	350	350
K_2CO_3 (%)	0.4	1.0	1.6	2.2	1.6	1.6	1.6	1.6	1.6	1.9	1.6
Dry lignin (%)	5.6	5.5	5.5	5.4	5.5	5.5	5.5	5.5	5.5	0	5.5
Phenol (%)	4.1	4.1	4.1	4.0	4.1	4.1	4.1	4.1	4.1	4.7	0

[a] Methanol mass fraction: 4.1%

3.3.2. Stability conditions of lignin HTL bio-oil

The stability of lignin HTL bio-oil can be studied by investigating its storage time (storage stability: natural aging) and storage temperature (thermal stability: accelerated aging) (**Grioui** *et al*., 2014). For storage stability, the samples of bio-oil were stored in a dark locker at RT for a period of 2 years; for thermal stability, the samples were aged using a heating oven (50°C and 80°C) for four periods of time (*i.e.* 1 h, 1 day, 1 week and 1 month), while the different bio-oil fractions (see **Figure 3.2**) were aged at 80°C for three periods of time (*i.e.* 1 h, 1 day and 1 week) (see Section 2.3 in Papers V and VI).

3.4. Analytical methods

3.4.1. Characterization of LignoBoost™ Kraft 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 contents of carbon, hydrogen and nitrogen were measured according to the method SS-EN 15104 and those of sulphur and chlorine according to the methods SS-EN 15289 and SS-EN 15289 A, respectively. The content of ash and the heat value were measured 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, 130°C, auto-stabilization method). The amounts of aromatic and aliphatic groups present were analysed by means of a ^{13}C NMR (Varian, 9.4 T and DMSO-d_6). The spectra obtained were processed with an exponential line broadening (10 Hz), signal phasing and baseline correction. Furthermore, the chemical composition of the lignin was analysed with ^{1}H–

^{13}C NMR (Bruker, 18.8 T and DMSO-d_6) at the NMR centre of Gothenburg University, Sweden. Heteronuclear Single Quantum Coherence (HSQC) data processing and plots were carried out using the default processing template, automatic phase and baseline correction of MestReNova V10.0.0 software.

3.4.2. Analytical methods applied to the liquid products

The liquid products obtained from the HTL process are composed of two phases, an aqueous and an oil, which were separated by centrifugation. A block diagram, showing the various steps of the analytical methods applied to these liquid products, is presented in **Figure 3.2**.

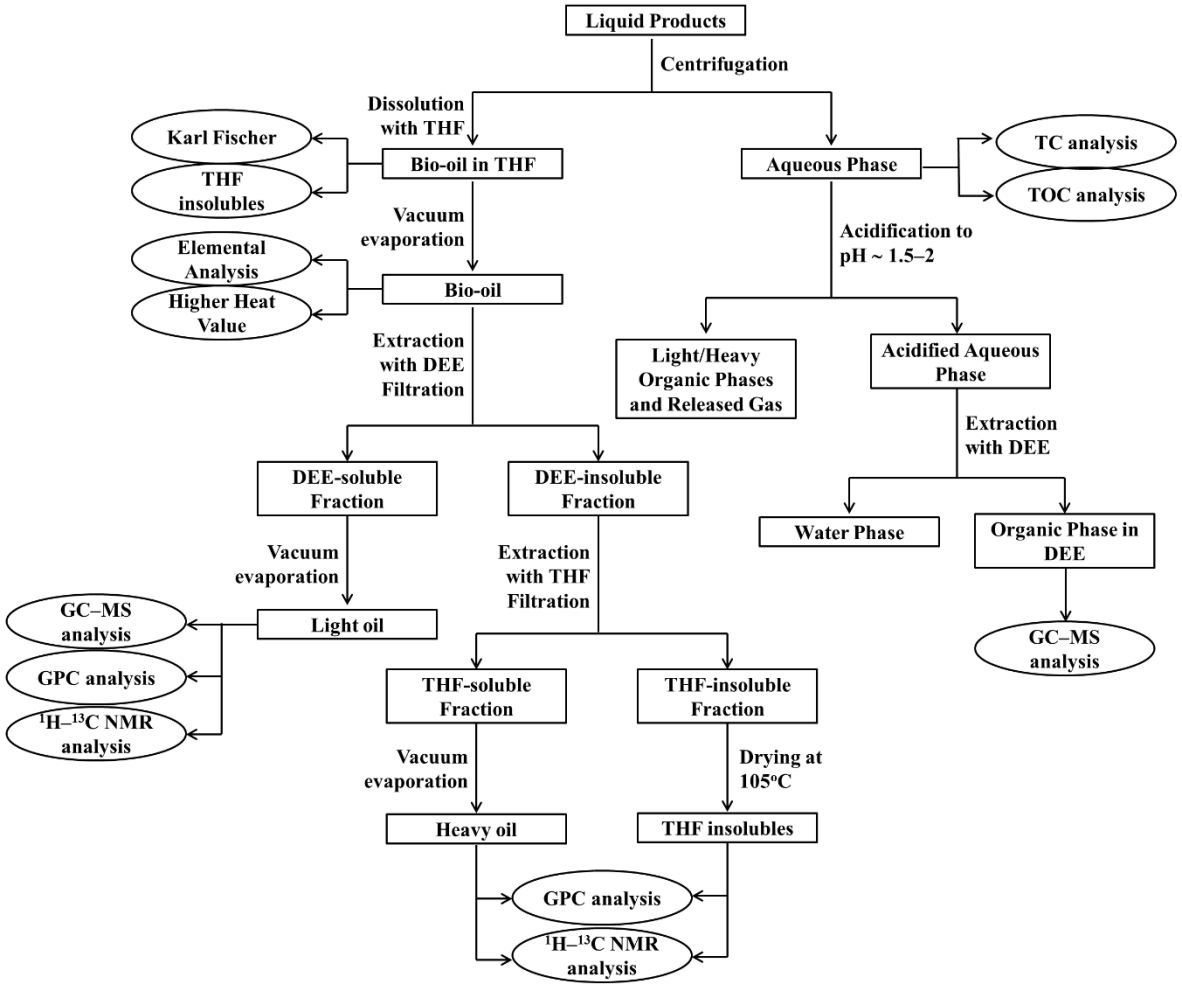


Figure 3.2 Block diagram of the analytical methods applied to the liquid products.

The amounts of total carbon (TC) and total organic carbon (TOC) present in the aqueous phase samples obtained after centrifugation were measured at SP (Borås, Sweden). In addition, the

water-soluble organics present in the aqueous phase (WSO) was identified by Gas Chromatography (GC, Agilent 7890A) coupled with Mass Spectrometry (MS, Agilent 5975C).

In the runs with lignin in the feed, it was observed that acidification led to further clarification of the aqueous phase: very small amount of two 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 WSO were carried out: syringol was used as an internal standard (IST) because (i) it is otherwise absent and (ii) it has a similar structure to that of the reaction products. Spectral interpretation was carried out using the NIST MS Search programme (Vers. 2.0) operating on the NIST/EPA/NIH Mass Spectral Database 2011 (NIST 11). An approximate quantitation of the water-soluble products in the acidified aqueous phase was 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 of the peak area was found to be 7.1%.

The lignin HTL bio-oil produced in the process was soluble in THF. The water content of the bio-oil samples obtained after centrifugation prior to, and following, the removal of THF was measured through Karl Fischer volumetric titration. The THF insolubles (TIS) in the bio-oil obtained after centrifugation, but prior to the removal of THF, were measured using Büchner funnels equipped with a Duran glass filter P2 (nominal maximum pore size 40–100 μm) and a P4 (nominal maximum pore size 10–16 μm). This allowed the quantity of the insolubles retained to be determined, along with a very rough indication of their size distribution. Furthermore, the elemental composition, ash content and heat value of the solvent-free bio-oil obtained after the removal of THF were analysed at SP, as above. The elemental composition of the stored bio-oil, on the other hand, was determined at the Mikroanalytisches' Laboratorium Kolbe (Germany); the ash content was measured using Nabertherm (Labotherm Programme Controller S27); and the HHV was calculated using Doulong's formula (**Jiang** *et al*., 2011a):

$$HHV\ [MJ/kg] = \left[338.2 \times \%C + 1442.8 \times \left(\%H - \frac{\%O}{8}\right)\right] \times 0.001$$

The lignin HTL bio-oil sample was partly soluble in DEE, and the DEE-soluble phase was analysed by means of GC–MS. Furthermore, the bio-oil was fractionated into "light oil", "heavy oil" and "THF insolubles" using DEE and THF as the solvents and Duran P4 glass as the filters. The Mw of the bio-oil and these fractions was then analysed using gel permeation chromatography (PL-GPC 50 plus). These fractions were also analysed for chemical composition using ^{1}H–^{13}C HSQC NMR (Bruker, 800 MHz and DMSO-d_6). These analyses were performed according to the methods mentioned above.

3.4.3. Quantitation of char

The reactor was cooled down and disassembled after each run before the catalyst particles were recovered. A portion of the catalyst was sampled, washed with water, dried in an oven at 105°C for 24 h, cooled down; the resulting pellets were then weighed. These were 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 be determined. Knowledge of the total amount of dry catalyst charged in the reactor prior to a run allows the total amount of char deposited on the catalyst in each experimental run to be calculated.

4. Results and Discussion

4.1. Outline of the results presented

An outline of this chapter is shown in **Figure 4.1**. Firstly, the physical and chemical characterisations of LignoBoost™ Kraft lignin are described; secondly, the influence of reaction conditions on the lignin HTL process are examined, including a discussion regarding carbon balances and product yields, analyses of the liquid products (*i.e.* the aqueous and oil phases) are made and a reaction mechanism including the capping agent (*i.e.* phenol) of the lignin HTL process is suggested. The stability studies of lignin HTL bio-oil are presented at the end of this chapter, and include storage stability at RT (raw bio-oil, 2 years) and stability at elevated temperature (raw bio-oil and bio-oil fractions, 50°C and 80°C, 1 h to 1 month). Finally, an aging mechanism that is suggested for lignin HTL bio-oil at increasing temperatures is discussed.

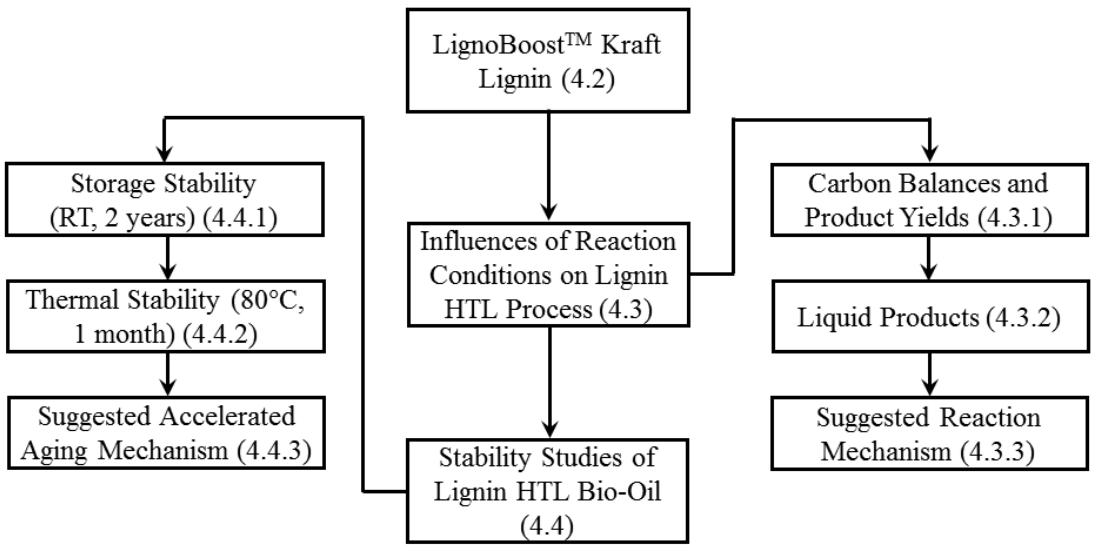


Figure 4.1 Outline of the results presented in this chapter.

4.2. LignoBoost™ Kraft lignin

The LignoBoost™ Kraft lignin used in this study had a moisture content of 32.6% and carbon, hydrogen, sulphur, potassium and ash contents of 65.6%, 5.7%, 1.85%, 0.07% and 0.8%, respectively. The oxygen content of lignin was approx. 26% (calculated value), the HHV was 27.7 MJ/kg and the Mw was 16700 Da, with a molecular weight distribution (MwD) of 3.2 (**Mattsson** *et al.*, 2016). The ^{13}C NMR spectrum (see Figure 2 in Paper I) showed that 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.

The ^{1}H–^{13}C HSQC NMR spectra of the LignoBoost™ Kraft lignin used (**Figure 4.2**) revealed important information of its structure: the peaks are divided into two general regions corresponding to the aliphatic (δ_C/δ_H 10–100/0–6 ppm) and aromatic (δ_C/δ_H 100–145/5–8 ppm) regions. The NMR spectrum in the aliphatic region consists of the major cross-peaks corresponding to methyl (-CH_3), methylene (-CH_2-), methine (-CH-) and aliphatic ether groups at the *α*-/*β*-/*γ*- positions on the propane chain as well as methoxyl groups attached to an aromatic ring (Ar-). In particular, the main region of -CH_2- groups between δ_C/δ_H 25–37/1.2–3.0 ppm corresponds to the main aliphatic network in lignin Ar–$\underline{CH_2}$–$\underline{CH_2}$–CH(R)–OH/OR located at the *α*-/*β*- positions to an aromatic ring. Moreover, the known aliphatic inter-unit linkages *β*–O–4' (*β*–aryl ether), *β*–*β*' (pioresinol and secoisolariciresinol), *β*–5' (phenyl coumarane) and 5–5'–O–4 (dibenzodioxocin) was found in the lignin structure, whereas the *β*–1' (diaryl propane 1,3-diol) linkage was not.

The NMR spectrum in the aromatic region shows that the main CH cross-speaks correspond to a guaiacol ring (**Figure 4.2**): Ar2 (δ_C/δ_H 110.7–110.8/6.9, 112.2–112.4/6.8–6.9 ppm), Ar5 (δ_C/δ_H 115.5–115.9/6.6–6.9 ppm) and Ar6 (δ_C/δ_H 119.3/6.7–6.8 ppm). Furthermore, other cross-peaks corresponding to stilbene (δ_C/δ_H 127–129/7.0–7.4 ppm) and possibly PAH (polycyclic aromatic hydrocarbon) structures (δ_C/δ_H 125–135/7.2–8.2 ppm) were also found in the lignin structure. These findings pertaining to the structure of lignin are consistent with data published in the literature (*e.g.* **Ando** *et al.*, 2016; **Balakshin** *et al.*, 2003; **Constant** *et al.*, 2016; **Giummarella** *et al.*, 2016; **Liitiä** *et al.*, 2003; **Löfstedt** *et al.*, 2016, **Narani** *et al.*, 2015; **Shen** *et al.*, 2016; **Yue** *et al.*, 2016).

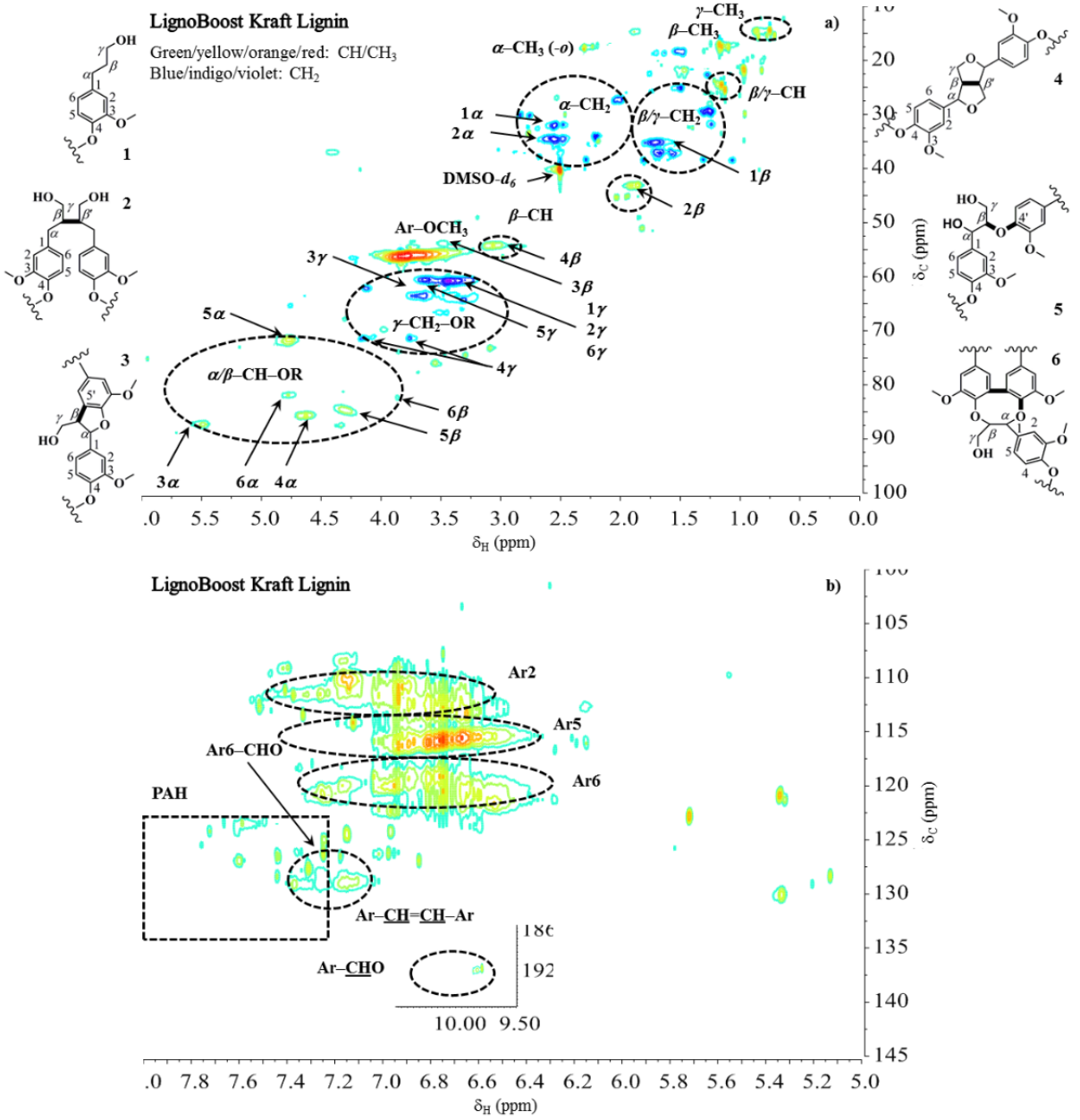


Figure 4.2 The ^{1}H–^{13}C HSQC NMR spectrum of LignoBoost™ Kraft lignin used. (a) Aliphatic region (δ_C/δ_H 10–100/0–6 ppm) and (b) aromatic region (δ_C/δ_H 100–145/5–8 ppm).

4.3. Influences of reaction conditions on the lignin HTL process

4.3.1. Carbon balances and product yields

The effects of the base catalyst and reaction temperature had on the lignin HTL process were investigated in this study. In the base concentration series (*i.e.* Runs A–D, see **Table 4.1**), the base concentration (K_2CO_3) was varied from 0.4% to 2.2%. In the temperature series (*i.e.* Runs

F–I, see **Table 4.1**), temperatures between 290°C and 370°C were used, being selected to cover the subcritical water conditions (*i.e.* 300°C < T < 374.1°C and P > 22.1 MPa).

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 for between 95% and 103% of the carbon input. Overall, these results showed that a reliable carbon balance was obtained in all runs, indicating that the loss errors suffered the analytical procedure was very small. The product yields (**Figure 4.3**) were calculated taking three different products into consideration: dry bio-oil (OIL), water-soluble organics in the acidified aqueous phase (WSO) and char (CHAR). The corresponding yields are defined here as the mass of phenol-free products relative to the mass of dry lignin fed into the system. The calculations were made using the average rate of char formation during the entire run (*i.e.* the average rates of start-up, steady-state and cooling down).

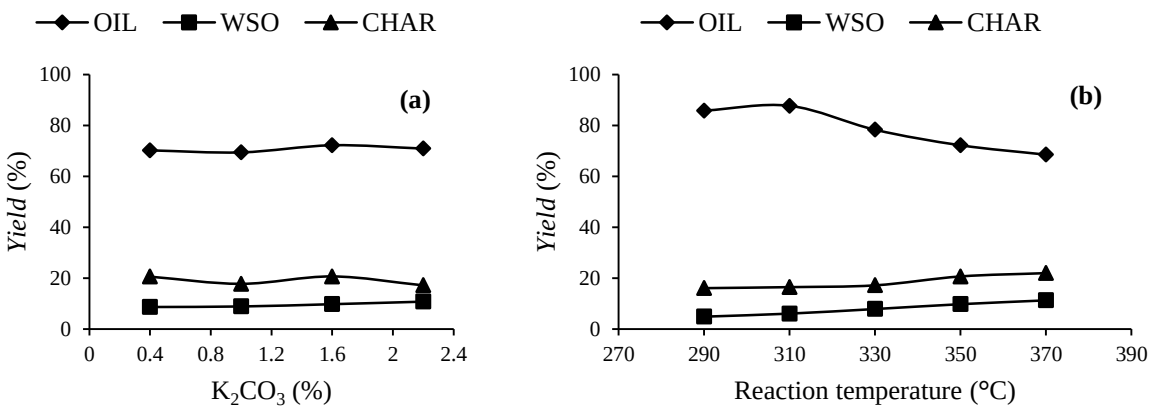


Figure 4.3 Yields (%) of oil (OIL), water-soluble organics in the acidified aqueous phase (WSO) and char (CHAR) as a function of (a) reaction temperature (at K_2CO_3 concentration of 1.6%) and (b) K_2CO_3 concentration (at the reaction temperature of 350°C).

In the K_2CO_3 concentration series (0.4–2.2%, **Figure 4.3a**), it was found that the yield of dry oil was approx. constant at around 70% and that of char was about 20% at a reaction temperature of 350°C, thus indicating that the yields of both oil and char were independent of the base concentration in the interval investigated (0.4–2.2% K_2CO_3). On the other hand, the yield of WSO found to increase slightly, from 9% to 11%, as the concentration of K_2CO_3 increased from 0.4% to 2.2%. In the temperature series (290–370°C, **Figure 4.3b**), however, the oil yield was around 85–88% at the two lower reaction temperatures (290°C and 310°C), decreasing to 69% as the reaction temperature increased to 370°C. The char and WSO yields, however,

increased from 16% to 22% and from 5% to 11%, respectively, as the reaction temperature increased from 290°C to 370°C. The reaction temperature therefore affected the yields of both the bio-oil and the WSO.

4.3.2. Liquid products

4.3.2.1. General properties of the liquid products

The liquid products obtained from the HTL process after centrifugation were comprised of an aqueous and oil phases in all of the runs with the exception of Run E (run without lignin), which had only a homogeneous aqueous phase. When the input and output pH levels are compared (**Table 4.1**), it is obvious that the pH decreased in the aqueous phase, showing that the reactions in the HTL process involve the consumption of hydroxyl ions (OH^-). The pH of the aqueous phase increased as the concentration of K_2CO_3 increased in Runs A–D, but it decreased as the reaction temperature increased in Runs F–I. This increasing consumption of OH^- in the temperature series indicates that the reaction rate increased with increasing reaction temperature. The higher reaction temperature (*i.e.* 350°C and 370°C) is, thus, supposedly the most effective for the conversion of lignin in subcritical water conditions.

Table 4.1 Steady-state output data of the liquid products obtained from the lignin HTL process.

	Base Concentration Series				**Reaction Temperature Series**					**Extra Runs**	
	A	**B**	**C**	**D**	**F**	**G**	**H**	**C**	**I**	**E**	**K[a]**
T (°C)	350	350	350	350	290	310	330	350	370	350	350
K_2CO_3 (%)	0.4	1.0	1.6	2.2	1.6	1.6	1.6	1.6	1.6	1.9	1.6
pH_f[b]	7.9	8.8	9.1	9.3	9.1	9.1	9.1	9.1	9.1	9.5	9.7
Oil/Total[c]	5.2	5.1	5.3	5.6	6.6	6.0	5.8	5.3	4.9	0	0
pH_a[d]	7.1	7.4	8.0	8.2	8.5	8.2	8.2	8.0	7.9	9.6	8.1
TC_a[d]	28	27	29	30	27	28	27	29	28	-	-
TOC_a[d]	27	26	27	27	25	26	25	27	26	-	-

[a] Methanol mass fraction: 4.1%

[b] pH of the feed

[c] Ratio between the mass flow rate of the output oil and the total mass flow rate (%) at steady-state.

[d] pH, total carbon (g/L) and total organic carbon (g/L) of the aqueous phase.

In the case of Run E (run without lignin), on the other hand, the pH of the product was 9.6, which was the same as for the feed, showing that virtually no reaction occurs with phenol involving OH^- occurs. This indicates that the reaction involving OH^- takes place only when lignin is present in the system. In the case of Run K (run with methanol instead of phenol in the system), some clogging problems were experienced and no oil phase was observed: a plausible explanation here is that, without a capping agent (such as phenol), reactive hydrolysis products

from lignin react and form larger structures that cause obstructions in the system. This indicates that the addition of phenol can suppress the cross-linking reactions and thereby improve the operational conditions drastically.

The oil phase after vacuum evaporation is known as lignin HTL bio-oil. It can be observed from the elemental analysis (**Table 4.2)** that the bio-oil obtained here was of rather high quality: it had lower contents of both water and sulphur as well as a HHV compared to Kraft lignin. The ash content in the dry bio-oil increased as the K_2CO_3 concentration increased due to the increase in the amount of potassium ion: this indicates that if a high concentration of K_2CO_3 is used, an additional washing stage may be necessary to obtain a bio-oil of high quality.

Table 4.2 Water content (%), elemental composition (%) and HHV of the lignin HTL bio-oil, calculated on a dry oil basis.

	A	**B**	**C**	**D**	**F**	**G**	**H**	**C**	**I**
T (°C)	350	350	350	350	290	310	330	350	370
K_2CO_3 (%)	0.4	1.0	1.6	2.2	1.6	1.6	1.6	1.6	1.6
Water content	1.2	1.1	2.0	1.8	9.8	1.3	2.4	2.0	2.1
Elemental composition									
C	74.6	74.2	74.9	74.8	70.0	72.6	73.9	74.9	76.0
H	6.9	6.9	6.6	6.5	6.5	6.4	6.1	6.6	6.8
N	<0.1	<0.1	<0.1	-	-	<0.1	<0.1	<0.1	<0.1
S	0.37	0.38	0.38	0.29	0.41	0.51	0.56	0.38	0.25
Cl	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Ash	1.0	2.1	2.8	3.5	2.4	2.0	2.4	2.8	1.8
O	17	16	15	15	21	18	17	15	15
Na	<0.01	<0.01	0.01	<0.01	0.01	0.01	0.01	0.01	0.01
K	0.5	1.0	1.6	1.9	1.5	1.4	1.7	1.6	1.4
HHV (MJ/kg)	31.93	31.83	31.90	31.86	31.66	31.12	31.03	31.90	32.73

Based on the elemental analysis of Kraft lignin and lignin HTL bio-oil, a Van Krevelen plot (**Figure 4.4**) showed that the atomic H/C of the bio-oils was kept as the same level as that of Kraft lignin irrespective of the K_2CO_3 concentration or reaction temperature. The atomic O/C of bio-oil, however, was lower than that of Kraft lignin, showing that a reduction of oxygen occurs during the HTL process. Moreover, the atomic O/C of the bio-oils did not show a significant change for different concentrations of K_2CO_3, whereas that value decreased when reaction temperature was decreased: the deoxygenation reaction increases with increasing reaction temperature. The low oxygen content of the lignin HTL bio-oil rendered it more chemically stable than the bio crude oil obtained by fast pyrolysis (see Section 2.5).

The ratio of potassium (K) that culminates in the wet bio-oil to that which enters the system (K present in lignin and K from the addition of K_2CO_3) decreased from 9.1% to 7.0% as the

concentration of K_2CO_3 increased from 0.4% to 2.2%. The potassium observed in the bio-oil may originate from some potassium salts that might have been precipitated, or the fact that potassium ions might act as counter ions to the organic acids present in the bio-oil. Furthermore, in the temperature series performed (290–370°C), this value was in the range of 6.5–9.2%, with no clear trend being discernible: a range which coincided approx. to that found when the reactor was operated at 350°C (base concentration series). In the ranges of the operating variables investigated, the results can be summarised as the ratio of potassium found in the oil being quite constant, with values in the range of approx. 7–9%. A low amount of potassium in bio-oil is advantageous for its quality and decreasing this value would therefore be beneficial: this is one aspect that might be investigated further as the downstream processing of lignin HTL bio-oil is developed.

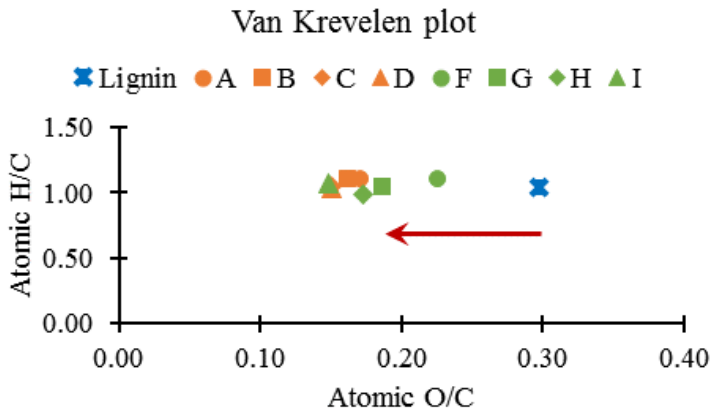


Figure 4.4 Van Krevelen plot of Kraft lignin and lignin HTL bio-oil at different K_2CO_3 concentrations and reaction temperatures.

The lignin HTL bio-oils obtained in this study were fractionated, using DEE and THF as solvents, to obtain a better understanding of the yield of the low and high Mw fractions. The yields of each fraction were calculated from the mass on a dry oil basis: the fresh bio-oil is comprised of ~63% light oil (LO), ~11% heavy oil (HO) and ~19% THF insolubles (TIS). Together with the product yields, calculated on a dry lignin basis (**Figure 4.3**), the HTL processed LignoBoost^{TM} Kraft lignin in subcritical water (290−370°C, 25 MPa) gives ~9% WSO (mainly monomers), 47% light oil (mainly monomers and dimers), 8% heavy oil (mainly oligomers), 14% THF insolubles, and 19% char. Thus, the low Mw part is the major product of the lignin HTL process, indicating that the HTL process is an efficient method for the depolymerisation of lignin.

Measuring the Mw of the bio-oil fractions (LO, HO and TIS) revealed that the Mw increases in the order: light oil, heavy oil and THF insolubles (**Figure 4.5**). Light oil comprises a high amount of monomers (Peak 1, ~60 Da) and low amounts of dimers (Peak 2, ~200 Da) and oligomers (Peak 4, ~2000 Da). The heavy oil comprises mainly oligomers, with a low amount of Peak 3 (~400 Da) and a higher amount of Peak 5 (~3600 Da). The THF insolubles have just one peak with high Mw oligomers (Peak 6, ~8600 Da). Compared to the Mw of LignoBoost™ Kraft lignin (~16700 Da), it can be established that lignin has been converted here to give fractions of lower Mw (*i.e.* LO and HO).

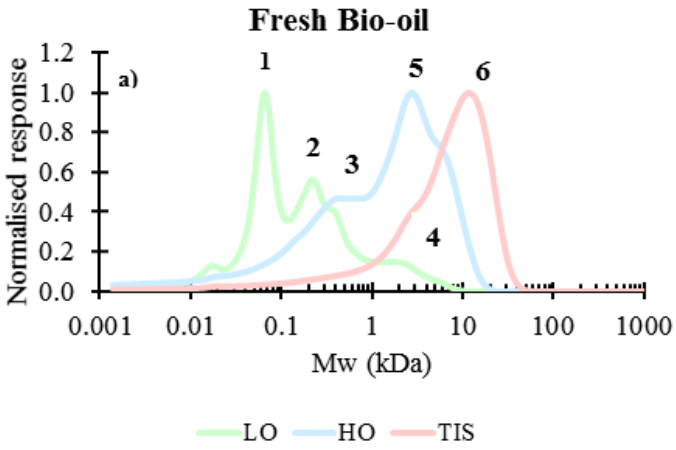


Figure 4.5 Typical MwD curves for lignin HTL bio-oil fractions: light oil, heavy oil and THF insolubles.

4.3.2.2. GC–MS analysis of the liquid products

In **Figure 4.6**, an example of a GC–MS Total Ion Current Chromatogram (TICC) is shown for the DEE extracts in the acidified aqueous phase (black line) and the DEE-soluble fraction in the lignin HTL bio-oil (blue line): as mentioned previously, in Chapter 3, the method used for determining the yield of the compounds may be considered as being semi-quantitative. The DEE-soluble fraction of the bio-oil identified by GC–MS was in the range of 21–40% of the original weight of bio-oil and comprised mainly of 1-ring aromatic compounds.

Besides phenol, which was used in the feed, the main compounds detected in these samples were anisoles (*i.e.* anisole and alkyl anisoles), alkyl phenols (methyl and ethyl groups), guaiacols (*i.e.* guaiacol and alkyl guaiacols), catechols (*i.e.* catechol and alkyl catechols) and phenolic dimers (*i.e.* Ar–CH_2–Ar and Ar–CH_2–CH_2–Ar). Moreover, although most of the compounds in the DEE-soluble fraction of the bio-oil were the same as in the aqueous phase, their relative concentration differed, depending on whether they were hydrophilic or hydrophobic. For

example, catechol was relatively more abundant in the aqueous phase because it has two hydroxyl groups attached to the aromatic ring: this makes it more hydrophilic than either anisole or guaiacol, which have only one methoxyl group.

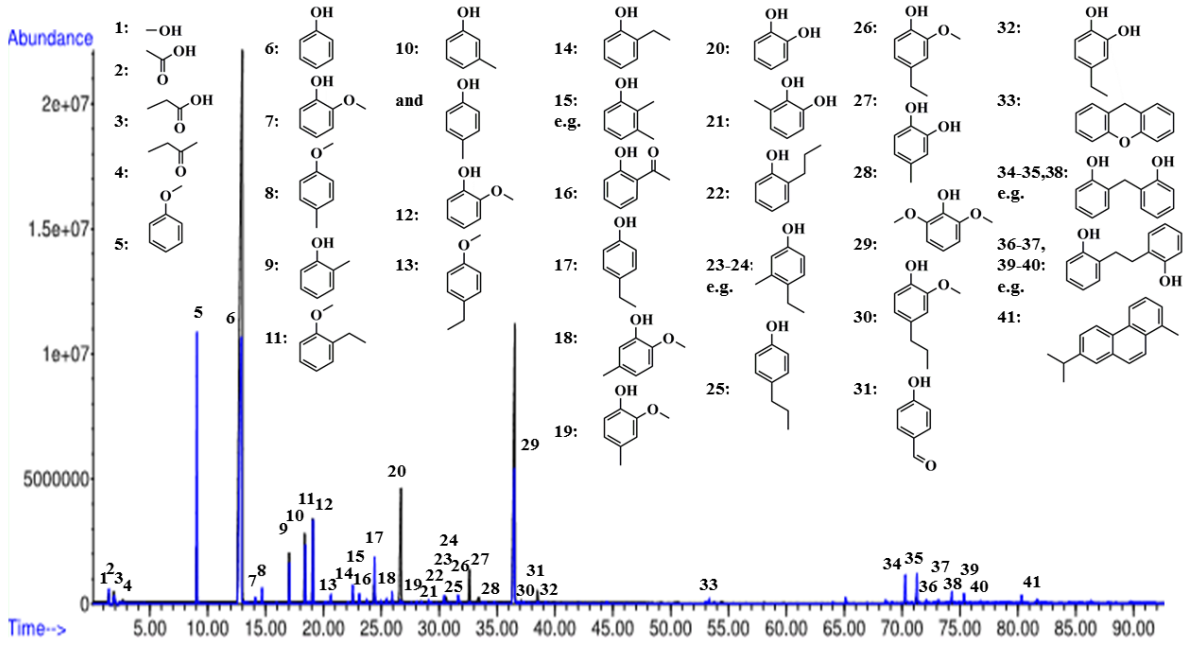


Figure 4.6 Typical GC–MS TICC in the DEE extracts of the acidified aqueous phase (black line) and the DEE-soluble fraction of lignin HTL bio-oil (blue line): sample from Run H. Peak 29 is syringol, the IST.

Table 4.3 Yields (%) of the main classes of the compounds found in the acidified aqueous phase and the DEE-soluble fraction in the lignin HTL bio-oil.

	A	**B**	**C**	**D**	**F**	**G**	**H**	**C**	**I**
T (°C)	350	350	350	350	290	310	330	350	370
K_2CO_3 (%)	0.4	1.0	1.6	2.2	1.6	1.6	1.6	1.6	1.6
Aqueous phase									
Phenol	2.18	2.08	1.96	1.65	1.81	1.71	1.64	1.96	1.70
Alkyl phenols	0.17	0.19	0.20	0.21	0.03	0.06	0.12	0.20	0.29
Guaiacols	0.10	0.07	0.06	0.04	0.13	0.11	0.07	0.06	0.02
Catechols	0.22	0.23	0.27	0.30	0.07	0.12	0.20	0.27	0.28
Phenolic dimers	0.01	0.01	0.01	0.01	0.02	0.02	0.01	0.01	0.00
Total (incl. phenol)	2.70	2.60	2.53	2.28	2.09	2.07	2.10	2.53	2.36
Total (excl. phenol)	0.52	0.52	0.57	0.63	0.29	0.36	0.46	0.57	0.65
DEE-soluble bio-oil									
Anisoles	2.39	5.08	5.23	9.42	2.04	3.09	4.72	5.23	6.17
Phenol	13.43	14.56	12.80	16.22	11.51	9.77	12.44	12.80	11.35
Alkyl phenols	4.26	5.54	5.83	6.44	0.95	1.61	3.60	5.83	7.75
Guaiacols	3.21	2.54	2.00	2.66	2.55	2.26	2.16	2.00	1.02
Catechols	0.59	0.58	0.42	0.80	0.14	0.25	0.19	0.42	0.62
Phenolic dimers	1.79	2.02	1.84	2.61	5.08	4.08	2.27	1.84	1.03
Total (incl. phenol)	26.70	31.34	28.71	39.52	22.54	21.47	25.76	28.71	28.67
Total (excl. phenol)	13.27	16.78	15.91	23.30	11.04	11.70	13.33	15.91	17.32

Several compounds found in the DEE-soluble fraction of bio-oil, such as alkyl anisoles, 1-ring aromatic compounds with propyl side groups, ethyl cresols, 2-acetylphenol and two 3-ring aromatic compounds, were not found in the aqueous phase. Furthermore, small amounts of methanol, acetic acid, 2-butanone, propanoic acid, salicylic acid and 4-hydroxybenzaldehyde were found in the aqueous phase (see Table 4 in Paper I and Table 2 in Paper II). The same set of compounds was found in Runs A–D (*i.e.* at different concentration of K_2CO_3) and Runs F–I (*i.e.* at different reaction temperatures). Since these compounds were not found in Run E (run without lignin), it may be concluded that the compounds found in the aqueous phase and bio-oil are derived from the chemical conversion of lignin.

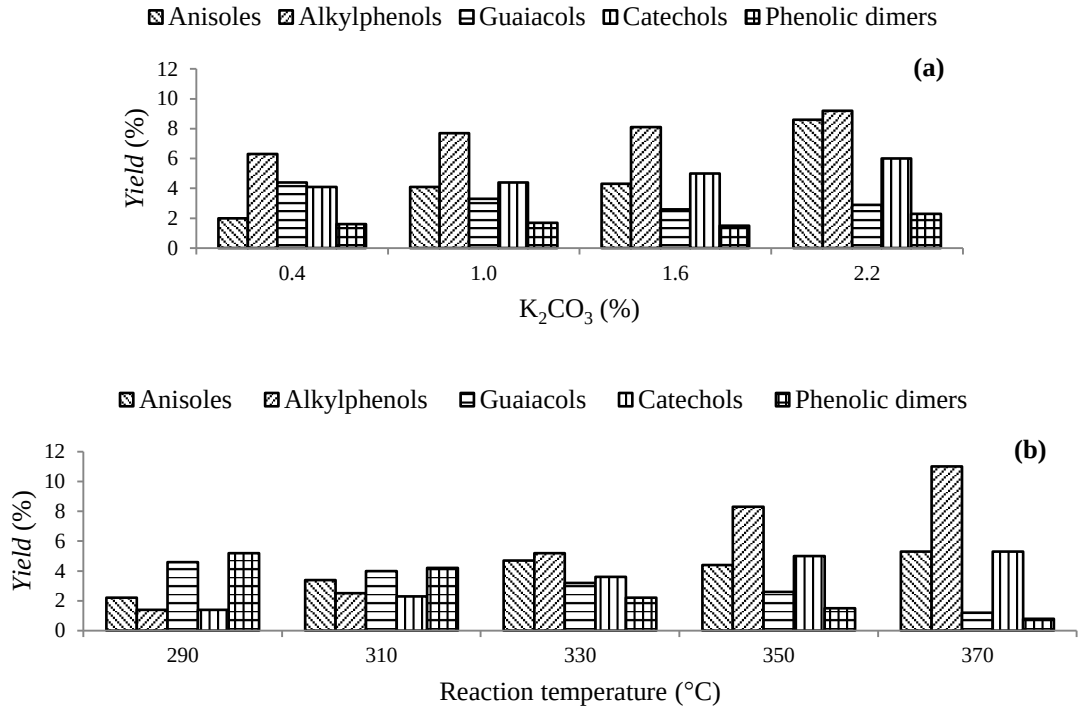


Figure 4.7 Yields of the different classes of aromatic compounds in WSO and DEE-soluble lignin HTL bio-oil, calculated on a dry lignin basis, as a function of (a) concentration of K_2CO_3 at 350°C and (b) reaction temperature at concentration of K_2CO_3 of 1.6%.

The yields of the main classes of the compounds found in the acidified aqueous phase and DEE-soluble fraction in the lignin HTL bio-oil (**Table 4.3**) showed different trends as the concentration of K_2CO_3 and reaction temperature increased, with an increase in the yield of anisoles, catechols and alkyl phenols, together with a decrease in the yield of guaiacols, being observed in particular. Taking into account the quantities of the main classes of compounds found in both the aqueous and bio-oil phases (**Figure 4.7**), the overall yield of 1-ring aromatic compounds increased remarkably from 17% to 27% as the concentration of K_2CO_3 increased

(0.4–2.2%) and from 10% to 23% as the reaction temperature increased (290–370°C). When the K_2CO_3 concentration increased, a relatively large increase was found for anisoles in particular (20–86 g/kg), while alkyl phenols (63–92 g/kg) and catechols (41–60 g/kg) increased to a lesser degree; when the reaction temperature increased, a relatively large increase was found for alkyl phenols (14–110 g/kg), whilst the increase for anisoles (22–53 g/kg) and catechols (14–53 g/kg) was less. The yield of phenolic dimers was found to increase with increasing K_2CO_3 concentration, whilst it decreased with increasing reaction temperature: the concentration of K_2CO_3 and reaction temperature therefore exerted different effects on the yields of the liquid products.

In the case of Run K (run with methanol instead of phenol as capping agent), a different composition of the liquid product was observed and the aqueous phase was analysed with qualitative GC–MS (area %). The dominating aromatics here were in the order of catechols (~30%) > guaiacols (~20%) > alkyl phenols (~2%); it was not possible to detect either anisole or phenolic dimers in this run.

4.3.2.3. 2D NMR analysis of the lignin HTL bio-oil

The chemical structures of the various fractions of lignin HTL bio-oil (*i.e.* light oil, heavy oil and THF insolubles) were analysed using ^{1}H–^{13}C HSQC NMR (**Figure 4.8**). In the NMR spectrum in the aliphatic region of the fresh light oil, the major cross-peaks corresponding to aromatic substituents were methylene, ethylene, methoxyl and methylene groups adjacent to the alcohol groups. No evidence was found of a methylene group adjacent to the carboxylic groups between δ_C/δ_H 50–60/3.5–4.1 ppm in the bio-oil: the reason for this may be found in the fact that hydrophilic compounds (*e.g.* compounds having carboxylic groups) ends up in the water phase which is separated from the bio-oil after exiting the HTL process. The NMR spectrum in the aromatic region is predominated by many cross-peaks assigned to aromatic CH at the *o*-/*m*-/*p*- positions of not only phenolic rings (such as phenols, catechols and phenolic dimers) but also other aromatic compounds (such as anisoles and guaiacols). Using the ^{1}H–^{13}C HSQC NMR spectra obtained for the model compounds (see Table S1 and Figure S1 in Paper V), the relative contents of the various compounds in the fresh light oil were found to be phenols > anisoles, guaiacols > catechols: this is consistent with the GC–MS results of the fresh light oil (see Section 4.3.2.2).

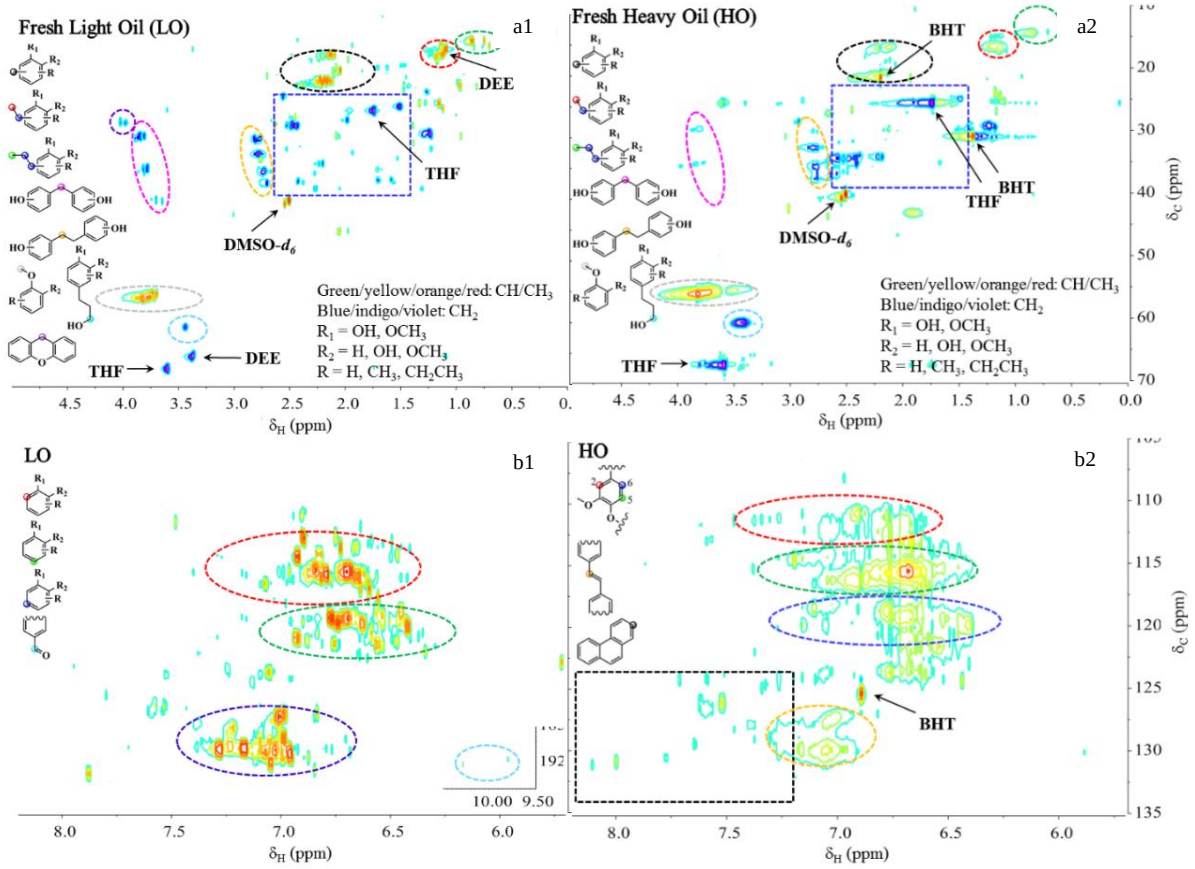


Figure 4.8 (a) The aliphatic region (δ_C/δ_H 10–70/0–5 ppm) and (b) the aromatic region (δ_C/δ_H 105–135/5.7–8.2 ppm) (b) in a typical ^{1}H–^{13}C HSQC NMR spectrum (800 MHz, DMSO-d_6) of fresh light oil (LO) and fresh heavy oil (HO).

The NMR spectrum of the fresh heavy oil shows the structural motifs, such as aliphatic methylene and methyl groups, faint signals of methylene bridges (Ar–CH_2–Ar) and aliphatic dihydroconiferyl alcohol-like groups (Ar–CH_2–CH_2–CH_2–OH) in the aliphatic region together with aromatic CH (Ar2, Ar5 and Ar6), alkene bridges (Ar–CH=CH–Ar) and PAH-like structures in the aromatic region. The heavy oil is generally assumed to be a mixture of various macromolecules, the structures of which are mainly an aromatic network connected by alkene (vinylic and allylic-like) and aliphatic linkages (C2–C4). It can be observed that the cross-peaks of the alkyl groups in all the bio-oil fractions (LO, HO and TIS) were found mostly at the α-position, which was not the case for LignoBoost^{TM} Kraft lignin, indicating that the dealkylation reactions occurred during the HTL process. Although a few aliphatic dihydroconiferyl alcohol-like groups (Ar–CH_2–CH_2–CH_2–OH) still exist in the fresh light oil and heavy oil, none of the typical inter-unit linkages that are present in native lignin can be detected when compared to the LignoBoost^{TM} Kraft lignin (see **Figure 4.2**), demonstrating virtually that all the inter-unit linkages present in the lignin have been cleaved during the HTL process (**Mattsson** *et al.*,

2016). It is reasonable to assume that the lignin was hydrolysed and dealkylated in the HTL process to produce small aromatics that were, in turn, repolymerised to form molecules of higher Mw.

4.3.3. A suggested reaction mechanism

The reaction system studied in this work (the HTL process, using phenol as the capping agent) is extremely complicated. Each of the compounds identified in the product stream may have been formed via several reaction pathways: some as a product of the disintegration of lignin, others as a result of the reaction with phenol and, of course, a combination of both. Although this makes it very difficult to elucidate the reaction pathways precisely, an attempt is made here below to clarify some of the reaction pathways that are plausible: it is, however, by no means complete.

It can be concluded, from all of the test runs carried out, that this reaction system gives high yields of alkyl phenols, guaiacols, catechols and phenolic dimers. The reaction conditions influence the composition of the product in different ways: an increase in the concentration of K_2CO_3 results in an increase in the yield of water-solubles, anisoles and phenolic dimers. An increase in the concentration of K_2CO_3 is assumed to promote not only the hydrolysis of lignin (due to the more polarised ether bond by K^+ and facilitated ionic cleavage), but also repolymerisation of the decomposed fragments of lignin (**Karagöz** *et al.*, 2005, 2006; **Roberts** *et al.*, 2010a, 2010b). On the other hand, an increase in the reaction temperature results in an increase in the yield of alkyl phenols and a decrease in phenolic dimers. At higher temperatures, phenol is assumed to trap more the reactive fragments (*e.g.* methyl and ethyl), thereby forming more alkyl phenols and phenolic dimers (**Saisu** *et al.*, 2003). Also, the more stable C–C bonds in lignin and oligomers are most likely to be cleaved at high temperature (**Fang** *et al.*, 2008), which explains the higher yield of alkyl phenols and lower yield of phenolic dimers obtained at higher reaction temperatures. The lowest yield of guaiacols and the highest yield of catechols, however, were obtained not only at the highest K_2CO_3 concentration but also the highest temperature. The increase of catechols and a simultaneous decrease of guaiacols could be due to the high degree of demethylation of methoxyl groups with increasing reaction temperatures and K_2CO_3 concentrations (**Lavoie** *et al.*, 2011).

When the experiments using phenol as the capping agent (see **Table 4.3**, Runs A–I) are compared with the one using methanol (Run K), it can be concluded that the composition of the product is very different: the reaction pathway is therefore influenced by the capping agent. This suggests that the capping agent is involved in the reactions which, in fact, is the purpose

of the capping agent: it should react with reactive entities of lignin (*i.e.* methanol, alkyl fragments, aldehydes, etc.) and, thus, hinder them from, for example, starting repolymerisation reaction. The phenol is most likely involved in several reactions with various reactive entities of lignin to form anisoles, alkyl phenols and phenolic dimers at the *o-/p-* positions of the phenolic rings (**Okuda** *et al.*, 2004; **Roberts** *et al.*, 2010a).

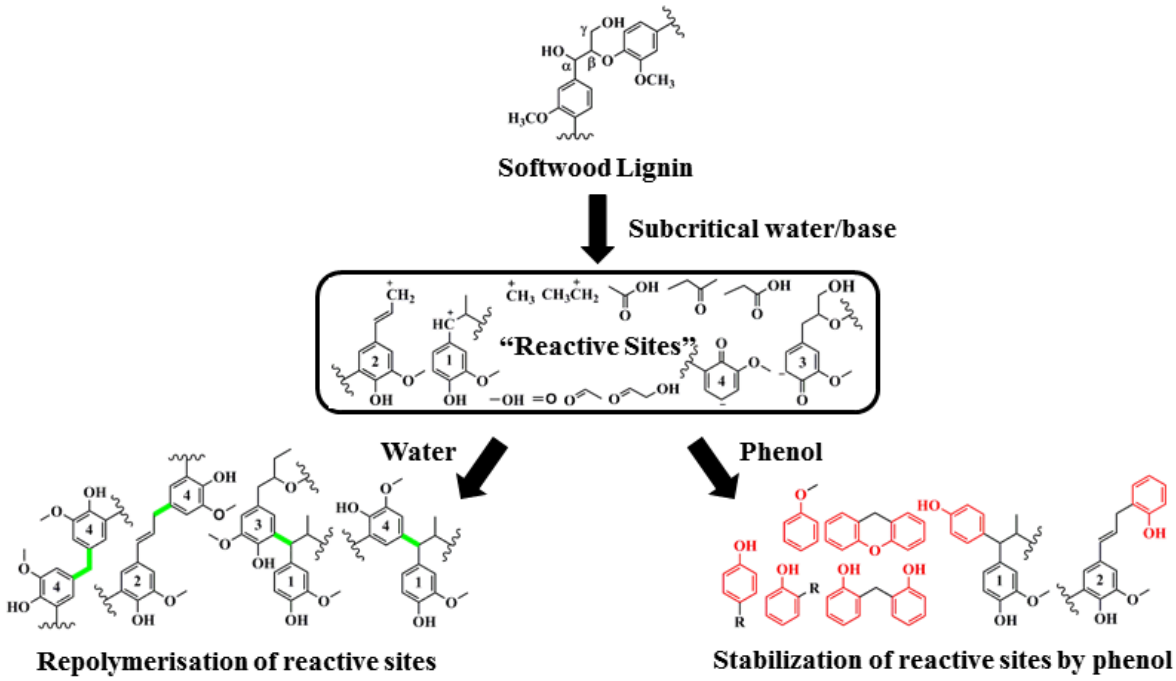


Figure 4.9 Suggested mechanism of lignin HTL process in the presence of phenol

Based on the experimental data obtained in this work, a possible overall reaction pathway for phenol in the lignin HTL process is suggested in **Figure 4.9**. It starts with the lignin being hydrolysed and dealkylated at its active sites (*i.e.* ether bond and propane chains) to form methoxylated benzenes (*i.e.* guaiacol structures), which react further to form hydroxylated benzenes (*i.e.* catechol structures) and reactive entities (aldehyde, alkyl fragments, methanol, etc.). These reactive entities are then trapped by phenol to form phenolic dimers, alkyl phenols, anisole, etc., preventing condensation/ repolymerisation from occurring in the medium, and also suppressing the formation of char. It should, however, be kept in mind that, the structures mentioned in **Figure 4.9** may also originate from the lignin structure via other reaction pathways.

4.4. Stability studies of lignin HTL bio-oil

4.4.1. Storage stability

4.4.1.1. Properties of the stored bio-oil

The storage stability of lignin HTL bio-oil and fractionated light oil was investigated at RT for a period of 2 years in order to obtain better knowledge at the natural aging of these types of bio-oils. Feeds with low concentrations of K_2CO_3 (Runs A and B, 0.4−1.0%) gave yields of bio-oil fractions that did not differ much between the fresh and stored samples (**Table 4.4**). Feeds with high concentrations of K_2CO_3 (Runs C, D, and F−I, 1.6−2.2%), on the other hand, showed a clear trend: after 2 years of storage, the yield of light oil decreased but that of heavy oil and THF insolubles increased. The MwD data of the bio-oil showed a decrease in the low Mw components and an increase in the high Mw components after 1 year of storage (see Figure 4 in Paper IV), indicating that the low Mw components were consumed in the repolymerisation/ condensation reactions: the high Mw components thus formed a larger part of the stored bio-oil, with the result that its average Mw increased. This was also consistent with the yields results that were calculated for the different fractions of bio-oil (see **Table 4.4**).

Table 4.4 The yields (%) of each fraction in the lignin HTL bio-oils before and after 2 years of storage at RT, calculated on a dry oil basis.

	A	**B**	**C**	**D**	**F**	**G**	**H**	**C**	**I**
T (°C)	350	350	350	350	290	310	330	350	370
K_2CO_3 (%)	0.4	1.0	1.6	2.2	1.6	1.6	1.6	1.6	1.6
Fresh									
Light oil	68.5	62.9	69.6	65.4	46.8	59.4	49.5	69.6	72.0
Heavy oil	23.6	11.2	4.4	4.9	14.4	11.2	13.9	4.4	9.5
THF insolubles	7.9	25.9	26.0	29.6	38.8	29.4	36.5	26.0	18.5
Stored									
Light oil	68.2	62.2	60.7	55.2	42.6	50.6	34.6	60.7	55.4
Heavy oil	24.9	12.8	9.0	8.8	18.6	17.7	23.9	9.0	13.8
THF insolubles	6.8	25.0	30.3	36.0	38.8	31.7	41.5	30.3	30.7

Furthermore, the elemental composition changes that occurred in the bio-oil during long-term storage were relatively small, even though this trend was not observed consistently in all of the runs (see Table 4 in Paper IV). At a reaction temperature of 350°C (Runs A−D, 0.4–2.2% K_2CO_3), two trends could be observed clearly, namely a decrease in the carbon content from 75% to 71% and an increase in the oxygen content from 16% to 19% (calculated value); the latter may be explained by the leakage of O_2 into the bio-oil during storage. Consequently, the atomic O/C increased after storage, but the atomic H/C was more or less stable, demonstrating

the possibility that oxidation reactions occur during storage (**Figure 4.10**). The DEE-soluble fractions of the bio-oil and light oil were analysed using GC–MS (**Figure 4.11**). A very small change in the yield of aromatic compounds was detected after the bio-oil was stored for 2 years. In general, there was an increase in the yields of anisole (from 3% to 4%) and phenol (from 12% to 15%) and a decrease in alkyl phenols (from 4% to 3%), catechols (from 0.5% to 0%), xanthene (from 0.2% to 0%), and phenolic dimers (from 3% to 1%), along with minor changes in the quantities of alkyl anisoles, guaiacols and retene. Even though anisole, alkyl phenols, catechols, xanthene and phenolic dimers are present as reactive compounds in the bio-oil, their reactivity is rather small. In addition, the total yield of aromatic compounds (excluding phenol) of the bio-oil decreased from 15% to 11% after storage.

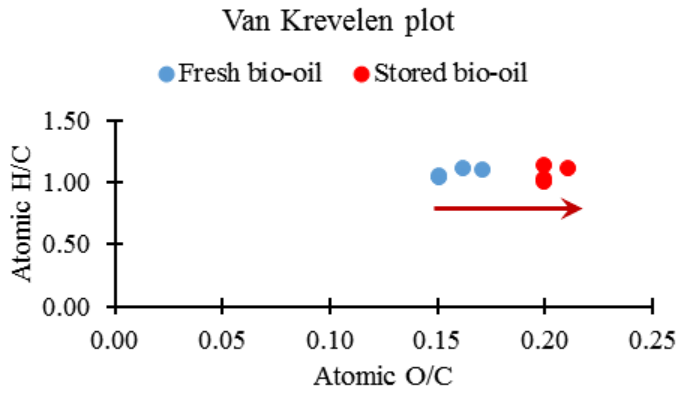


Figure 4.10 Elemental composition of the samples of lignin HTL bio-oil, both fresh and stored for 2 years at RT, from Runs A–D (K_2CO_3 concentration 0.4–2.2%).

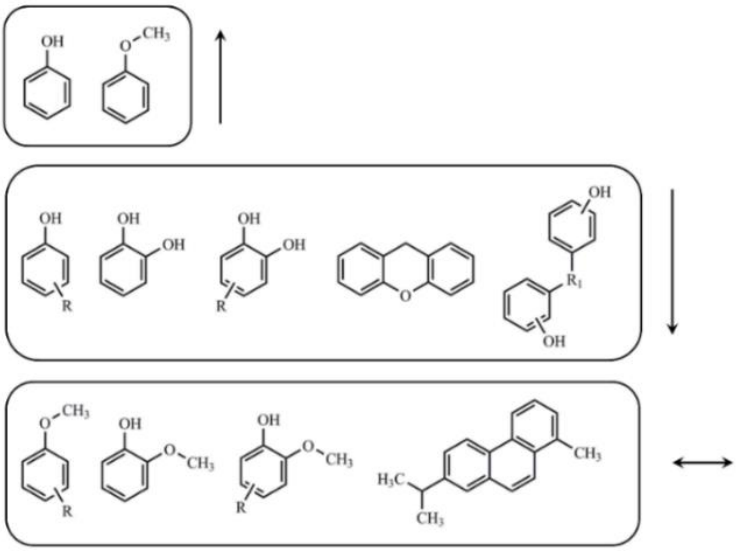


Figure 4.11 General variations found in the different compounds, as identified by GC–MS, in the DEE solubles of lignin HTL bio-oil after long-term storage at RT.

4.4.1.2. Influence of THF insolubles on the stability of bio-oil

It is obvious from the results of the yields of bio-oil fractions (see **Table 4.4**) and aromatic compounds identified by GC–MS (see Table 5 in Paper IV) at different concentrations of K_2CO_3, that the base concentration in the system affected the stability of the bio-oil: the higher the concentration of K_2CO_3 (1.6−2.2%) in the feed, the larger the change in the yield of the different fractions and GC–MS aromatic compounds. This decrease in the yield of bio-oil fractions and GC–MS aromatic compounds was correlated to the increase of the ash content in the bio-oil (from 1.0% to 3.5%, see Table 4 in Paper IV). Ash/insolubles have been reported as promoting the catalytic repolymerisation reactions of pyrolysis bio-oil, thereby affecting its stability during long-term storage (**Yang** *et al*., 2015). The same trend was found in this study: the bio-oil was more stable when it had low contents of ash/insolubles (low base concentration 0.4% and 1.0%).

This was supported further by the light-oils that were aged in which neither ash nor THF insolubles were present during long term storage: here, only a slight decrease in the total yield of GC–MS aromatic compounds (excluding phenol) was detected, *i.e.* from 15% to 14% (see Table 5 in Paper IV). This showed that the stored light oil had a more stable chemical composition than the stored bio-oil and that, by removing THF insolubles from bio-oil, this could potentially retard the aging process or enhance its stability. Lignin HTL bio-oil is therefore not as stable as conventional fossil fuels when stored long-term at RT: it is, however, much more stable than biomass-pyrolysis bio-oil (*cf.* **Chaala** *et al*., 2004, **Chen** *et al*., 2014; **Yang** *et al*., 2015).

Table 4.5 Yield (%) of each fraction of raw bio-oil before and after accelerated aging at different temperatures for different periods of time, calculated on a dry oil basis.

Aging temperature (°C)	**Fresh**	**50°C**				**80°C**			
Aging time		**1 h**	**1 d**	**1 w**	**1 m**	**1 h**	**1 d**	**1 w**	**1 m**
Light oil	64.1	63.5	60.0	59.9	62.3	62.9	58.4	61.7	58.1
Heavy oil	19.4	17.0	19.6	19.7	16.8	18.1	21.5	17.2	19.7
THF insolubles	16.5	19.5	20.4	20.4	20.9	19.0	20.1	21.1	22.2

4.4.2. Thermal stability

The thermal stability of lignin HTL bio-oil was investigated by carrying out two experimental series using accelerated aging of this type of bio-oil: (a) raw bio-oils that were aged at 50°C and 80°C for periods of 1 h, 1 d, 1 w and 1 m, and (b) bio-oil fractions (*i.e.* light oil and heavy

oil) that were aged at 80°C for periods of 1 h, 1 d and 1 w. All fractions were analysed by GPC, GC–MS and 2D NMR to determine the changes in Mw and chemical composition during aging.

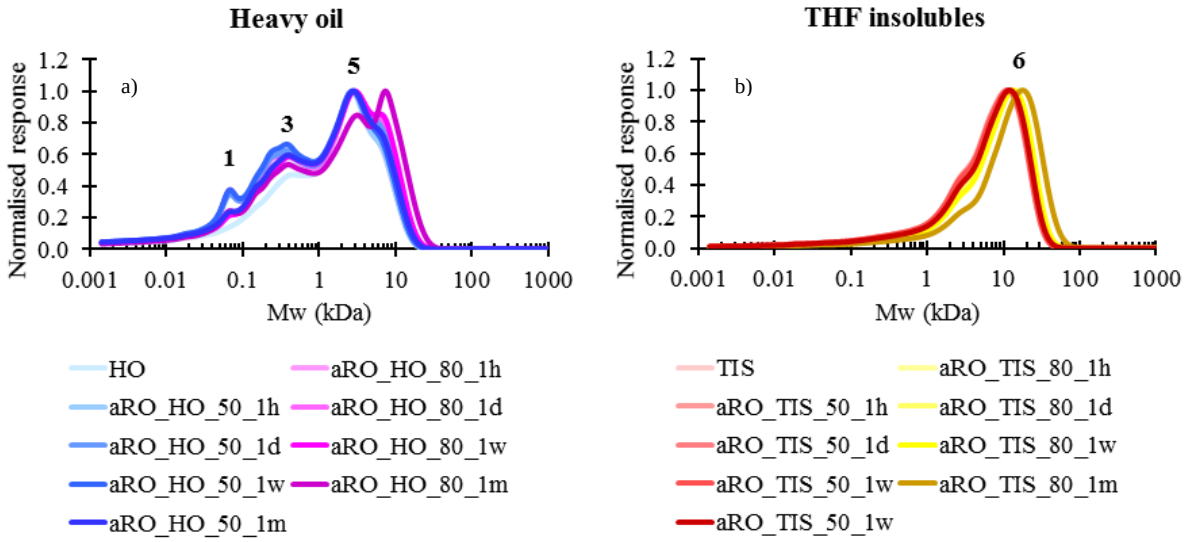


Figure 4.12 MwD curves for (a) fresh heavy oil (HO) and aged raw oil_heavy oil (aRO_HO), and (b) fresh TIS insolubles (TIS) and aged raw oil_THF insolubles (aRO_TIS).

4.4.2.1. Accelerated aging of the raw bio-oil

The raw bio-oil was analysed regarding the water content and elemental composition before and after aging at 80°C for 1 m (see Table 2 in Paper VI): no significant change was found. The aged raw bio-oil was fractionated into light oil (aRO_LO), heavy oil (aRO_HO) and THF insolubles (aRO_TIS) in order to assess its compositional changes (see **Figure 4.14**): it was found that the yield of light oil decreased whereas the THF insolubles increased after aging (**Table 4.5**). A higher aging temperature (80°C) and a longer aging time (1 m) resulted in larger changes in the yields of the bio-oils fractions. These aged raw oil fractions (*i.e.* light oil, heavy oil and THF insolubles) were analysed by GPC (**Figure 4.12**). After aging at 80°C for 1 m, minor changes in the Mw of these raw oil fractions could be detected: the MwD curves for the heavy oil (aRO_HO) and THF insolubles (aRO_TIS) in particular showed a significant shift toward signals characteristic of species of higher Mw. This indicates that the severest condition (80°C and 1 m) can alter the MwD of the bio-oil. However, the MwD curves for the fresh (LO) and aged light oils (aRO_LO) showed that there were no changes in the Mw (see Figure 2a in Paper V).

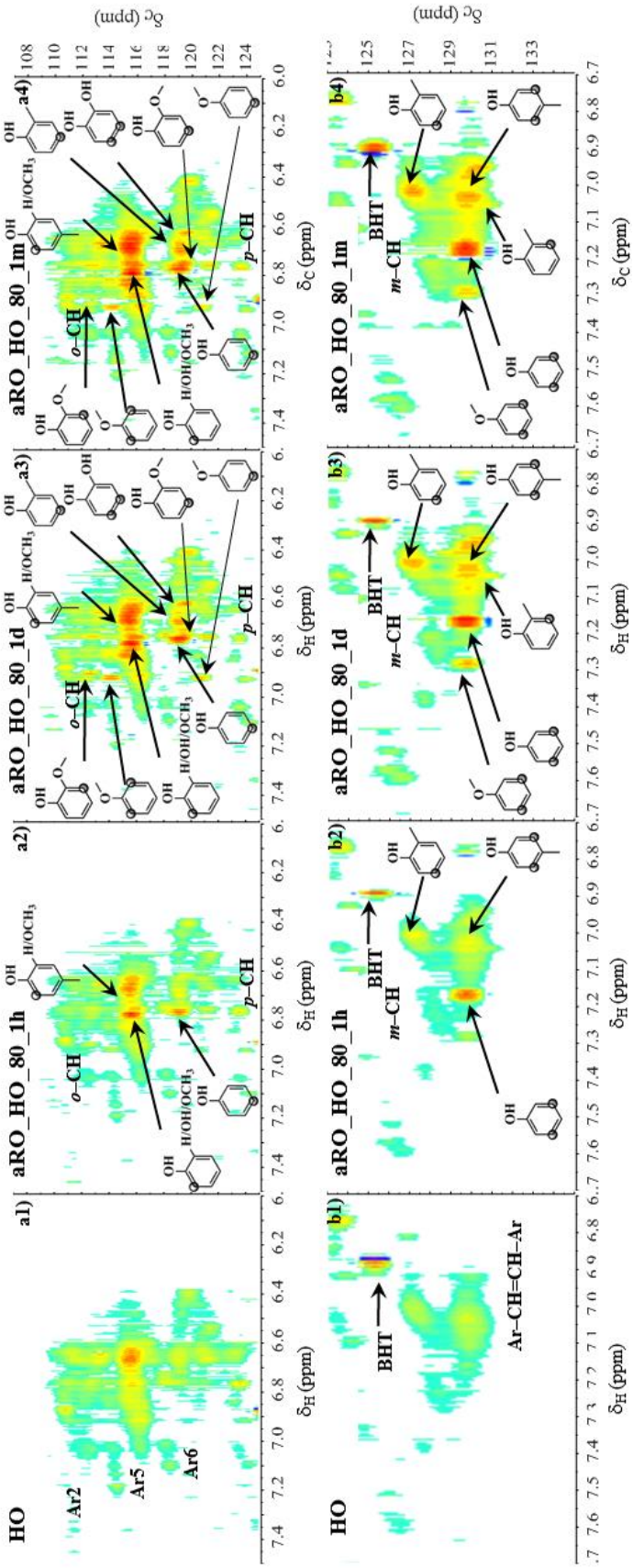


Figure 4.13 $^{1}H–^{13}C$ HSQC NMR spectra (800 MHz, DMSO-d_6) of the fresh heavy oil (HO) (a1, b1, c1 and d1) and aged raw oil_heavy oil at 80°C for 1 hour (aRO_HO_80_1h) (a2, b2, c2 and d2), 1 day (aRO_HO_80_1d) (a3, b3, c3 and d3) and 1 month (aRO_HO_80_1m) (a4, b4, c4 and d4).

The chemical composition of the DEE soluble fractions in the fresh and aged bio-oil were analysed by GC–MS (see Table 3 in Paper VI). The reactivity of the compounds in the bio-oil was found to be in the order: phenolic dimers (Ar–CH_2–Ar) > phenol > anisole > phenolic dimers (Ar–CH_2–CH_2–Ar) > guaiacol > alkyl phenols, alkyl anisoles, alkyl guaiacols, xanthene, catechol and retene. At the severest condition (1 m and 80°C), the yields of anisole (6.3% to 5.7%), phenol (16.0% to 14.1%) and phenolic dimers (Ar–CH_2–Ar, 2.3% to 0.1%; Ar–CH_2–CH_2–Ar; 0.5% to 0.2%) were found to be reduced. The large decrease in the yield of phenolic dimers shows that these bridging phenolic structures have a high reactivity/ instability in the conditions investigated.

The chemical structure of the aged bio-oil fractions was analysed using ^{1}H–^{13}C HSQC NMR (see Figures 3–5 in Paper VI). Comparing the ^{1}H–^{13}C HSQC NMR spectra of the fresh light oil (LO) with the aged light oil at 80°C for 1 month (aRO_LO_80_1m) showed that there were no new cross-peaks in the aliphatic region of the aged fraction: there was just a slight reduction in the existing structural motifs such as the aromatic substituents methyl, methoxyl and aldehyde groups. In the aromatic region, phenol and anisole were found to decrease slightly after aging, which corresponds well with the GC–MS data.

When the ^{1}H–^{13}C HSQC NMR spectra of the aged heavy oil (aRO_HO_80) are compared to those of fresh heavy oil (HO) (**Figure 4.13**), structural changes can be clearly observed in the aromatic region of the aged fraction: the new molecules, with cross-peaks of high signal intensity, show similarities with the alkylated phenol structures found in the light oil (see **Figure 4.8**). The intensity of these molecules increased when the raw oil was aged at 80°C for 1 m. In the aliphatic region, the structures of the aromatic substituents (such as methoxyl and methyl groups) were found to be increased in the aged fraction. This suggests that anisole, guaiacol and alkylated phenolic structures form parts of a new "phenolic macromolecule" that was formed from the light oil after aging. Moreover, other cross-peaks, such as the aldehyde groups, were found to be reduced in intensity with longer aging time.

Taking into account all the results obtained from the yields, and the properties of the aged bio-oil, it can be concluded that, compared to biomass-pyrolysis bio-oil, lignin HTL bio-oil is more stable at 80°C after 1 m of storage (*cf.* **Alsbou** and **Helleur**, 2014; **Boucher** *et al*., 2000; **Garcìa-Pèrez** *et al*., 2006; **Joseph** *et al*., 2016; **Li** *et al*., 2015; **Meng** *et al*., 2015). During the accelerated aging of bio-oil (80°C and 1 m), various oligomerisation/polymerisation reactions of reactive compounds occur not only in the light oil but also in the heavy oil (see **Table 4.5**) and form molecules of high Mw (*i.e.* heavy oil and THF insolubles, see **Figure 4.12**). The

reactive compounds in the light oil are phenolic dimers, phenol and anisole, which react to form the new phenolic-molecules in the heavy oil fraction of the aged raw oil: this implies that these new molecule structures originate from the aged light oil (see Section 4.4.2.2). On the other hand, the fresh heavy oil is also repolymerised during accelerated aging: it forms high Mw THF insolubles, which were found to give the same structural molecules as the THF insolubles in the fresh bio-oil, *i.e.* a more condensed network of aromatic structures (such as PAH and di-substituted ether aromatic structures (*i.e.* guaiacol-like structures) with alkene and aliphatic bridges) (**Mattsson** *et al.*, 2016). Consequently, the structure of the heavy oil obtained in the accelerated aging process of raw bio-oil is a combination of the DEE insolubles (from aged light oil) and THF solubles (from aged heavy oil) structures (**Figure 4.14**).

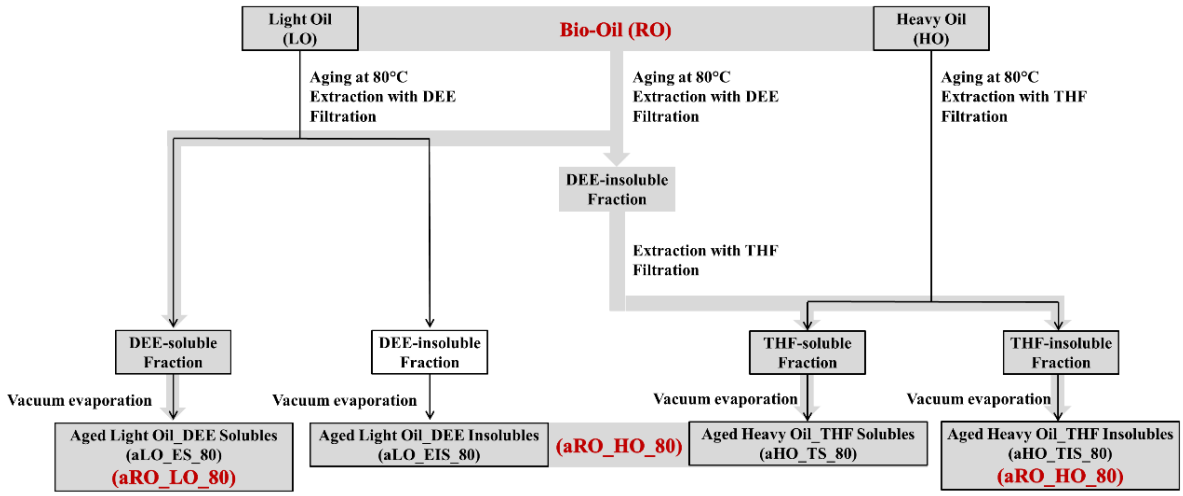


Figure 4.14 Block diagram of the solvent fractionation of the lignin HTL bio-oil used and its fractions.

4.4.2.2. Accelerated aging of the bio-oil fractions

After aging, the light oil and heavy oil were fractionated (see **Figure 4.14**). The data obtained for these fractions before and after aging (see Table 1 in Paper V) showed a slight decrease in the yields of the bio-oil fractions after aging for 1 w: from 100% to 99.5% for the light oil and from 100% to 96.9% for the heavy oil. This shows that the formation of high Mw structures was slower in the light oil than in the heavy oil after aging, although the formation rate is rather slow in both fractions. The light oil (LO, aLO_ES_80 and aLO_EIS_80) and heavy oil (LO, aLO_ES_80 and aLO_EIS_80) at fresh and aged states were analysed by GPC to estimate the change in Mw (see Figure 4 in Paper V). The MwD curves for the fresh (LO) and soluble fractions in the aged light oil (aLO_ES) were found to be almost identical. Two aspects should be noted here: the MwD curves for the insolubles in the aged light oil (aLO_EIS_80) were

found to have the same Mw as the fresh heavy oil (HO, ~5600 Da), and the aged heavy oil (aHO_TIS_80) was found to have a significantly lower Mw (~11000 Da) than the THF insolubles found in the fresh bio-oil (TIS, ~17000 Da). The molecules with a high Mw in the bio-oil have thus become larger after aging, indicating that the molecules with a low Mw have, to some extent, been repolymerised to form molecules with a higher Mw.

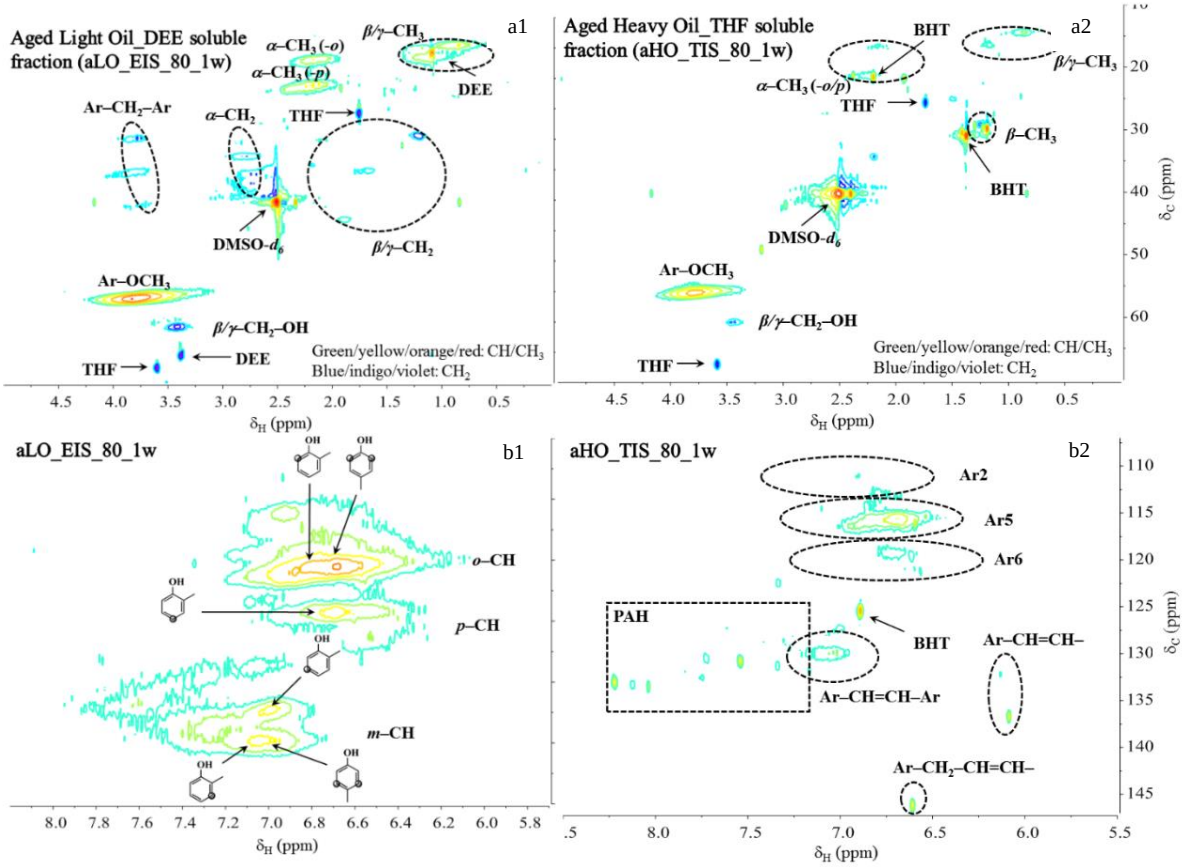


Figure 4.15 (a) Aliphatic region and (b) aromatic region in the ^{1}H–^{13}C HSQC NMR spectrum (800 MHz, DMSO-d_6) of the aged light oil_DEE insolubles stored at 80°C for 1 week (aLO_EIS_80_1w) and of the aged heavy oil_THF insolubles stored at 80°C for 1 week (aHO_TIS_80_1w).

The chemical composition of the light oil (LO) and aged light oil (aLO_ES_80) were analysed by GC–MS (see Table 2 in Paper V). The most reactive classes of compounds were found to be in the order: xanthene > anisoles >> guaiacols, phenols, phenolic dimers (Ar–CH_2–Ar, methylene bridge) >>> catechol, phenolic dimers (Ar–CH_2–CH_2–Ar, ethylene bridge). In particular, there was a decrease in the yields of xanthene, anisoles, guaiacols, phenols and phenolic dimers (Ar–CH_2–Ar) of about 87%, 36%, 13%, 10%, 8%, respectively, after 1 w of aging at 80°C: this is consistent with the yield results given in **Figure 4.11** for the bio-oil stored at RT for 2 years. The chemical structures of the aged light oil (aLO_ES_80) and aged heavy

oil (aHO_TS_80) were recorded using $^{1}H–^{13}C$ HSQC NMR and compared with the fresh states (LO and HO) (see Figures S2 and S3 in Paper V). A minor reduction in the amount of methyl, methylene and methoxyl groups, together with the guaiacol regions Ar2 and Ar6, were found in the 1 w sample of the aged heavy oil (aHO_TS_80_1w), indicating that aromatic repolymerisation/ condensation occurs in these positions on the guaiacol ring in the bio-oil.

The DEE insolubles in the aged light oil (aLO_EIS_80_1w) and THF insolubles in the aged heavy oil (aHO_TIS_80_1w) were also analysed by $^{1}H–^{13}C$ HSQC NMR (**Figure 4.15**). The DEE insolubles formed in the aged light oil comprised of aromatic methyl, methoxyl and aliphatic methylene groups, as well as di-substituted aromatic methylene and ethylene bridged structures. In the aromatic region, the highest signal intensity of the aromatic CH cross-peaks corresponds to alkylated phenolic structures at the *o*-/*p*-/*m*- positions. This suggests that the alkylated phenols and phenolic dimers (Ar–CH_2–Ar) form the main structures of the DEE insolubles in the aged light oil. On the other hand, the THF insolubles in the aged heavy oil (aHO_TIS_80_1w) were found to have similar chemical structures to those of the fresh THF insolubles, with structural motifs such as aromatic CH, vinylic/allylic, a PAH-like structures, branched *β*-methyl groups (similar to *t*Bu, *i*Pr), methoxyl groups and minor signs of aromatic and aliphatic methyl groups (**Mattsson** *et al*., 2016). This indicates that the structures of the THF insolubles in the aged heavy oil have a different origin to those in the aged light oil.

In summary, these results show that although the light oil has a low tendency to react/ repolymerise, small amounts of DEE insolubles were, in fact, formed after a longer aging time (1 w). It was found that these new DEE insolubles structures (Mw ~6000 Da) were significantly different to those of the fresh heavy oil (Mw ~5600 Da). The DEE insolubles structures were formed from the aromatic monomers in the light oil (*i.e.* anisoles, guaiacols, phenols, phenolic dimers (Ar–CH_2–Ar) and xanthene). From a chemical perspective, the THF insolubles structures (Mw ~11000 Da) were nevertheless virtually identical to the fresh THF insolubles formed in the HTL reactor (Mw ~17000 Da), although the Mw in the latter was higher. The structural network that was formed was based on an aromatic network connected by aliphatic and alkene bridges, so it is plausible that the main structure of the aromatic ring is "guaiacol-like" and condensed PAH structures, substituted with "*t*-Bu-like" and methyl groups. The formation of these THF insolubles structures is assumed to be driven by the reactive guaiacol-like structures that are present in the fresh heavy oil (**Mattsson** *et al*., 2016). Compared to pyrolysis bio-oil, the light oil obtained by the HTL of lignin is relatively stable after aging at 80°C for 1 w (*cf.* **Meng** *et al*., 2015).

4.4.3. A suggested accelerated aging mechanism

Even though studies show lignin HTL bio-oil to be rather stable, some rather small changes can be observed during aging. It has been found that the conversion rate increased with increasing temperature and, furthermore, that the "aging" rate was much lower in the low Mw fraction (*i.e.* light oil) than in the raw, or high Mw, fraction of the bio-oil (*i.e.* heavy oil). This indicates that the high Mw fractions have elements that are reactive.

Based on the chemical composition (GC–MS, 2D HSQC NMR) of lignin HTL bio-oil and its fractions, the substituted aromatic rings with Ar–OCH_3, Ar–CH_3 and Ar–CHO were found to have a high reactivity during aging at the severest aging condition (1 m and 80°C). This demonstrates that these structural motifs (high and low Mw) may participate in the reactions with the THF insolubles, leading to the formation of heavier Mw structures in both the light and heavy oils. The 2D HSQC NMR investigation revealed that there was an increase in the amount of the aliphatic methylene groups (Ar–CH_2–Ar and α-CH_2) and a significant increase in the aromatic-intense peaks from the phenol, anisole and alkylated phenolic structures present in the bio-oil. These results indicate that a possible pathway is the formation of new C–C linkages at the *o*-/*p*- positions in the phenolic nucleus, leading to a large network of phenolic structures. The facts that (a) the content of water did not increase and (b) the content of acid compounds in the lignin HTL bio-oil was found to be low, suggest that acid-catalysed repolymerisation/ condensation reactions during the accelerated aging of lignin HTL bio-oil is less likely. The main mechanism of these reactions may, therefore, be a radical mechanism. It is possible that the radicals were generated either in the HTL process or by the stereo-electronic effect of the aromatic ring (**Ben** and **Ragauskas**, 2012; **Wright** *et al*., 2009).

Considering the studies carried out on the thermal stability of the bio-oil fractions (*i.e.* light oil and heavy oil) and the raw bio-oil at elevated temperature (80°C) allows the conclusion to be reached that the aging mechanism in the medium with, and without, THF insolubles differs. During the accelerated aging of the light oil fraction without THF insolubles present, a less significant change in the yield of light oil was detected (*i.e.* a decrease of 0.5% after 1 w). In the case of raw oil with THF insolubles present, however, aging gave a higher change in the yield of light oil (*i.e.* a decrease of 2.4% after 1 w). The same trend was also found for the heavy oil fraction. This suggests that THF insolubles are involved in the accelerated aging of raw bio-oil: a larger change can thus be observed in the aged raw bio-oil than in the aged bio-oil fractions.

5. Conclusions

The HTL of LignoBoost^{TM} Kraft lignin in subcritical water, using $ZrO_2/K_2CO_3/KOH$ as the catalytic system and phenol as the capping agent, was found to result in a bio-oil (~75%) and a fraction of water-soluble chemicals (~9%).

The water-soluble chemicals produced were mainly anisoles, alkyl phenols, guaiacols and catechols. The bio-oil produced, being partially deoxygenated, had a high heat value and a low water content, both of which are beneficial to downstream processes such as hydrotreating and hydrocracking. The bio-oil was consisted mainly of a low Mw fraction (light oil, ~63%), the monomeric part of which had about the same chemical composition as the aqueous phase. The monomerics in both the aqueous phase and the bio-oil accounted for ~19% based on dry lignin, which provides a good potential for the production of phenolic-based chemicals.

The influence of the reaction conditions (*i.e.* K_2CO_3 concentration and reaction temperature) on the yield and quality of the bio-oil produced via HTL was investigated. The optimum conditions for an effective HTL process was found to be a K_2CO_3 concentration of 1.6–2.2% and a reaction temperature of 350°C. Phenol was used as the capping agent, which improved the operational conditions drastically and reduced the formation of high Mw molecules.

It was suggested that the reaction pathway for the conversion of lignin by HTL in the presence of a base and a capping aging follows the ionic mechanism: hydrolysis (the cleavage of ether bonds) and dealkylation (the cleavage of C–C bonds on the propane chains) reactions in the lignin structure that form mainly lignin aromatic structures (guaiacol and catechol) along with reactive structures of high and low Mw. Simultaneously, phenol acts as a capping agent by cross-linking the reactive fragments (aldehyde, alkyl fragments, methanol, etc.) which form more stable phenolic structures (phenolic dimers, alkyl phenols and anisole). This prevents repolymerisation from occurring in the medium and thus suppresses the formation of high Mw insoluble structures and char.

The stability properties of the produced bio-oil were studied in terms of storage (RT, 2 years) and heat (50 and 80°C, 1 h to 1 month). In general, the bio-oil obtained from lignin HTL was remarkably stable. It could also be concluded that the THF insolubles (ash/ char) had a high impact on the stability of the bio-oil: the results of this study show that the removal of THF insolubles enhances the stability of bio-oil substantially.

The accelerated aging mechanism of this bio-oil was suggested as following a radical mechanism: which differs, depending on the presence or absence of HF insolubles/ residues. The aging rate of the low Mw light oil is, however, less than that of the high Mw heavy oil. The structure of the heavy oil fraction in the aged raw bio-oil was found to be a combination of the DEE insolubles, formed from the aged low Mw light oil (*i.e.* a "phenolic macromolecule structure"), and the original high Mw heavy oil structure (a partly deoxygenated aromatic network linked with alkyl and alkene bridges). A possible pathway taken by these reactions can be via a condensation reaction at the *o*-/*p*- positions on the phenolic rings, thereby forming new C–C linkages.

In summary, HTL can be considered as being an effective process for producing high quality bio-oil from Kraft lignin. The effective separation of phases in this HTL process produces a bio-oil with a high level of stability with respect to both storage and heat, enabling it to be stored/ transported prior to being processed further into bio-fuels and various phenolic-based chemicals.

6. Acknowledgements

I would like to extend my warmest thanks to:

Professor Hans Theliander, my examiner and supervisor, for his invaluable guidance and the numerous productive discussions we had throughout the work.

Chalmers Energy Initiative–LignoFuel Project, Valmet Power AB, The Swedish Energy Agency and Ångpanneförenings Forskningsstiftelse for their financial support.

Assistant Professor Marco Maschietti, my former co-supervisor, for his diligent supervision, inspirational ideas and interesting discussions during the first period of my Ph.D. study.

Dr. Cecilia Mattsson, my later co-supervisor, for her useful suggestions, new analytical ideas and interesting discussions during the second period of this study.

Associate Professor Sven-Ingvar Andersson, Adjunct Professor Emeritus Lars Olausson, Professor Lennart Vamling, Associate Professor Lars-Erik Åmand and Mr. Tallal Belkheiri for all the help and guidance they provided.

Ms. Eva Kristenson and Ms. Malin Larsson for their assistance in administrative matters.

Mr. Bengt Erichsen, Ms. Lena Fogelquist and Mr. Tommy Friberg for their skilful help with practical work.

Ms. Carina Olsson for her help with Karl Fischer.

Assistant Professor Lars Nordstierna for his analysis with ^{13}C NMR.

Mr. Maxim Mayzel and Ms. Cecilia Persson for their analyses with 2D NMR.

Ms. Maureen Sondell for linguistic review of the papers and the thesis.

All my colleagues at Chalmers, both in the division of Forest Products and Chemical Engineering and Chemical Environmental Science, for their friendly working environment.

My family and all my friends for their constant support.

Last, but not least, my husband Marcus Lyckeskog and my son Alvin Lyckeskog for their endless encouragement and support. Thank you!

7. References

Alsbou, E., Helleur, B., 2014. Accelerated aging of bio-oil from fast pyrolysis of hardwood. *Energy Fuels* 28, 3224–3235.

Ando, D., Nakatsubo, F., Takano, T., Yano, H., 2016. Elucidation of LCC bonding sites via γ-TTSA lignin degradation: crude milled wood lignin (MWL) from Eucalyptus globulus for enrichment of lignin xylan linkages and their HSQC-NMR characterization. *Holzforschung* 70, 489–494.

Azadi, P., Inderwildi, O.R., Farnood, R., King, D.A., 2013. Liquid fuels, hydrogen and chemicals from lignin: A critical review. *Renewable Sustainable Energy Rev*. 21, 506–523.

Ba, T., Chaala, A., Garcia-Perez, M., Roy, C., 2004. Colloidal properties of bio-oils obtained by vacuum pyrolysis of softwood bark. Storage stability. *Energy Fuels* 18, 188–201.

Balakshin, M.K., Capanema, E.A., Chen, C.-L., Gracz, H.S., 2003. Elucidation of the structures of residual and dissolved pine Kraft lignins using an HMQC NMR technique. *J. Agric. Food Chem.* 51, 6116–6127.

Beauchet, R., Monteil-Rivera, F., Lavoie, J.-M., 2012. Conversion of lignin to aromatic-based chemicals (L-chems) and biofuels (L-fuels). *Bioresour. Technol.* 121, 328–334.

Ben, H., Ragauskas, A. J., 2012. In situ NMR characterization of pyrolysis oil during accelerated aging. *ChemSusChem* 5, 1687−169.

Boucher, M.E., Chaala, A., Pakdel, H., Roy, C., 2000. Bio-oils obtained by vacuum pyrolysis of softwood bark as a liquid fuel for gas turbines. Part II: Stability and ageing of bio-oil and its blends with methanol and a pyrolytic aqueous phase. *Biomass Bioenergy* 19, 351–361.

Carr, A.G., Mammucari, R., Foster, N.R., 2011. A review of subcritical water as a solvent and its utilisation for the processing of hydrophobic organic compounds. *Chem. Eng. J.* 172, 1–17.

Chaala, A., Ba, T., Garcia-Perez, M., Roy, C., 2004. Colloidal properties of bio-oils obtained by Vacuum Pyrolysis of Softwood Bark: Aging and thermal stability. *Energy Fuels* 18, 1535−1542.

Chen, D., Zhou, J., Zhang, Q., Zhu, X., 2014. Evaluation methods and research progresses in bio-oil storage stability. *Renewable Sustainable Energy Rev.* 40, 69−79.

Constant, S., Wienk, H.L.J., Frissen, A.E., Peinder, P., Boelens, R., Es, D.S., Grisel, R.J.H., Weckhuysen, B.M., Huijgen, W.J.J., Gosselink, R.J.A., Bruijnincx, P.C.A., 2016. New insights into the structure and composition of technical lignins: a comparative characterisation study. *Green Chem.* 18, 2651–2665.

Davoudzadeh, F., Smith, B., Avni, E., Coughlin, R.W., 1985. Depolymerization of lignin at low pressure using Lewis acid catalysts and under high pressure using hydrogen donor solvents. *Holzforschung* 39, 159–166.

Dimmel, D., 2010. Overview, in: Heitner, C., Dimmel, D.R., Schmidt, J.A., (Eds.), Lignin and lignans: Advances in chemistry. CRC Press, Boca Raton, USA.

Fang, Z., Sato, T., Smith Jr.R.L., Inomata, H., Arai, K., Kozinski, J.A., 2008. Reaction chemistry and phase behavior of lignin in high-temperature and supercritical water. *Bioresour. Technol.* 99, 3424–3430.

Garcìa-Pèrez, M., Chaala, A., Pakdel, H., Kretschmer, D., Rodrigue, D., Roy, C., 2006. Evaluation of the influence of stainless steel and copper on the aging process of bio-oil. *Energy Fuels* 20, 786–795.

Gellerstedt, G., 2009a. The worldwide wood resource, in: Ek, M., Gellerstedt, G., Henriksson, G., (Eds.), Pulp and paper chemistry and technology, Vol. 1, Wood chemistry and wood biotechnology. Walter de Gruyter, Berlin, Germany.

Gellerstedt, G., 2009b. Chemistry and chemical pulping, in: Ek, M., Gellerstedt, G., Henriksson, G., (Eds.), Pulp and paper chemistry and technology, Vol. 2, Pulping chemistry and technology. Walter de Gruyter, Berlin, Germany.

Gellerstedt, G., Henriksson, G., 2008a. Lignins: major sources, structure and properties, in: Belgacem, M.N., Gandini A., (Eds.), Monomers, polymers and composites from Renewable Resources, Elsevier, Amsterdam, Holland.

Gellerstedt, G., Li, J., Eide, I., Kleinert, M., Barth, T., 2008b. Chemical structures present in biofuel obtained from lignin. *Energy Fuels* 22, 4240–4244.

Giummarella, N., Zhang, L., Henriksson, G., Lawoko, M., 2016. Structural features of mildly fractionated lignin carbohydrate complexes (LCC) from spruce. *RSC Adv.* 6, 42120–42131.

Grioui, N., Halouani, K., Agblevor, F. A, 2014. Bio-oil from pyrolysis of Tunisian almond shell: Comparative study and investigation of aging effect during long storage. *Energy Sustainable Dev.* 21, 100−112.

Henriksson, G., 2009. Lignin, in: Ek, M., Gellerstedt, G., Henriksson, G., (Eds.), Pulp and paper chemistry and technology, Vol. 1, Wood chemistry and wood biotechnology. Walter de Gruyter, Berlin, Germany.

Jegers, H.E., Klein, M.T., 1985. Primary and secondary lignin pyrolysis reaction pathways. *Ind. Eng. Chem. Process Des. Dev.* 24, 173–183.

Jiang, X., Naoko. E., Zhong. Z., 2011a. Structure properties of pyrolytic lignin extracted from aged bio-oil. *Chin. Sci. Bull.* 56, 1417–1421.

Jiang, X., Zhong, Z., Ellis, N., Wang, Q., 2011b. Aging and Thermal Stability of the Mixed Product of the Ether-Soluble Fraction of Bio-Oil and Bio-Diesel. *Chem. Eng. Technol.* 34, 727−736.

Joseph, J., Rasmussen, M.J., Fecteau, J.P., Kim, S., Lee, H., Tracy, K.A., Jensen, B.L., Frederick, B.G., Stemmler, E.A., 2016. Compositional changes to low water content bio-oils during aging: An NMR, GC/MS, and LC/MS study. *Energy Fuels* 30, 4825–4840.

Kang, S., Li, X., Fan, J., Chang, J., 2013. Hydrothermal conversion of lignin: A review. *Renewable Sustainable Energy Rev.* 27, 546–558.

Karagöz, S., Bhaskar, T., Muto, A., Sakata, Y., Oshiki, T., Kishimoto, T., 2005. Low-temperature catalytic hydrothermal treatment of wood biomass: analysis of liquid products. *Chem. Eng. J.* 108, 127–137.

Karagöz, S., Bhaskar, T., Muto, A., Sakata, Y., 2006. Hydrothermal upgrading of biomass: Effect of K_2CO_3 concentration and biomass/water ratio on products distribution. *Bioresour. Technol.* 97, 90–98.

Kleinert, M., Barth, T., 2008a. Phenols from lignin. *Chem. Eng. Technol.* 31, 736–745.

Kleinert, M., Barth, T., 2008b. Towards a lignincellulosic biorefinery: Direct one-step conversion of lignin to hydrogen-enriched biofuel. *Energy Fuels* 22, 1371–1379.

Kleinert, M., Gasson, J.R., Barth, I., 2009. Optimizing solvolysis conditions for integrated depolymerisation and hydrodeoxygenation of lignin to produce liquid biofuel. *J. Anal. Appl. Pyrolysis* 85, 108–117.

Kudsy, M., Kumazawa, H., Sada, E., 1995. Pyrolysis of Kraft lignin in molten $ZnCl_2$-KCl media with tetralin vapor addition. *Can. J. Chem. Eng.* 73, 411–415.

Lavoie, J.-M., Baré, W., Bilodeau, M., 2011. Depolymerization of steam-treated lignin for the production of green chemicals. *Bioresour. Technol.* 102, 4917–4920.

Li, H., Xia, S., Li, Y., Ma, P., Zhao, C., 2015. Stability evaluation of fast pyrolysis oil from rice straw. *Chem. Eng. Sci.* 135, 258–265.

Liitiä, T.M., Maunu, S.L., Hortling, B., Toikka, M., Kilpeläinen, I., 2003. Analysis of technical lignins by two- and three-dimensional NMR spectroscopy. *J. Agric. Food Chem.* 51, 2136–2143.

Lora, J., 2008. Industrial commercial lignins: sources, properties and applications. In: Belgacem, M.N., Gandini, A., (Eds.), Monomers, polymers and composites from Renewable Resources. Elsevier, Amsterdam.

Löfstedt, J., Dahlstrand, C., Orebom, A., Meuzelaar, G., Sawadjoon, S., Galkin, M.V., Agback, P., Wimby, M., Corresa, E., Mathieu, Y., Sauvanaud, L., Eriksson, S., Corma, A., Samec, J.S.M., 2016. Green diesel from Kraft lignin in three steps. *ChemSusChem* 9, 1392–1396.

Ma, Z., Custodis, V., Bokhoven, J.A., 2014. Selective deoxygenation of lignin during catalytic fast pyrolysis. *Catal. Sci. Technol.* 4, 766–772.

Mattsson, C., Andersson, S.-I., Belkheiri, T., Åmand L.-E., Olausson, L., Vamling, L., Theliander, H., (2016) Using 2D NMR to characterize the structure of the low and high molecular weight fractions of bio-oil obtained from LignoBoost™ Kraft lignin depolymerized in subcritical water. *Biomass Bioenergy* 95, 364–377.

Meng, J., Moore, A., Tilotta, D., Kelley, S., Park, S., 2014. Toward understanding of bio-oil aging: Accelerated aging of bio-oil fractions. *ACS Sustainable Chem. Eng.* 2, 2011–2018.

Meng, J., Moore, A., Tilotta, D.C., Kelley, S.S., Adhikari, S., Park, S., 2015. Thermal and storage stability of bio-oil from pyrolysis of torrefied wood. *Energy Fuels* 29, 5117–5126.

Miller, J.E., Evans, L.R., Littlewolf, A., Trudell, D.E., 1999. Batch microreactor studies of lignin and lignin model compound depolymerisation by bases in alcohol solvent. *Fuel* 78, 1363–1366.

Miller, J.E., Evans, L.R., Mudd, J.E., Brown, K.A., 2002. Batch microreactor studies of lignin depolymerization by bases: 2. Aqueous solvents. Sandia National Laboratories Report, SAND2002-1318.

Möller, M., Nilges, P., Harnisch, F., Schröder, U., 2011. Subcritical water as reaction environment: fundamentals of hydrothermal biomass transformation. *ChemSusChem* 4, 566–579.

Narani, A., Chowdari, R.K., Cannilla, C., Bonura, G., Frusteri, F., Heeres, H.J., Barta, K., 2015. Efficient catalytic hydrotreatment of Kraft lignin to alkylphenolics using supported NiW and NiMo catalysts in supercritical methanol. *Green Chem.* 17, 5046–5057.

Oasmaa, A., Kuoppala, E., 2003. Fast pyrolysis of forestry residue. 3. Storage stability of liquid fuel. *Energy Fuels* 17, 1075−1084.

Öhman, F., Wallmo, H., Theliander, H., 2007. A novel method for washing lignin precipitated from Kraft black liquor – Laboratory trials. *Nord. Pulp Pap. Res. J.* 22, 9–16.

Okuda, K., Umetsu, M., Takami, S., Adschiri, T., 2004. Disassembly of lignin and chemical recovery–Rapid depolymerization of lignin without char formation in water–phenol mixtures. *Fuel Process. Technol.* 85, 803–813.

Pandey, M.P., Kim, C.S., 2011. Lignin depolymerization and conversion: A review of thermochemical methods. *Chem. Eng. Technol.* 34, 29–41.

Pińkowska, H., Wolak, P., Złocińska, A., 2012. Hydrothermal decomposition of alkali lignin in sub- and supercritical water. *Chem. Eng. J.* 187, 410–414.

Roberts, V., Fendt, S., Lemonidou, A.A., Li, X., Lercher, J.A., 2010a. Influence of alkali carbonates on benzyl phenyl ether cleavage pathways in superheated water. *Appl. Catal., B* 95, 71–77.

Roberts, V.M., Knapp, R.T., Li, X., Lercher, J.A., 2010b. Selective hydrolysis of diphenyl ether in supercritical water catalyzed by alkaline carbonates. *ChemCatChem* 2, 1407–1410.

Roberts, V.M., Stein, V., Reiner, T., Lemonidou, A., Li, X., Lercher, J.A., 2011. Towards quantitative catalytic lignin depolymerisation. *Chem –Eur. J.* 17, 5939–5948.

Saisu, M., Sato, T., Watanabe, M., Adschiri, T., Arai, K., 2003. Conversion of lignin with supercritical water–phenol mixtures. *Energy Fuels* 17, 922–928.

Samanya, J., Hornung, A., Jones, M., Vale, P., 2011. Thermal stability of sewage sludge pyrolysis oil. *Int. J. Renewable Energy Res.* 11, 66–74.

Shabtai, J.S., Zmierczak, W.W., Chornet, E., 1999a. Process for conversion of lignin to reformulated hydrocarbon gasoline. International Patent WO9910450A1.

Shabtai, J.S., Zmierczak, W.W., Chornet, E., Johnson, D.K., 1999b. Conversion of lignin. 2. Production of high-octane fuel additives. *Am. Chem. Soc., Div. Fuel Chem.* 44, 267–272.

Shabtai, J.S., Zmierczak, W.W., Chornet, E., 2000. Process for conversion of lignin to reformulated, partially oxygenated gasoline. International Patent WO0011112A1.

Schmiedl, D., Unkelbach, G., Graf, J., Schweppe, R., 2009. Studies in catalyzed hydrothermal degradation processes on sulphur-free lignin and extractive separation of aromatic SYNTHONs. In: 2nd Nord. Wood Biorefin. Conf., pp. 189–196, Helsinki, Finland.

Shen, X.-J., Wang, B., Pan-li, H., Wen, J.-L., Sun, R.-C., 2016. Understanding the structural changes and depolymerization of Eucalyptus lignin under mild conditions in aqueous $AlCl_3$. *RSC Adv.* 6, 45315–45325.

Silva, E.A.B., Zabkova, M., Araújo, J.D., Cateto, C.A., Barreiro, M.F., Belgacem, M.N., Rodrigues, A.E., 2009. An integrated process to produce vanillin and lignin-based polyurethanes from Kraft lignin. *Chem. Eng. Res. Des.* 87, 1276–1292.

Thring, R.W., Chornet, E., Overend, R.P., 1993. Thermolysis of glycol lignin in the presence of tetralin. *Can. J. Chem. Eng.* 71, 107–115.

Tomani, P., 2010. The LignoBoost process. *Cellul. Chem. Technol.* 44, 53–58.

Toor, S.S., Rodendahl, L., Rudolf, A., 2011. Hydrothermal liquefaction of biomass: A review of subcritical water technologies. *Energy* 36, 2328–2342.

Toor, S.S., Rosendahl, L., Nielsen, M.P., Glasius, M., Rudolf, A., Iversen, S.B., 2012. Continuous production of bio-oil by catalytic liquefaction from wet distiller's grain with solubles (WDGS) from bio-ethanol production. *Biomass Bioenergy* 36, 327–332.

Unkelbach, G., Schmiedl, D., Schweppe, R., Hirth, T., 2010. Catalyzed hydrothermal degradation of lignins from biorefineries to aromatic compounds. In: 11th Eur. Workshop Lignocellul. Pulp, pp. 57–60.

Villar, J.C., Caperos, A., García-Ochoa, F., 2001. Oxidation of hardwood Kraft-lignin to phenolic derivatives with oxygen as oxidant. *Wood Sci. Technol.* 35, 245–255.

Vigneault, A., Johnson, D.K., Chornet, E., 2007. Base-catalyzed depolymerization of lignin: Separation of monomers. *Can. J. Chem. Eng.* 85, 906–916.

Wright, J.S., Shadnia, H., Chepelev, L.L., 2009. Stability of carbon-centered radicals: Effect of functional groups on the energetics of addition of molecular oxygen. *J. Comput. Chem.* 30, 1016–1026.

Yang, Z., Kumar, A., Huhnke, R.L., 2015. Review of recent developments to improve storage and transportation stability of bio-oil. *Renewable Sustainable Energy Rev.* 50, 859−870.

Yong, T.L.-K., Matsumura, Y., 2013. Kinetic analysis of lignin hydrothermal conversion in sub- and supercritical water. *Ind. Eng. Chem. Res.* 52, 5626–5639.

Yue, F., Lu, F., Ralph, S., Ralph, J., 2016. Identification of 4−O−5-units in softwood lignins via definitive lignin models and NMR. *Biomacromolecules* 17, 1909−1920.

Zmierczak, W.W., Miller, J.D., 2006. Process for catalytic conversion of lignin to liquid bio-fuels and novel bio-fuels. US Patent US2011237838A1.