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Hydrothermal liquefaction of lignin into bio-oil

EFFECT OF PHENOL AND CATALYST OF THE BIO-OIL PRODUCED

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CONTENTS

SUMMARY

The objective of this study was to investigate a novel process for the conversion of a solid biomaterial to a bio-oil. Lignin, which is the second most abundant material in wood, obtained from the chemical recovery cycle of a kraft paper pulp mill was used as the starting material. The conversion process is accomplished in the pilot process plant located at Chalmers University of Technology, Gothenburg, (Sweden). The treatment applied is a depolymerization process carried out by a hydrothermal liquefaction at subcritical conditions in water with presence of phenol as a capping agent and a base catalyst.

The aim of this study was to gain a better understanding of the mechanism pathways that take place and to observe the effect on the bio-oil product. The parameters investigated was phenol levels and different catalyst mixtures (Na/K). A study of different solvent used to extract lipophilic compounds from the aqueous phase was also accomplished with the aim of finding other more suitable solvents then those previously used.

Keywords: Lignin, Kraft Process, LignoBoost, bio-oil, renewable energy, hydrothermal liquefaction, phenol

1. Introduction

1.1. Introduction and motivation

The uncontrolled exploitation of fossil reserves combined with the concerns of the global climate change, has motivated the quest for renewable recourses and for new transportation fuels. Nowadays a substantial part of the research is focused on biomass and how to processing it to obtain suitable products for supply the future energy demand [1].

Biomass is a renewable energy source and may origin from, animal and vegetal material which mainly composed of carbon, hydrogen, oxygen, nitrogen and a small portion of sulphur. One advantage about the use of biomass as an energy source is the possibility of in some cases turn a waste into a resource, besides of that the organic material used is not edible and have no competition with feed supplies. Moreover, the emissions of CO_2 produced in the combustion can be considered roughly be the same amount that is taken up during plant growth [1].

Wood is an abundant material present in the nature which is composed of cellulose, hemicellulose and lignin. Lignin can be described as an amorphous polymer that gives rigidity to the cell wall. It is composed of cross-linked phenolic polymers such as sinapyl (3,5-dimethoxy 4-hydroxycinnamyl), coniferyl (3-methoxy hydroxycinnamyl), and p-coumaryl (4-hydroxycinnamyl) alcohols connected by ether (C-O-C) and carbon-carbon (C-C) bonds (Figure 1). It is not possible to define its chemical structure with precision because the method of isolation may change its structure. However, the used softwood lignin contains no sinapyl units [2,3].

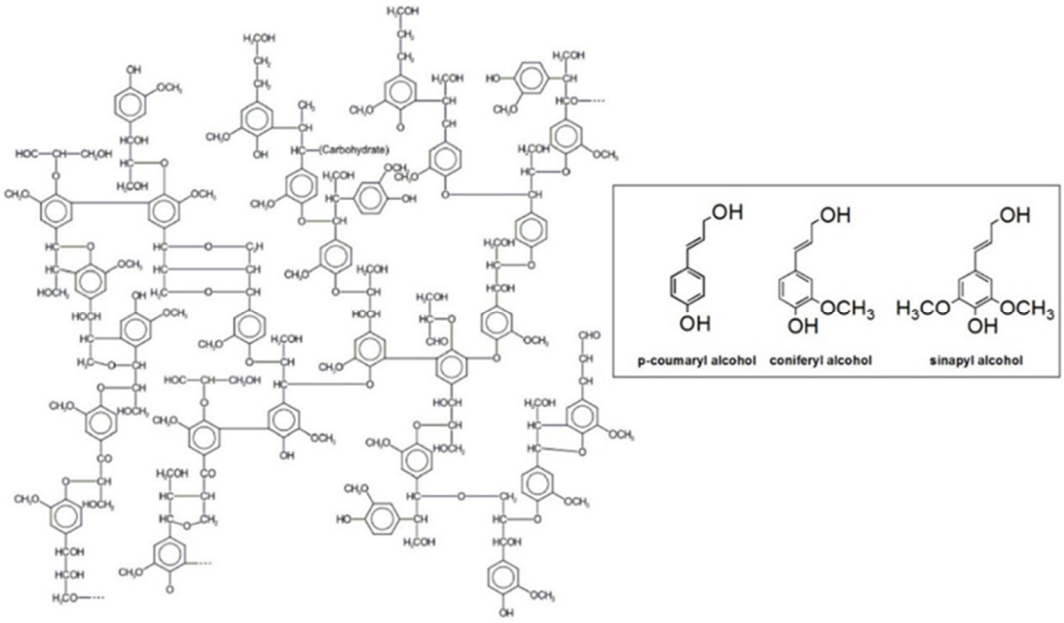


Figure 1.: The structure of native lignin and the aromatic building blocks [4].

In the Kraft pulping process black liquor is obtained. This liquor is generated in the chemical cooking process of the wood chips for the obtaining of the Kraft pulp and contain spent cooking chemicals and dissolved wood components mainly lignin. The biomass used in this study is the lignin present in the black liquor [5]. Today a new biorefinery process for precipitation of high quality kraft lignin from the black liquor exists i.e. the LignoBoost process [5]: The LignoBoost kraft lignin could be a useful source for the conversion of lignin into value-added products as bio-fuel and green chemicals.

Biorefineries are facilities that in a sustainable way produce fuel from biomass, through its decomposition into smaller chemical structures. Their popularity has been growing in the last years and its concept of operation is similar to the petroleum refineries. Besides of accomplish conversion processes also integrates an equipment to produce transportation biofuels, power, and chemicals [6]. Conversion of lignocellulosic biomass into suitable fuel can be carried out in different ways, most of the processes are through the thermochemical treatments although enzymatic depolymerization methods have also been applied.

The main goal in this work is to depolymerize lignin to generate a product with higher amount of stored energy by removal of oxygen and the reduction of char formation. This it can be achieved through processes such as pyrolysis, hydrogenolysis, gasification, oxidation among others [7].

It is known that the behaviour of water at high temperatures and high pressure is similar to an organic solvent (close to the supercritical point), this allow that nonpolar substance will be readily dissolved and extracted. This occurs when temperature and pressure are high enough and water close to its critical point behave either as liquid or as a gas, it shares properties of both [8]. This change in water behaviour is used in the process of conversion of lignin derived of LignoBoost into bio-fuel i.e. hydrothermal liquefaction (HTL).

HTL is the process used in the transformation of lignin in the pilot unit of Chalmers University of Technology. The process consists in decompositions reactions taking place in subcritical water with the aid of a capping agent and the presence of a soluble and heterogeneous catalysts [9].

1.2. Aim

The objective of this thesis work was to investigate the subcritical depolymerization (350 °C, 25 MPa) of LignoBoost Kraft lignin into the products bio-oil, water soluble organics (WSO) and char. This study was carried out at Chalmers University of Technology using a pilot plant.

- To study the soluble catalyst impact on the subcritical depolymerization of LignoBoost Kraft lignin by using NaOH/Na_2CO_3 and KOH/K_2CO_3 separately or as a mixture.
- The amount of capping agent phenol was also studied to see how it affects the quality and yields of the products from the subcritical depolymerization of LignoBoost Kraft lignin.
- Development of an improved analytical GC-MS method for the aqueous phase (WSO) fraction was made. To gain a better understanding of polar and nonpolar organic structures found in aqueous phase. By switching organic solvents for extraction, comparing diethyl ether (DEE) with methyl-*tert*-butyl ether (MTBE).

2. Background and Theory

2.1. LignoBoost Kraft Lignin

Lignin is extracted from Kraft black liquor, which contains most of the organic compounds obtained during the cooking process, for their use as a solid fuel or as a raw material for the production. Lignin revalorisation allows to take advantage of their great potential as a fuel since it is the largest contributor to the heating value of black liquor [10,11]. A new process to produce lignin with higher purity has been designed by Chalmers University of Technology and by the institute of research, Innventia. The "LignoBoost" process avoid the problems, such as the plugging of the filter and the presence of impurities, which usually occurred by precipitation of lignin through the traditional process [5].

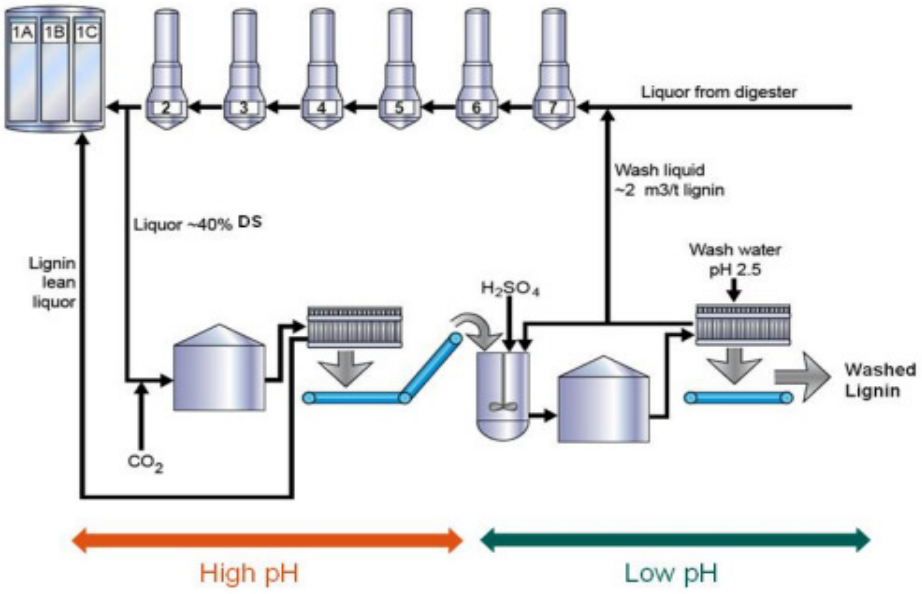


Figure 2.: Diagram of LignoBoost Process [10].

The procedure starts with the acidifying of Kraft lignin from black liquor evaporation plant with the addition of CO_2 (roughly pH 10) to produce the precipitation of the lignin suspensions and to carry out their posterior filtration [5,12]. In the traditional process the lignin washing is applied direct after the filtration, but in the LignoBoost process it is needed to submit the filter-cake to a dewatering and a later re-dissolution. After that, is the process of acidification repeated, using H_2SO_4 in this case, to get a low pH and decreasing their solubility.

Finally, realize the filtration and the displacement washing [5,8]. The second re-dissolution is carried out to avoid the large gradients in pH and the ionic strength since they are the main cause of plugging. With this novel process, it is got a higher yield of lignin due to the decreasing of the pH in the re-

dissolution phase. Further, the sodium content can be reduced to low levels avoiding the plugging problems thanks to the spent acids coming from the "re-slurry of cake" [5,12].

LignoBoost Kraft lignin structure presents mainly ether bonds and carbon-carbon bonds as it can be observed in the following tables (Table 1).

Table 1.: Different chemical bonds in LignoBoost Kraft lignin.

Ether bonds	
β-aryl ether	β-O-4'
Diaryl ether	4-O-5'

Carbon-carbon bonds	
Dihydroxy biphenyl	5-5'
Phenyl coumarane	β-5' (β-5' α-O-4')
Pinoresinol	β-β' (α-O-γ' β-β' γ-O-α')
-	β-β' (α-O-α' β-β')
Secoisolariciresinol	β-β'
Diaryl propane 1,3-diol	β-1'

Other structures	
Dibenzodioxocin	5-5'-O-4
Spiro-dienone	β-1' α-O-α'

2.2. Lignin Depolymerization

There are different options to take advantage of lignin, it can already be through combustion producing heat and power, or thought thermochemical treatments hydrogenolysis, gasification, pyrolysis, oxidation, hydrolysis among others [8].

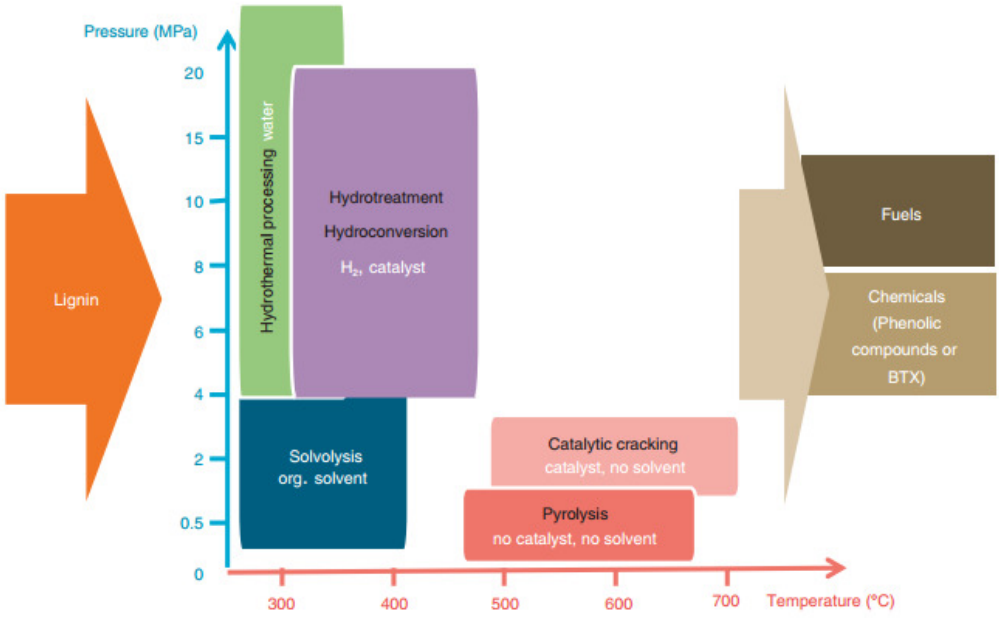


Figure 3.: Different thermochemical pathways of lignin conversion [13].

As previously discussed, the main pathway to convert lignocellulosic biomass into value-added fuel is through thermochemical treatments. It is difficult to describe an accurate mechanism of depolymerization reaction due to especially to ignorance of the lignin structure, or in this case LignoBoost Kraft lignin structure.

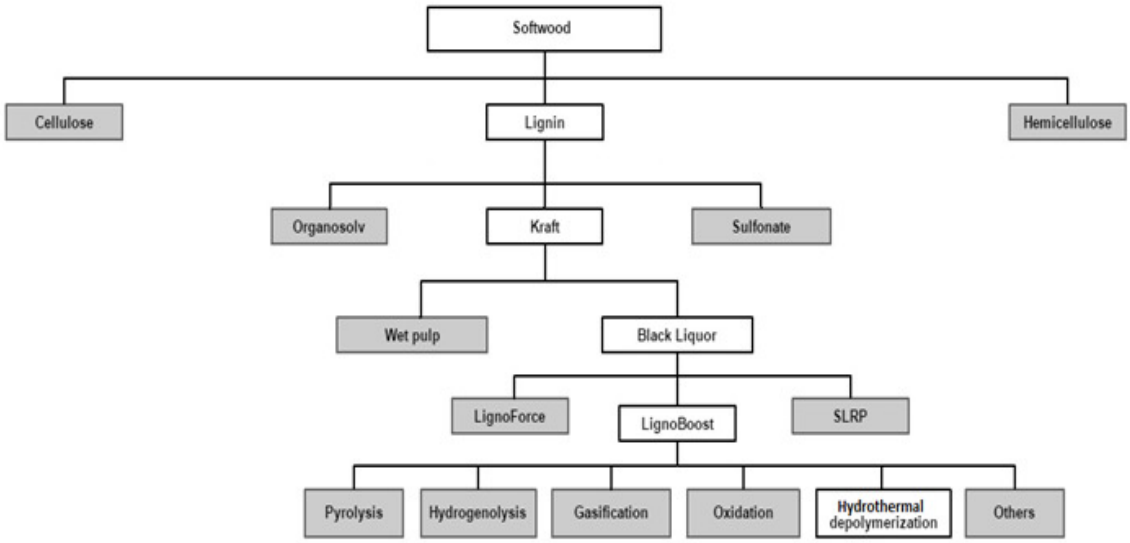
A classical pathway to obtain bio-oils from biomass is pyrolysis, which consists in a thermal decomposition in absence of oxygen with or without presence of a catalyst. Products obtains from this process include char, bio-oil and gases such as hydrogen, carbon monoxide, carbon dioxide, methane. To get mainly bio-oil as product it is needed to keep temperature between 450-800ºC and to have rapid heating rates [14].

Another possible route is gasification that consists basically in a conversion of biomass into syngas (carbon monoxide/hydrogen) by reaching temperatures above 700 ºC, without combustion and with the presence of active agents as oxygen or steam. A thermal treatment in the presence of oxygen is the oxidation process and in this way, mainly phenolic aldehydes are obtained. The oxidation temperatures range has to be between 100-320 ºC and pressures from 0.5 to 20 MPa. Hydrogenolysis route it could be also used for lignin valorisation, it has the same mechanism as pyrolysis but with presence of hydrogen and in lower range temperatures. For this method, is needed a hydrogen source to carry out a ring hydrogenation

after the cleavage of interunit linkages and the deoxygenation. Combustion pathway is an option that use the lignin valorisation just in an energetic way producing mainly power and heat [15, 17, 18].

The conversion of lignin in the presence of water is known as hydrothermal process and it could be carried out using sub or supercritical water, a significant advantage of this method is that it doesn't require a preliminary drying process. Besides, the high concentration of H^+ and OH^- ions at subcritical conditions accelerates many reactions as for instance hydrolysis. This is the process elected to accomplish the conversion of lignin into bio-oil [16].

Following, there is a brief scheme which sum up the options chosen to submit the lignin to its depolymerization process.



Scheme 1.: Wood depolymerization routes.

2.2.1. Hydrothermal Liquefaction

A thermal treatment is one of the pathways to decompose different organic materials. In this pilot plant, lignin is subjected to high pressure and temperature with the aim of break the linkages of their structure to get a product with the simplest structures as possible.

Hydrothermal liquefaction (HTL) process accepts all biomasses from modern society and is generally carried out at temperatures of (280-370ºC) and between 10 and 25 MPa of pressure. The chemistry of this process depends on directly of substrate composition and the main purposes of this treatment is to decrease of the oxygen content in biomass. To achieve this goal, it is needed a dehydroxylation and decarboxylation reactions producing H_2O and CO_2. HTL is basically pressure cooking where biomass is introduced into a pre-heated reactor under high pressure (for approx. 5.5 min) and then quickly cooled down [19,20,21].

Some of the advantages that presents this treatment are mainly, an energy efficiency of 85-90%, that bio-crude from HTL has high heating values, and the HTL oil is storage stable and recovers a high percentage of the feedstock carbon content [17].

2.2.2. Subcritical Water

When water, it is found below the critical point (374 ºC, 22.1 MPa) it is designated subcritical water (SCW), and it is designated near-critical water when the temperature is slightly lower than the supercritical water. Some of the properties of water in these states of pressure and temperature are:

- Dissolve organic compounds
- Dissolve inorganic salts
- Low dielectric constant
- Low viscosity
- High density
- Catalyses acid-base reactions
- High diffusivity

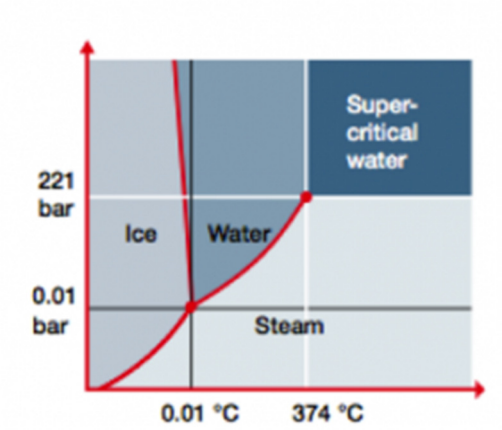


Figure 8.: Water phase diagram [22].

Furthermore, SCW allows the possibility of replace common solvents that are harmful for the environment or that are not economically affordable in commercial processes.

2.2.3. Capping agent

Another factor to consider is the presence of a capping agent, phenol is the most common used in this kind of process and this function in the process is avoid the repolymerization/condensation reactions leading to high molecular weight structures like char or coke [8].

Many of the produced molecules during the HTL process are unstable and reactive and can recombine into larger ones [16], for that reason it was needed the search of a compound to avoid these reactions between reactive molecules. The mechanism of a capping agent as phenol acts so that react with the lignin-degraded intermediates, such as formaldehyde (CH_2O), stabilizing them and to prevent repolymerization and char formation. Presence of phenol also promote the alkylation reactions giving compounds such as alkyl phenols. There are, however, some disadvantages as phenol is an expensive chemical and not environmentally friendly [23,24].

It has been attempted to look for other alternatives of capping agent, as the utilization of methanol, but it was concluded that although improved char suppression moderately, it has a negative effect on oil yield when is used in high amount. For that reason, phenol is continued using [25].

2.2.4. Catalyst

About the catalysis, as previously discussed, it is known that in these conditions of pressure and temperature water acts as a catalyst, but other catalysts can be added. The most common homogeneous catalysts used are potassium or other alkali metals like sodium. The addition of catalysts reduces the production of solid residue considerably and it is demonstrated that the catalyst produce an increase in the liquid-product yield [8,27].

The use of heterogeneous catalyst such as zirconia pellets (ZrO_2) is to improve the dispersion and accessibility of lignin in the medium [20]. However, the main advantage is the relative ease of catalyst separation from the product stream that aids in the creation of continuous chemical processes [26].

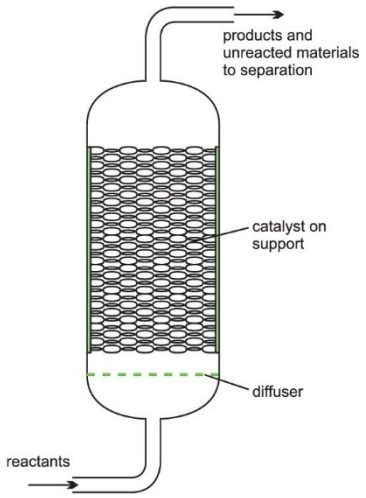


Figure 9.: Cage in fixed bed reactor [28].

2.2.5. Reaction mechanism

During lignin conversion, a depolymerization reactions take place. The main reactions that take place in this process are hydrolysis, alkylation, demethoxylation and demethylation. Hydrolysis is a decomposition reaction that produces the breaking of a bond in a molecule with the use of water. The molecule of water attack the ether bond C-O-R yielding structural fragments based on guaiacol aromatic rings. A possible route of this reaction mechanism is shown below using a hypothetical part for representation of lignin structure [29]. (Figure 4)

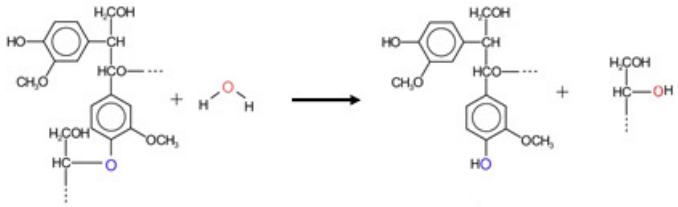


Figure 4.: Hydrolysis reaction on hypothetical lignin fragment

Demethylation takes place at the lignin guaiacol methoxyl groups, by this reaction guaiacol is transformed to catechol ring structures.

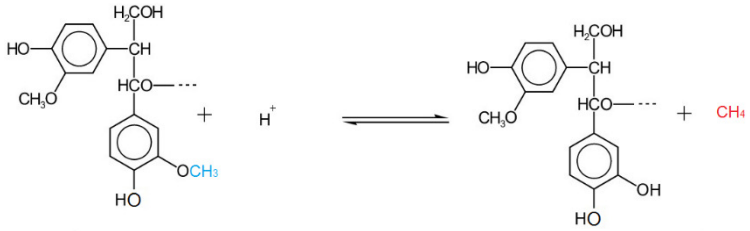


Figure 6.: Demethylation reaction on hypothetical lignin fragment

Demethoxylation are also believed to occur on the guaiacol structure in lignin. This reaction removes the methoxyl group and yield a phenolic aromatic ring as a product.

Finally, alkylation is another of the possible routes that lignin can follow from depolymerization. The molecules obtained from the other reaction processes and other reactive fragments such as ethanol (C_2H_5OH), acetic acid (CH_3COOH) and propanone ($CH_3(CO)CH_3$) is postulated to react with highly reactive phenolic ring structures formed during lignin depolymerization and yield for instance ethyl or methyl substituents at these aromatic rings [23].

2.3. Chromatographic methods

2.3.1. Gas chromatography-mass spectrometry (GC-MS)

Gas chromatography-mass spectrometry (GC-MS) is an analytical method used for the analysis of unknown organic compound mixtures. This method is a chromatographic method that separates compound by means of volatility and retention by the stationary phase in the column. Molecule proprieties such as polarity, weight, size, saturated compounds, boiling point, inter alia.

The GC-MS is composed of a gas chromatograph and a mass spectrometer. The sample is introduced by an automatic injector, separation then takes place by using a capillary column and a carrier gas (in this case helium) by a temperature gradient program, finally the molecules are ionized and

fragmented and quantified in the mass detector. This method can identify compounds in a practically unequivocal way, as it provides a characteristic spectrum of each molecule. It must be considered that one restriction of this combined method is just useful for analytes with molecular weight lower than 400 u.

2.3.2. Gel permeation chromatography (GPC)

Gel permeation chromatography (GPC) is a type of size exclusion chromatography (SEC) that separates materials on the basis of size. The technique is often used for the analysis of polymers such as lignin and bio-oil for determination of molecular weight (Mw) and polydispersity (PD).

GPC use a solvent as mobile phase (i.e. THF, DMSO and aq. NaOH) that leads the molecule to the column which is filled with a microporous packing material (stationary phase). Here separation takes place smaller molecules enter the porous material and are retarded by the stationary phase and the larger molecules are therefore eluted first due to lower retention of the stationary phase.

Finally, Mw of compounds can be detected with an ultraviolet (UV) in the case of aromatic molecules (bio-oil, lignin) and infrared (IR) detectors (sugar or have no aromatic rings). A restriction of this method is that molecular weights obtained depend highly on system and standards and solvent used.

3. Materials and Method

3.1. Materials

Lignin conversion is carried out in a process pilot plant in Chalmers University of Technology and the raw material used comes from Bäckhammar LignoBoost plant, in Sweden. Regarding to feed slurry, were used potassium carbonate (K_2CO_3 ≥ 99,5 %) and potassium hydroxide (KOH, ≥ 85 % dry content) as homogeneous catalysts, besides of phenol (crystallized ≥ 99,5 %) used as capping agent, were all sourced from Scharlau. In the reactor, zirconia pellets (ZrO_2) from Harshaw Chemie BV (length: 3 mm, diameter: 3 mm, BET surface area 48 m^2/g) were used as heterogeneous catalyst. Other compounds used in the analytical methods were hydrochloric acid (HCl, 1 mol/L), tetrahydrofuran (THF, ≥ 99,9 %) and diethyl ether (DEE, ≥ 99,9 %) from Scharlau. Finally, the analytical standards for GC-MS and GPC were from Sigma-Aldrich. The chemicals were all used as provided, without further purification [20].

3.2. Experimental conditions

The process pilot plant works under operational conditions pressure of 25 MPa and roughly 350 ºC of temperature. This plant is equipped with two pressure diaphragm pumps (one of them as a replacement) to impulse the stream from the storage tank, where the slurry is blended and pre-heated until 40 ºC, to the reactor with a flow rate of approx. 2 kg/h. Before entering, the slurry is heated until 80 ºC through an electric preheater and mixed with a hot steam recirculated from the reactor [8]. The recirculation ratio is calculated applying an energy balance before and after the mixing point, giving thus that the recirculation flow has to be 4-5 times higher than the main stream and so to get an easy way to heated up reactor temperature.

$$Q = w \cdot C_p \cdot (T_1 - T_2) \; (1)$$

$$Q_3 + Q_8 = Q_4 \; ; \; w_3 \cdot C_p \cdot (T_3 - T_4) + w_8 \cdot C_p \cdot (T_8 - T_4) = \; w_4 \cdot C_p \cdot ({T_c}^a - T_4) \; ; \; w_2 = \sim 4 \, w_1$$

[a] T_c is the mixing temperature of the main flow and the recirculation stream

The reactor corresponds to a fixed-bed catalytic reactor of 0,5 dm^3 (0,294 dm^3 of free volume) capacity which give a residence time of approx. 10-13 min. Further, is it surrounded for a heating jacket that allows keep the extreme conditions of temperature. In the outlet of the reactor the flow is led to a cooler to reduce the temperature and pressure until the ambient conditions, this is carried out boosting a cold stream through screw pump. There are three valves to reduce the pressure of the outlet flow but only one is it used to pick up the samples, besides of rupture discs to relieving pressure in case of a failure in the process. Moreover, all tubes were isolated with fibre glass to reduce the heat losses and coated with aluminium tape.

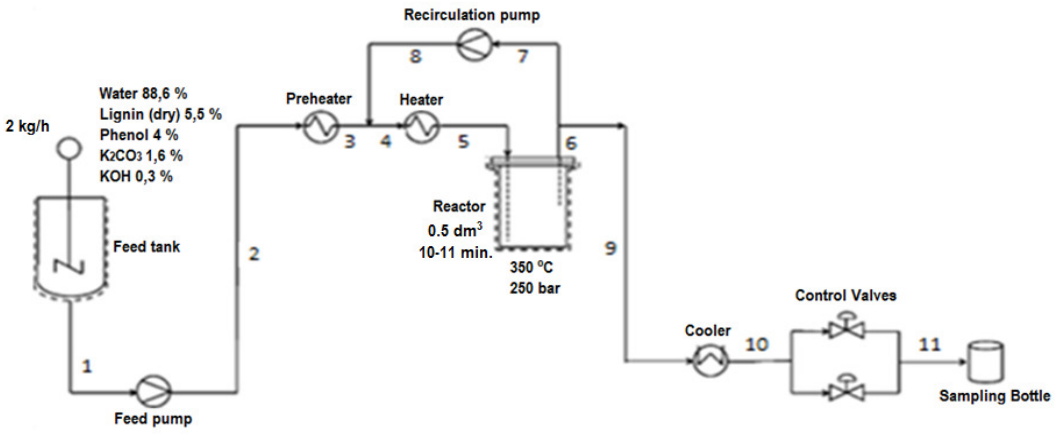


Figure 10.: Schematic flow diagram of the pilot plant [29].

The running process takes 4-5 hours (90 min approx. get the stationary state), but before that it is required implement a first run using the slurry without presence of the lignin to get the pilot plant ready. After the pre-slurry running, the prepared mixture begins the process and samples were taken every 20 minutes in borosilicate bottles of 1000 mL. Once the process is over, the samples collected after reached stationary state were mixed together to represent an average. Is important to weight the samples collected in the outlet to check for possible leakages. Then, the product is subjected to centrifugation with the aim of separate the oil phase and the aqueous phase to proceed of its analysis. Finally, is it carried out the cleaning plant procedure to ensure its fine-tuning for the future running processes.

In this study, the effects of phenol (Table 2) and soluble catalyst (Table 3) have been investigated with the aim of improve the quality and quantity of the product obtained.

Table 2.: Phenol series with constant catalyst loading. (P= 25 MPa, T= 350 ºC)

	Phenol series			
	Run 51	Run 50	Run 53	Run 54
Phenol[a] (%)	2	3	4	5

[a] KOH mass fraction: 0,3%, K_2CO_3 mass fraction: 1,6%, dry lignin bases mass fraction: 5,5%

Table 3.: Catalysts series with constant phenol levels. (P= 25 MPa, T= 350 ºC)

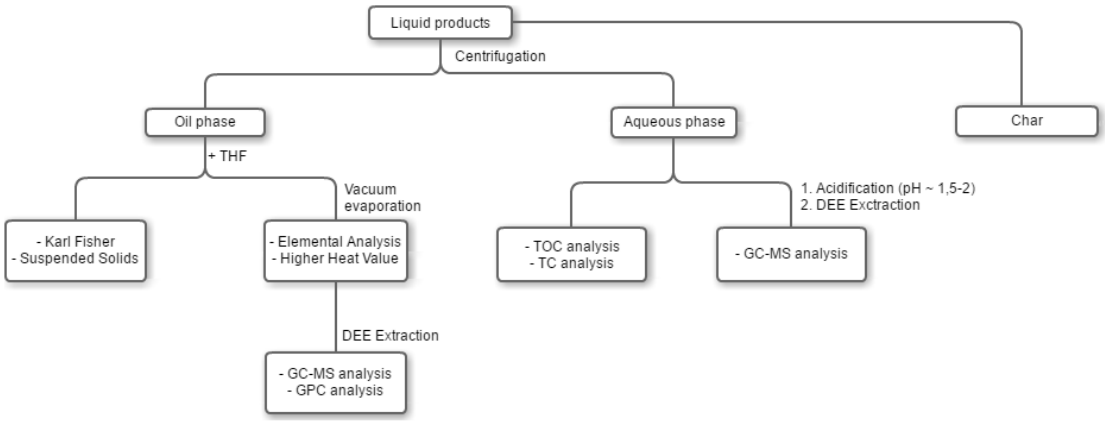
	Catalysts series							
	Run 53 (100% KOH/K_2CO_3)		**Run 58 (80% $NaOH/Na_2CO_3$)**		**Run 57 (90% $NaOH/Na_2CO_3$)**		**Run 56 (100% $NaOH/Na_2CO_3$)**	
KOH/K_2CO_3 [a] (%)	0,3	1,6	0,1	0,3	0,03	0,2	-	-
$NaOH/Na_2CO_3$ [a] (%)	-	-	0,2	1	0,2	1,1	0,2	1,2

[a] Phenol mass fraction: 4%. Dry lignin bases mass fraction: 5,5%.

3.3. Analytical methods

3.3.1. General comments

By utilisation of fractionation and analytical methods of the produced HTL products (bio-oil, WSO and char) important information of the product composition can be obtained.



Scheme 2.: Analytical methods used in different products of lignin conversion.

The liquid products collected from the reactor process were subjected to centrifugation obtaining a separation between aqueous phase and oil phase. At the same time amount of char is measured gravimetrically burning the material stuck in the ZrO_2 pellets present in the reactor cage.

Oil phase was added THF for enable transfer from the centrifugation bottles to a flask. Detailed description of the different chemical analysis of the various fraction is described below (Scheme 2).

Some considerations taken into account for this study and their posterior analysis methods were:

- In the phenol series, a concentration of 1.6% of K_2CO_3/KOH is used for efficient catalysis effect [20].
- Lignin is stable and can be stored.
- It was considered that no reactions take place in the feed tank.
- As IST for the GC-MS is used syringol because in softwood trees is not a possible product and it has a similar behaviour of the detected aromatic compounds.
- Same integration parameters of detected peaks in GC-MS for all batches.

3.3.2. Determination of char

For char determination, the pathway followed is: cool down the reactor and remove the zirconia pellets from inside. The procedure consists in take a portion of the catalyst and weight it before to put it inside the oven (500 ºC for 12 h) where is going to be regenerated by means of burning char. When oven was cooled down, pellets were reweighted and with the knowledge of the total amount of zirconia pellets that were used it can be calculated the char content [20].

3.3.3. Elemental analysis of bio-oil and total organic carbon (TOC) and total Carbon (TC) determination of water phase

The elemental composition of the bio-oil was determined at Mikroanalytisches Laboratorium Kolbe (Germany), which uses a CHNOS Analyzer (from Elementar) to measure the contents of carbon and hydrogen, and an ion chromatography (IC) system (from Method) to measure the sulphur content. The content of ash in the bio-oil was measured in triplicate according to the method E1755-01 [20], using Nabertherm (Labotherm ® Programm Controller S27). The oxygen content was calculated by difference allowing to calculate higher heating value (HHV).

The TC and TOC of the water phase samples obtained after centrifugation were measured at SP (Borås, Sweden) according to the SS-EN 1484 method [20]. Analysis results were recalculated considered that they were diluted 1/250 times.

3.3.4. Solvent fractionation of bio-oil

Bio-oil fractionation is required to separate the lignin-derived bio-oil into light oil (the low Mw fraction) and heavy oil (the high Mw fraction) through of their solubility in diethyl ether (DEE) or tetrahydrofuran (THF). The bio-oil was first extracted with DEE, with a solvent-to-feed ratio of (20/1), and then separated in two fractions, the DEE soluble fraction (Light oil) which was recovered thought vacuum evaporation and the DEE insoluble fraction. Then, insolubility fraction was extracted with THF and filtrated, with a solvent-to-feed ratio of (20/1), and getting the THF soluble fraction (Heavy oil) also recovered with vacuum evaporation and the THF insoluble fraction with drying at 105ºC [20].

3.3.5. Determination of insoluble material in bio-oil

For the quantification of THF insoluble fraction (Suspended solids), the procedure followed begins withdrawing a 2 g sample of bio-oil and dissolved in 40 g THF and filtered under vacuum through Büchner funnels by means of two-step process. Before filtration steps a glass filters P2 (nominal maximum pores size 40-100 μm) and glass filters P4 (nominal maximum pores size 10-16 μm) were dried in the oven (105 ºC – 1h), cooled in a desiccator and weighted. In the first step the diluted oil is filtrated with the dried filter glass P2 and filtrated again through dried filter glass P4. After every filtration step, filters were washed with

THF and dried again under same conditions, cooled in a desiccator and weighted again. The difference of both weights is the mass of retained solids (Suspended solids) [20].

3.3.6. Water content of bio-oil

The bio-oil water content was measured through Karl Fischer volumetric titration, for this analysis 1 g was withdraw, dissolved in THF (about 20 g) and filtered under vacuum using a Büchner funnel equipped with Duran glasses filters P2 (nominal maximum pores size 40-100 μm). Filtration step is required to avoid the accumulation of solid particles in Karl Fisher equipment. It was considered that between 1-7 % of diluted oil was loss due to volatility and it was assumed to be pure THF, then oil/THF ratio was recalculated [20]. THF was also submitted to Karl Fischer analysis to know the water derived from the solvent, which presented 0.03 % of water content. Mass of water was calculated in the sample and in the THF and mass of water in oil was calculated by difference. All samples were measured with replicate and standard deviation of content water percentage in the samples was lower than 0.05 %.

3.3.7. Chemical composition in bio-oil and water phase by GC-MS

For light bio-oil analysis a sample of 1 g was withdraw and dissolved in DEE with a solvent-to-feed ratio of 40 and mixed with a known amount of IST (Internal Standard), the compound elected was syringol (1,3-Dimethoxy-2-hydroxybenzene) since is not an aromatic unit present in softwood lignin and it is not produced in the reaction. This mixture was filtered using a syringe with a 0.45 μm filter and injected in the gas chromatography (GC, Agilent 7890A) coupled to a mass spectrometer (MS, Agilent 5975 C) with a FID detector (electron ionization mode). The analysts are separated in a chromatographic column HP-5MS (length: 30 m; internal diameter: 0.25 mm; thickness of stationary phase: 0.25 μm) by injecting 1 μL of sample via an auto sampler (Agilent 7693A), using helium at 1 mL/min as the carrier gas. The injector temperature was set at 300ºC and temperature programme of the GC oven was 45ºC for 2.25 min, 2ºC/min up to 300ºC, 300ºC for 10 min. The MS source and quadrupole temperatures were set at 250ºC and 150ºC, respectively. Spectra interpretation was carried out using the NIST MS Search programme (version 2.0) operating on the NIST/EPA/NIH Mass Spectral Database 2011 (NIST 11) [20]. The contents of the main components were determined semi-quantitatively: each sample was analysed in duplicated and the average was then used.

For mass compounds calculation, equation 1 was applied using the peaks areas found in GC-MS results and the known amount of IST.

$$A_{compound} \cdot \frac{m_{IST}}{A_{IST}} = m_{compound} \quad (1)$$

To know the real content of mass compounds in the oil phase was not taken into account the water content (Chapter 3.3.7), for that it was needed to find the percentage of mass compound present in the oil

with water content and make the correction using equation 2. GC-MS results of HTL bio-oil samples presents a standard deviation average of 0.03.

$$\frac{m_{compound\ \ (Oil\ wit\,h\ water\ \ content\ )\,(\%)}}{1-water\ \ content} = m_{compound\ \ (wit\,hout\ \ water\ \ content\ )(\%)} \quad (2)$$

For aqueous phase GC-MS analysis 10 g of water previously acidified was withdrawn and mixed with a known amount of IST (syringol). Aqueous phase was filtered with a syringe with a 0.45 μm filter and extracted the organic phase with methyl tert-butyl ether (MTBE) in a separated funnel, with a solvent-to feed ratio of 1. Then, was injected in the GC-MS and as with the oil phase analysis the amount known of IST for the sample vials preparation, allowed to find the mass of compounds applying the equation 1 and using the peaks areas found in GC-MS results. Finally, for acidification correction equation 3 was applied in both replicas accomplished giving a standard deviation average lower than 0.01.

$$m_{WSO\ \ (HCl\ presence\ )\ (\%)} \cdot \frac{m_{aq}+m_{HCl}}{m_{aq}} = m_{WSO\ \ (wit\,hout\ \ HCl\ presence\ )(\%)} \quad (3)$$

3.3.8. Molecular weight determination of bio-oil with GPC

About 10 mg of bio-oil fraction were dissolved in the mobile phase (1 mL, DMSO/LiBr 10 mM) and diluted to 0.25 mg/mL, filtrated with a syringe filter (GHP Acrodisc, diam. 13 mm, pore size 0.2 μm). The sample solutions were analysed for molecular weight (Mw) and molecular weight distribution (MwD) thought gel permeation chromatography (PL-GPC 50 plus) connected to refractive index (RI) and ultraviolet (UV) detectors (280 nm, Polymer Laboratories, Varian Inc.). Two PolarGel-M columns and a guard column (300 x 7.5 mm and 50 x 7.5 mm, 8 μm) were coupled in series. A 10-point calibration curve with Pullulan standards (polysaccharide calibrations kit, PL2090-0100, Varian) was used to determine the molecular weight (Mw) of the samples. All of the samples were found soluble in the mobile phase (DMSO/LiBr). The same systematic error obtained from all the samples (same concentration, solvent, analysis time) allows the average value of the molecular weight determined by GPC for the oil to be compared [20].

3.3.9. Total yields calculation

The calculations of yields were based on dry lignin feed using mass balances and the results obtained from analytical techniques, including GC-MS and TOC/TC. For the water soluble organic (WSO) content, the TOC results were used with the assumption that the primary organic compounds in the aqueous phase had phenol-like molecular structures. The monomer fractions were used to determine by the

quantification obtained with GC-MS results. For “phenol free” is considered that the amount of phenol quantified from GC-MS product results is excluded. Finally, it was assumed that all reacted phenol is deposited in bio-oil [24].

Higher heating value

HHV is determined for investigation of the quality of the bio-oil, which is a key parameter. As in the Doulong’s formula [20] it can be observed that to get a high heat of combustion, the oxygen quantity must be as low as possible. For this calculation, it was need the results of elemental analysis.

$$HHV\ \left[\frac{MJ}{kg}\right] = \left[\ 338.2\ x\ \%C + 1442.8\ x\ \left(\%H - \frac{\%O}{8}\right)\right] x\ 0.001 \quad (5)$$

Char

The procedure of char calculation was removing the zirconia pellets from the reactor, and weight them before and after be submitted to a burning process.

HTL Bio-oil

The main product of interest of this process is HTL Bio-oil. For its calculation was used the weight after centrifugation, dry and phenol free and the weight of phenol that it has reacted.

$$Bio - oil\ (wt.\%) = \frac{Bio{-}oil\ weight\ after\ \ centrifugation\ \ \ {-}weight\ of\ \ reacted\ \ phenol}{Dry\ \ lignin\ \ weight} \cdot 100 \quad (7)$$

Light oil

$$Light\ oil\ (wt.\%) = \frac{Bio - oil\ soluble\ in\ DEE}{Bio - oil\ weight} \cdot 100 \quad (8)$$

Heavy oil

$$Heavy\ oil\ (wt.\%) = \frac{Bio - oil\ soluble\ in\ THF}{Bio - oil\ weight} \cdot 100 \quad (9)$$

Suspended solids

$$SS\ (wt.\%) = \frac{Bio - oil\ insoluble\ in\ THF}{Bio - oil\ weight} \cdot 100 \quad (10)$$

WSO

Water soluble organic yield was found in the procedure of extraction with DEE and regarding to the total dry lignin weight in steady state. Amount of water soluble organic content calculated from TC and TOC analysis results attached in APPENDIX 2.

$$WSO\ (wt.\%) = \frac{Total\ WSO\ weight\ in\ aqueous}{Dry\ lignin\ weight} \cdot 100\ (11)$$

Monomers

Finally, to quantify monomers another last formula was used.

$$Monomers\ (wt.\%) = \frac{Monomers\ wt.}{Dry\ lignin\ weight} \cdot 100\ (12)$$

4. Results and Discussion

The operation considerations begin for the use of the Hydrothermal Liquefaction (HTL) as a thermal treatment to promote the decomposition reactions in the lignin structure. Reaction medium consists of water in a sub-critical point, as stated above, since their catalytic behaviour ease the conversion of lignin into bio-oil. Phenol presence is also needed owing to is it used as capping agent, and finally, the procedure of catalysis is carried out with potassium as a homogenous catalyst. There are, besides, a zirconia (ZrO_2) pellets in a cage inside the reactor which act as a heterogeneous catalyst.

Moreover, in all the processes is very important keep under control the conditions of operation. Temperature and the rate of heating, besides the pressure, play an important role in the process. Is for that reason that exist a range of temperature and pressure where the process is optimum. Residence time is also an important factor; its optimization is necessary to ensure a complete depolymerization without allowing further reactions to occur. All these variables have been considered during this process to ensure its proper functioning.

4.1. The catalysis impact on HTL bio-oil: potassium vs. sodium based systems

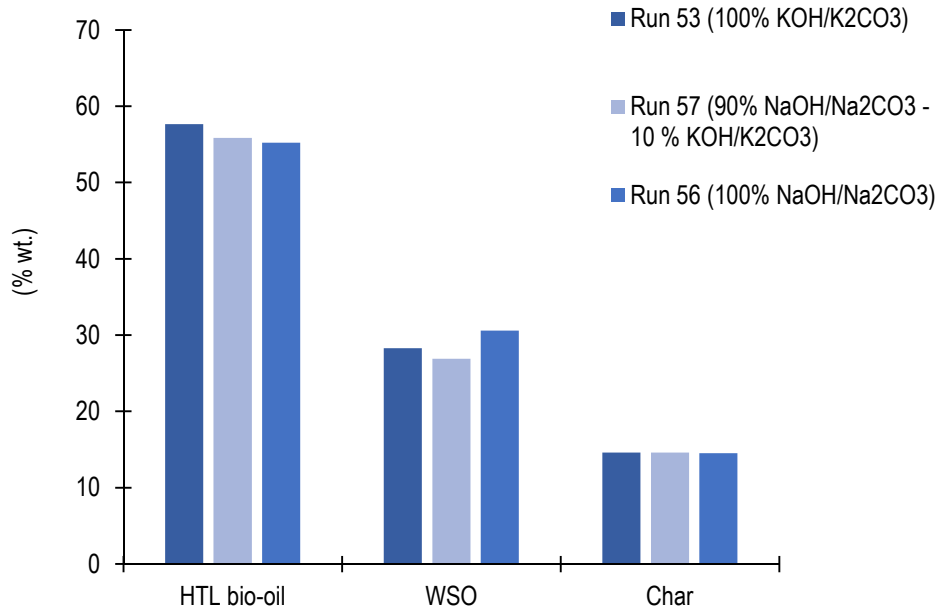
4.1.1. Total yields

Accumulated bio-oil product was used for a closure of mass balance to 100%. As can be seen variation between -0.29 to 2.64 wt.% indicate a very good work carried out with the pilot plant as well as an accurate laboratory work, in addition to verification that there are no leaks in the system.

Table 4.: Yield calculation for bio-oil, WSO, char and accumulated bio-oil products. [a]

	Phenol (wt.%)	Catalyst	pH output	HTL bio-oil (wt.%)	WSO (wt.%)	Char (wt.%)	Accumulated (wt.%)
Run 53	4	KOH/K_2CO_3	7.45	57.65	28.30	14.59	- 0.53
Run 56	4	$NaOH/Na_2CO_3$	7.44	55.20	30.57	14.52	- 0.29
Run 57	4	10 % KOH/K_2CO_3 90 % $NaOH/Na_2CO_3$	-	55.84	26.92	14.60	2.64
Run 58	4	20 % KOH/K_2CO_3 80 % $NaOH/Na_2CO_3$	-	n.c.	n.c.	15.33	n.c.

[a] calculated on dry lignin basis.



Graphic 1.: Graph of product yields for bio-oil, WSO and char calculated on lignin basis.

Different soluble catalyst systems were tested in the bio-oil pilot plant. Previously only potassium based system have been used with good results. The intention was to investigate the change to sodium based catalyst system. The use of sodium based catalyst would be preferred due to lower cost and the possibility to use the Kraft pulp mill chemical recovery process.

Generally, the product yields obtained in the catalyst series present roughly constant results (55.2–57.65%) regarding to the catalyst effect. In addition, run 58 was not calculated due to lack of data from elemental analysis and total carbon content analysis.

Regarding the bio-oil yields was batch 53 with 100% of KOH/K_2CO_3 catalyst was found to have a slightly higher product yield (57.6%) bio-oil product compared to 100% $NaOH/Na_2CO_3$ catalyst (55.2%). Regarding the water soluble organic content (WSO) the highest product yield was with 100 % $NaOH/Na_2CO_3$

(30.5%). The mixed catalyst system with 10% KOH/K_2CO_3 and 90% $NaOH/Na_2CO_3$ in batch 57 presents equal quite good results with bio-oil yield of 55.8% and WSO yield of 26.9%, this indicate a viable option for future studies to find the most efficient combination parameters between potassium and sodium catalyst.

Char content results were practically constant, concluding that char do not influence on different kind or of catalyst system (i.e. sodium vs. potassium).

Overall this was very good results indicating that a change from potassium to sodium catalyst system is possible without losses in bio-oil and WSO yields.

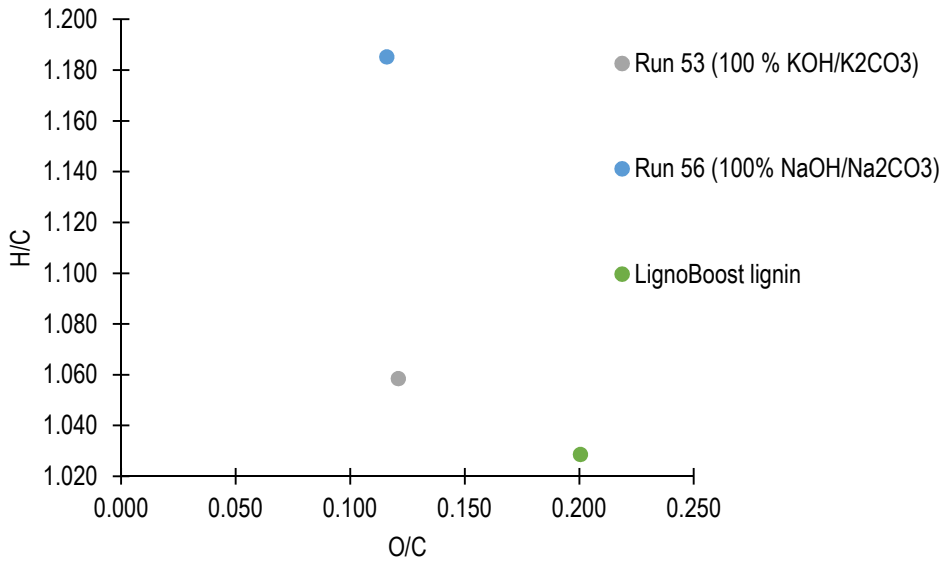
4.1.2. Chemical composition of the bio-oil

Below in Table 5, there are the results of the water content as well as higher heating value and elemental composition in the different HTL bio-oil products reported. Measurements of water was made by Karl Fisher method and the calculations of water content are found in APPENDIX 3. The higher heating value (HHV) is calculated with equation 5 see section 3.3.10.

Table 5.: Results of elemental analysis, water content and higher heating value for the bio-oils.

	Phenol (wt.%)	Catalyst	Water[a] (wt.%)	C (%)	H (%)	O[a] (%)	S (%)	Na (%)	K (%)	HHV[a] (MJ/kg)
Run 53	4	KOH/K_2CO_3	1.37	74.28	6.60	18.16	0.32	0.14	0.50	31.37
Run 56	4	$NaOH/Na_2CO_3$	6.7	74.05	7.37	17.61	0.32	0.62	0.03	32.5
Run 57	4	10% KOH/K_2CO_3 90% $NaOH/Na_2CO_3$	1.35	-	-	-	-	-	-	-
Run 58	4	20% KOH/K_2CO_3 80% $NaOH/Na_2CO_3$	0.74	-	-	-	-	-	-	-
LignoBoost	-	-	32.6	65.6	5.7	26	1.85	0.23	0.07	27.67

[a]calculated

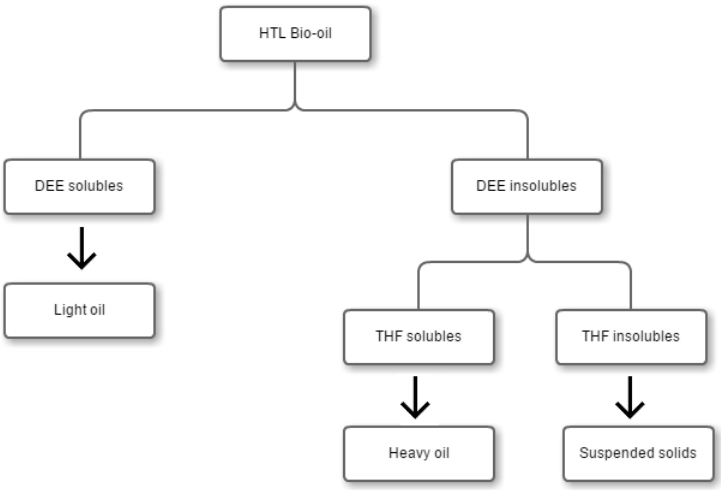


Graphic 6.: Van Krevelen diagram of bio-oil catalyst series.

The elemental composition data was used for a Van Krevelen diagram there the atomic H/C and O/C ratios was used. The bio-oils from 100% potassium vs. 100% sodium catalyst was compared with starting material LignoBoost Kraft Lignin. The shift in atomic ratio O/C from 0.2 for LignoBoost to 0.12 for the bio-oils (100% sodium and 100% potassium) indicate a depolymerisation process of LignoBoost Kraft lignin by hydrolysis reaction (lower oxygen content).

Clearly differences were seen regarding to elemental analysis results. The batch 56 with 100% $NaOH/Na_2CO_3$ present a lower oxygen content and an increase of hydrogen content yielding a higher HHV vs. the 100% KOH/K_2CO_3 (batch 53), this results indicate a positive effect of change of catalyst to sodium based system and provided an improvement in the quality of the product. The increase in H/C ratio for 100% sodium batch vs. 100% potassium based catalytic system indicate that different reaction mechanism may occur during depolymerization of lignin.

4.1.3. Solvent fractionation and molecular weight determination of bio-oil



Scheme 3.: Bio-oil fractionation procedure. (DEE diethyl ether, THF tetrahydrofuran).

By using solvent fractionation of the bio-oil with DEE and THF it is possible to get a mass balance of the different bio-oil fractions as light oil, heavy oil and THF insolubles as it is seen in scheme 3.

After fractionation procedure, bio-oil is separated depending on their solubility in DEE or THF. Different proportions of the bio-oil fractions were calculated, in the case of heavy oil the amount was calculated thought difference between percentage of light oil and THF insolubles due to loss of solvent and volatile compounds during fractionation (Table 7).

By using sodium based catalytic system instead of potassium it was found that the THF insolubles was reduced with 7% from 10.8% to 3.7%. Instead of a large formation of THF insolubles an increase in heavy oil fraction was found from 24.5% to 37.7%. These results indicate that potassium participate in the formation of THF insolubles. Then 90% or 80% sodium catalyst was mixed with 10% or 20% potassium an increase of THF insolubles could be found to 8.8% resp. 12.0% which further indicate the importance of the potassium catalytic effect for formation of THF insolubles.

Regarding the light oil yield here to the change to sodium catalyst system from potassium gave a reduction in yields from 64.6 to 58.6%. Similarly, with the THF insolubles light oil was also increased with addition of 20% potassium to the sodium system (80%) indicating that potassium has a higher catalytic activity in formation of light-oil from lignin depolymerization.

All bio-oils was also analysed with GPC for Mw determination. It is known from previous studies of the bio-oil that peak A and B in the GPC chromatogram belongs to the light-oil and peak C that is biphasic corresponds to the high Mw fractions (heavy oil and THF insolubles). All batches (53, 56-58) was found to

be depolymerized compered to starting material LignoBoost Kraft lignin. This could be determined by comparing the peak distribution in Graphic 2 and Table 6. LignoBoost peak C (16900 Da) have higher Mw compared to all bio-oil batches (peak C 4686-6524 Da).

Graphic 2.: GPC results of bio-oil from the catalyst series.

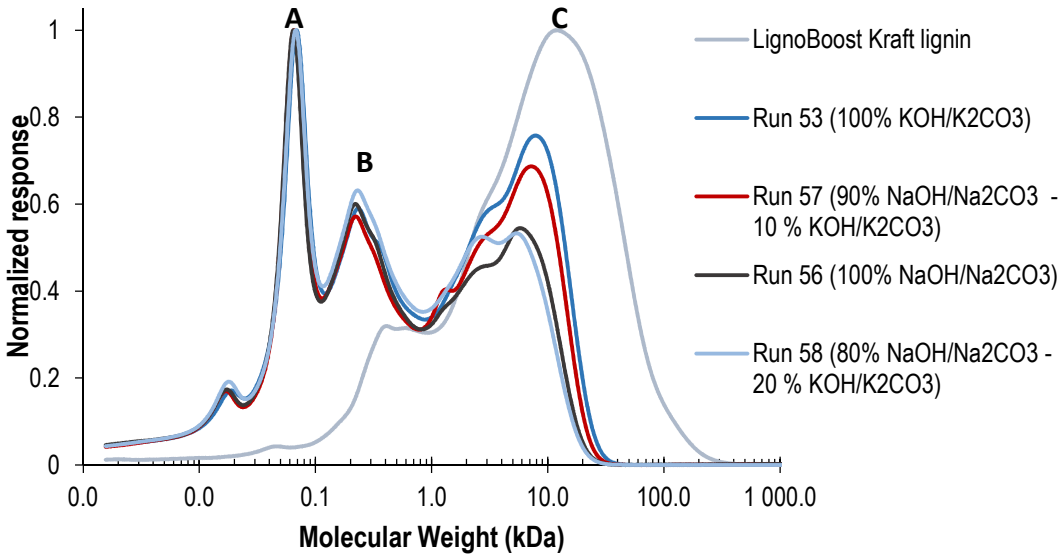


Table 6.: Molecular weight of THF insolubles/heavy oil peak "C".

	Catalyst	Mw (kDa)
Run 53	KOH/K_2CO_3	6524
Run 56	$NaOH/Na_2CO_3$	5191
Run 57	10 % KOH/K_2CO_3 90 % $NaOH/Na_2CO_3$	5913
Run 58	20 % KOH/K_2CO_3 80 % $NaOH/Na_2CO_3$	4686
LignoBoost	-	17775

Table 7.: Results of HTL bio-oil fractionation.

	Phenol (wt.%)	Catalyst	Light oil (%)	Heavy oil calculation (%)	Suspended solids (%)
Run 53	4	KOH/K_2CO_3	64.61	24.55	10.84
Run 56	4	$NaOH/Na_2CO_3$	58.56	37.67	3.7
Run 57	4	10% KOH/K_2CO_3 90% $NaOH/Na_2CO_3$	59.60	31.65	8.75
Run 58	4	20% KOH/K_2CO_3 80% $NaOH/Na_2CO_3$	65.61	22.41	11.98

[a] calculated on bio-oil weight.

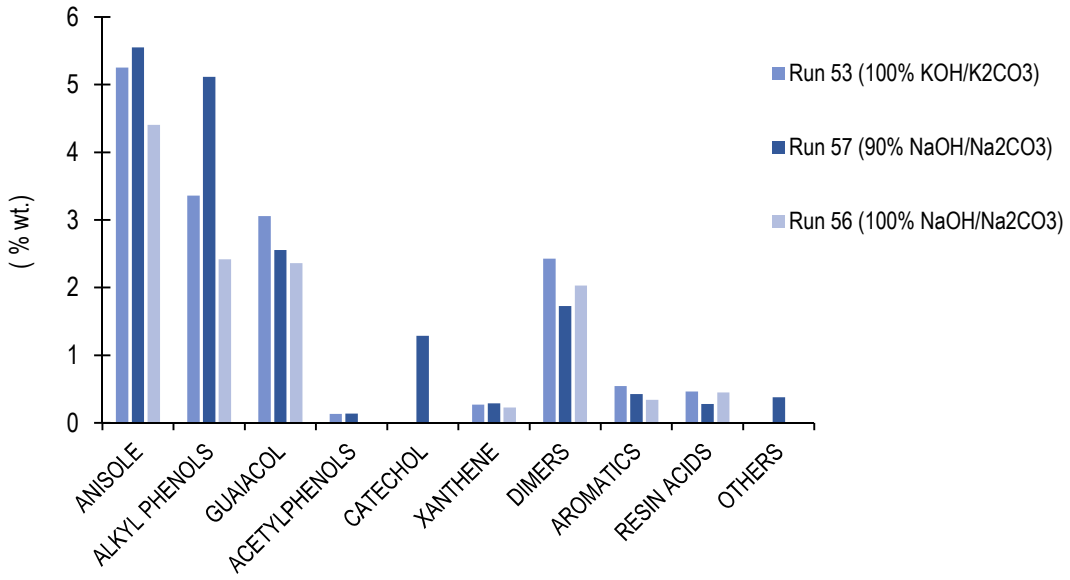
In case of the mixed catalyst batch 58 (K/Na 20/80), which presents the lowest molecular weight (peak C 4686 Da) but at the same time has the higher yields of suspended solids, demonstrated that the molecules of suspended solids have been more affected for depolymerisation by combination of K/Na catalyst system. This fact show as a mixture of both catalyst can get better results than working separately.

Finally, bio-oil fractionation evidenced an improvement due to mixture catalyst presence giving the best results in the batch 58 (20% KOH/K_2CO_3, 80% $NaOH/Na_2CO_3$) where the higher light oil product (65.61%) and lower heavy oil (22.41%) were obtained. Batch with presence of just potassium catalyst present also good results but that could be improved.

4.1.4. Bio-oil analysis with GC-MS catalyst series results

By GC-MS bio-oil analysis, the effect of different catalyst impact on the small organic compounds formed during depolymerization can be analysed.

By compare the 100% potassium with 100% sodium catalyst batches it could be seen that sodium produced slightly lower yields of guaiacol (3.1% to 2.5%) and phenolic dimer (2.5% to 2.2%) alkyl phenol (3.2% to 2.4%), anisole (5.2% to 4.2%) and phenolic dimer (2.5% to 2.2%) compound classes (Graphic 4). This correspond well with the catalytic reactivity of potassium vs. sodium (i.e. potassium has higher catalytic reactivity). However, by mixing the catalyst in a 90/10 ratio of K/Na another monomeric pattern could be found i.e. a large increase of alkyl phenols (2.5-3% to 5%) and catechol (0% to 1.5%) together with a smaller increase in anisole (4.5-5% to 5.5%). By using a mixture of 90/10 ratio of K/Na catalyst yielded promotion of certain degradation pathways of lignin in subcritical water. In our case, it seems that reaction pathways like demethylation to catechol together with alkylation reactions to alkyl phenols is favoured.



Graphic 4.: GC-MS oil phase results of catalyst series.

Standard deviation was calculated for all analysed compounds using equation 13 and presented as an average for all compounds analysed in each batch see Table 8.

$$\sigma = \sqrt{\frac{1}{n-1}\sum_{i=1}^{n}(x_i - \bar{x})^2} \quad (13)$$

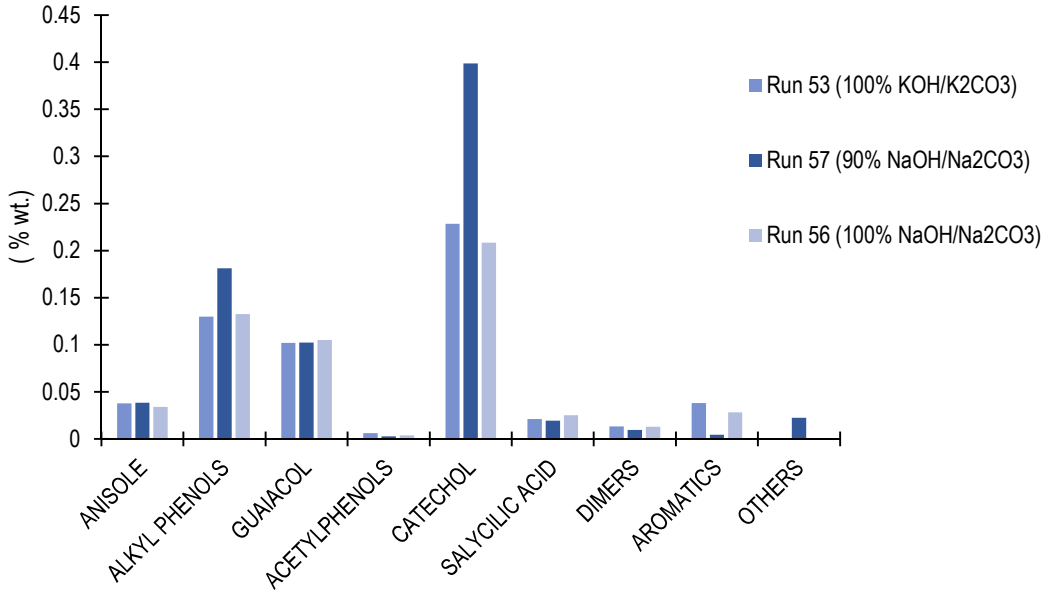
Table 8.: Bio-oil phase standard deviation of GC-MS results of catalyst series.

	σ
Run 53	0.0192396
Run 56	0.1626793
Run 57	0.0178465

4.1.5. Aqueous phase analysis with GC-MS

By GC-MS analysis of aqueous phase, the most hydrophilic compound which is catechol can be observed due to its hydrophilic nature. Results show a clearly increment of the compounds product in the mixed catalyst with 10/90 ratio of K/Na, especially catechol were found to be largely increased from approx. 0.2% to 0.4%. Compounds are favoured with the effect of both catalysts; potassium catalyst is more reactive than sodium catalyst but at the same time sodium catalyst contribute to specific formation of certain compounds. This use of combination of K/Na catalyst could be an opportunity to a process

improvement until this study potassium catalyst was considered to be the superior catalyst above sodium catalyst.



Graphic 5.: GC-MS aqueous phase results of lignin conversion with different catalyst series.

Standard deviation was calculated for all analysed compounds using equation 13 and presented as an average for all compounds analysed in each batch see Table 9.

Table 9.: Mean value of aqueous phase standard deviation of phenol series.

	σ
Run 53	0.0009050
Run 56	0.0008363
Run 57	0.0099085

4.1.6. Total yield of organic compounds in the bio-oil and WSO fraction

To provide a better overview of the total yield of released phenolic monomers in the bio-oil and WSO fractions, the GC-MS mass fraction yields were recalculated on the basis of dry lignin excluding phenol (see Table 10). By comparing 100% potassium with 100% sodium it's clear that potassium based catalytic system have slightly higher yield of monomer v.s. sodium catalyst approx. 4% difference in total monomeric yielded. However, by use a mixture of K/Na of 10/90 an increase of approx.2% of monomers were found vs. the 100% sodium case. As it has been in other chemical analysis of the HTL bio-oil the mixture of both catalyst Na/K give results that can really compete with the old runs with 100% potassium as catalytic system.

Table 10.: Total monomer yields in bio-oil and WSO fractions calculated based on dry lignin.[a]

	Run 53	Run 57	Run 56
Catalyst	100% KOH/K_2CO_3	90% NaOH/Na_2CO_3	100% NaOH/Na_2CO_3
Dry lignin (g)	146.71	147.31	149.02
Monomer wt. aq. Phase (wt. %)	0.58	0.77	0.54
Monomer wt. oil Phase (wt. %)	12.44	15.07	9.52
Monomer total (g)	33.41	31.50	28.41
Monomer yield (wt. %)	22.77	21.38	19.06

[a] calculated on dry lignin basis without phenol.

4.2. Variation of phenol in HTL runs

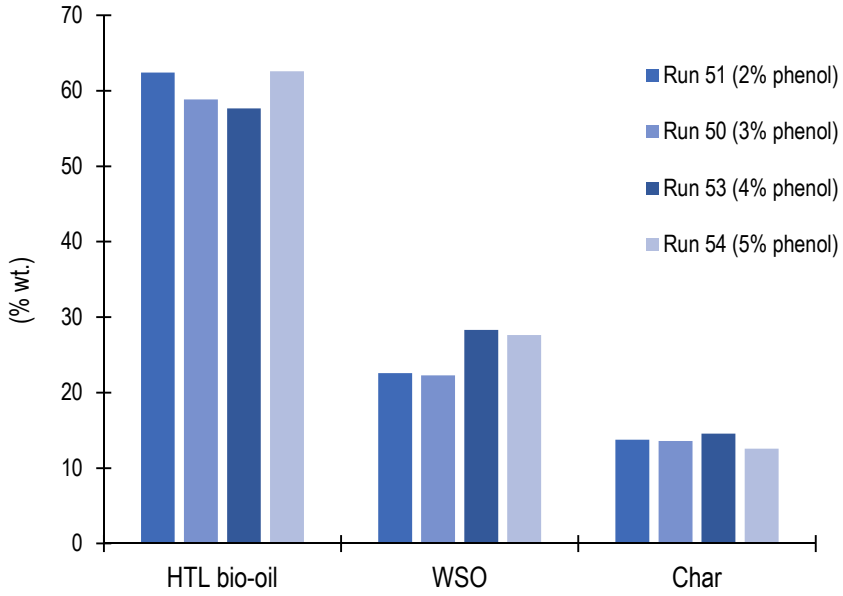
4.2.1. Total yields

Product yields were calculated using the total content of lignin and phenol in the steady state and reported in Table 11. Total product yields calculations are outlined in section 3.3.9 together with data in APPENDIX 1. Generally, yields discussion are reported in section 4.1.1.

Table 11.: Yield calculation for bio-oil, WSO, char and accumulated bio-oil products. [a]

	Phenol (wt.%)	Catalyst	pH output	HTL bio-oil (wt.%)	WSO (wt.%)	Char (wt.%)	Accumulated (wt.%)
Run 51	2	KOH/K_2CO_3	7.54	62.40	22.57	13.76	1.26
Run 50	3	KOH/K_2CO_3	7.17	58.83	22.28	13.58	5.30
Run 53	4	KOH/K_2CO_3	7.45	57.65	28.30	14.59	-0.53
Run 54	5	KOH/K_2CO_3	7.77	62.60	27.63	12.58	-2.80

[a] calculated on dry lignin basis.



Graphic 5.: Representation of different product fractionation phenol series.

High yields of HTL bio-oil was produced 58-62% in all runs where phenol was varied between 2% to 5%, a slight decreasing trend of HTL bio-oil product was detected as phenol amount was increased from 2% to 5%.

Regarding to water soluble organics, it presents a slight increase (22.5 to 28.3%) with phenol increase, as to char yields (12.6-14.6%) are rather constant and not sensitive for variation in phenol levels.

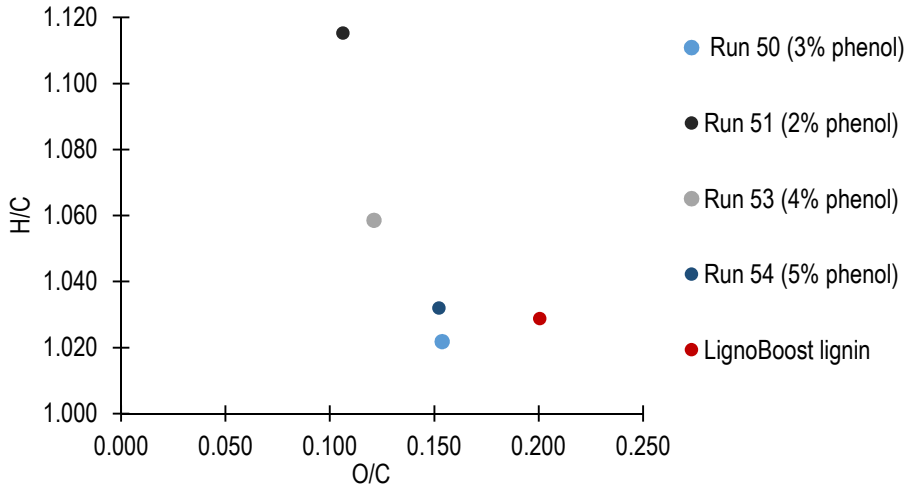
The mass balance in the yield calculations were very good as can be seen in the accumulated yield calculations in Table 11 (0.5 – 5.3%). This small variation in mass balance indicate that the pilot plant system does not present any important leak and analysis work was accurate.

4.2.2. Chemical composition of the Bio-oil

Table 12.: Results of elemental analysis and calculated higher heating value (HHV) from the bio-oils in the phenol series.

	Phenol (wt.%)	Catalyst	Water[a] (wt.%)	C (%)	H (%)	O[a] (%)	S (%)	Na (%)	K (%)	HHV[a] (MJ/kg)
Run 51	2	KOH/K_2CO_3	2.84	74.85	7.01	16.82	0.39	0.28	0.66	32.39
Run 50	3	KOH/K_2CO_3	1.59	72.00	6.17	20.74	0.34	0.18	0.57	29.52
Run 53	4	KOH/K_2CO_3	1.37	74.28	6.60	18.16	0.32	0.14	0.50	31.37
Run 54	5	KOH/K_2CO_3	1.59	72.14	6.25	20.63	0.30	0.16	0.52	29.69
LignoBoost	-	-	32.6	65.6	5.7	26	1.85	0.23	0.07	27.67

[a] calculated



Graphic 6.: Van Krevelen diagram of elemental composition of different HTL bio-oil products of phenol series.

By analysing the elemental composition of bio-oil and the starting LignoBoost Kraft lignin it is possible to retain the content of carbon (C), hydrogen (H), nitrogen (N), sulphur (S), sodium (Na) and potassium (K) in the total bio-oil, and from these results oxygen content is calculated by difference.

In the Van Krevelen diagram (Graphic 6) it can be seen that runs with 2 to 5% phenol have lower oxygen content than LignoBoost Kraft lignin i.e. the O/C atomic ratio have been left shifted from LignoBoost Kraft lignin ratio 0.2 to 0.1-0.15 in the various bio-oils. Regarding to H/C atomic ratio, this is increased in runs with 4 and 5% phenol addition. However, the runs with 2 and 3% phenol addition are more similar to LignoBoost Kraft lignin in atomic H/C ratio. This indicate that it could be differences in the reactions proceeding during the depolymerization of LignoBoost Kraft lignin and that these are dependent on low or high phenol addition.

Other parameters also important are the yields of Na, K and S since lower levels of these compounds mean that the produced bio-oil has good properties for further refining in fossil oil refineries. However, just in case of potassium this has been seen to increased vs. LignoBoost Kraft lignin (Table 12). This probably is due to the addition of the soluble catalyst system KOH/K_2CO_3 for depolymerization of LignoBoost Kraft lignin in the pilot plant.

4.2.3. Solvent fractionation and molecular weight determination of bio-oil

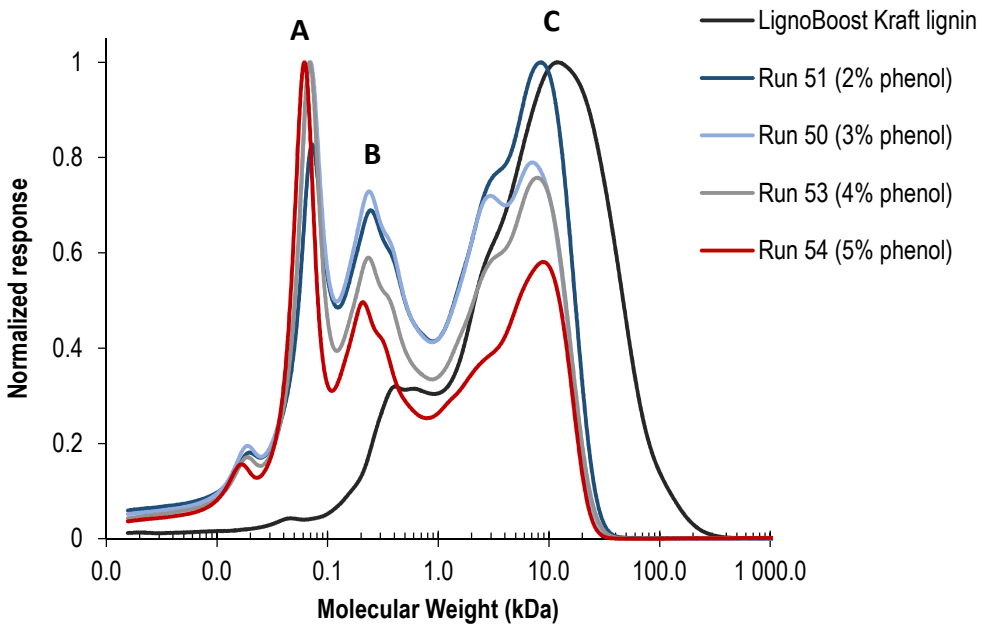
By using solvent fractionation of the bio-oil with DEE and THF it is possible to get a mass balance of the different bio-oil fractions as light oil, heavy oil and THF insoluble outlined in Scheme 3.

After fractionation procedure, bio-oil is separated depending on their solubility in DEE or THF. Different proportions of the bio-oil fractions were calculated, in the case of heavy oil the amount was calculated thought difference between percentage of light oil and suspended solids due to loss of solvent and volatile compounds during fractionation.

By analysing data, it was found that batch of 2% phenol has the highest yield of light oil (70.99%, run 51), regarding to the others batches, a slightly decreasing trend can also be observed in light oil yield from 2 to 5%phenol (Table 14).

By increasing phenol leads to higher yield of the heavy oil fraction in the same way that THF insoluble presents a decrease (11.26 to 9.04%) with increasing amount of phenol (2% to 5%). This indicate that phenol is involved in the reaction that stops formation of the unwanted THF insolubles.

Molecular weight determination with GPC were also made of the bio-oil produced in the pilot plant. By using this analysis, it is also possible to estimate the Mw of the different fractions (light oil, heavy oil and THF insolubles. In Graphic 7 are peak A and B corresponding to the Mw of the light oil (60-200 Da) and peak C (Table 13) are composed of both heavy oil and THF insolubles the high Mw structures formed during depolymerization. Lastly, by comparing Mw of LignoBoost Kraft lignin with bio-oil runs (50, 51 and 53-54) it can be seen that all batches are clearly depolymerized to lower Mw structures (peak A-B 60-200 Da and peak C 3587-6869 Da) vs starting material LignoBoost Kraft lignin (16 900 Da, Graphic 7 and Table 13).



Graphic 7.: GPC results of molecular weight determination in the phenol series.

Table 13.: Molecular weight of THF insolubles/heavy oil peak “C”.

	Mw (Da)
Run 51	6869
Run 50	6048
Run 53	6524
Run 54	6556
LignoBoost	17775

Table 14.: Results of HTL bio-oil solvent fractionation of the bio-oils in the phenol series.[a]

	Phenol (wt.%)	Catalyst	Light oil (%)	Heavy oil calculation (%)	Suspended solids (%)
Run 51	2	KOH/K_2CO_3	70.99	17.75	11.26
Run 50	3	KOH/K_2CO_3	60.88	29.08	10.04
Run 53	4	KOH/K_2CO_3	64.61	24.55	10.84
Run 54	5	KOH/K_2CO_3	60.90	30.06	9.04

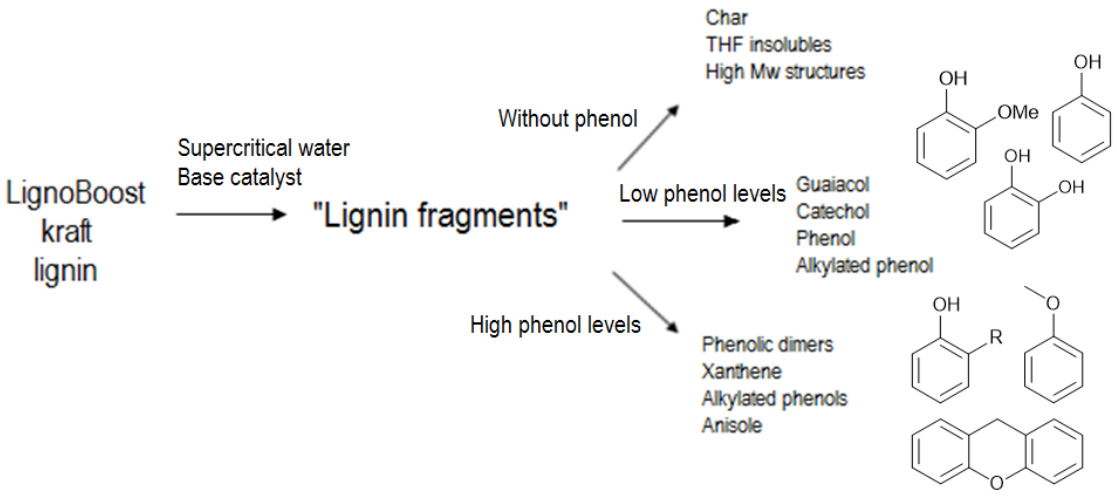
[a] calculated on bio-oil weight.

4.2.1. Bio-oil analysis with GCM-MS phenol series results

By using GC-MS analysis is possible to analyse the DEE extractable organic compounds formed during subcritical lignin depolymerization.

Generally, it can be seen a high quantity of anisole, alkyl phenols, guaiacols and phenolic dimers in the extracted DEE fraction from the bio-oil (Graphic 9). Regarding to the evolution of mass compound detection in function of phenol presence, anisoles and guaiacols are decreasing opposite to alkyl phenols and phenolic dimers which appear to increase proportionately.

Regarding to the behaviour of compounds with low levels of phenol (2% and 3%), high levels of released guaiacol monomers are expected due to softwood lignin is composed of 95% guaiacyl-propane units (e.g., coniferyl alcohol). Low phenol content does not favour the formation of phenolic dimers and aromatic molecules as xanthene, this is due to these products are produced from the interaction of phenol with subcritical water and the catalyst as it can be seen in Scheme 4.



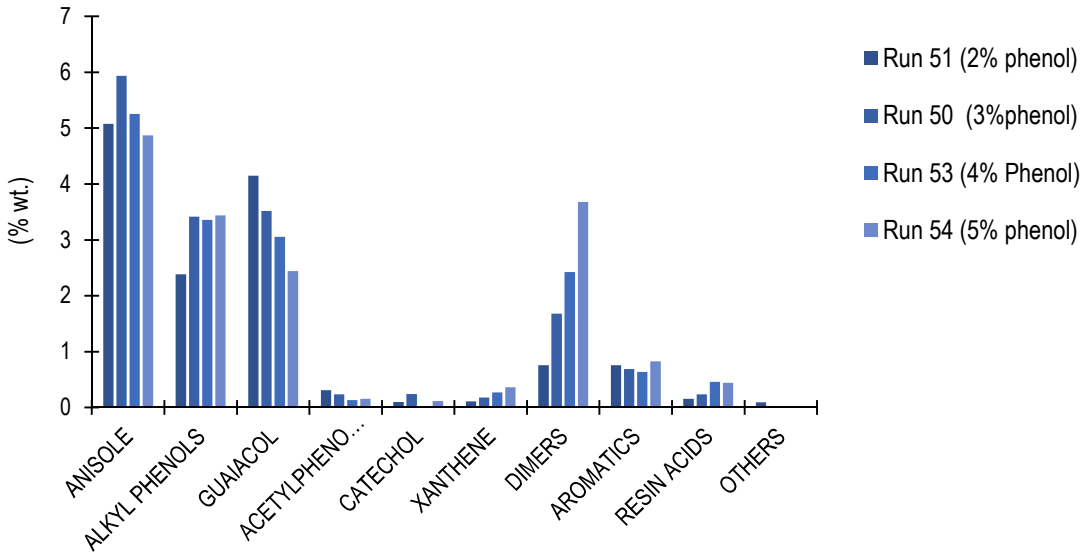
Scheme 4.: Main products of LignoBoost Kraft lignin depolymerisation.

High levels of phenol content (5%) promote the production of alkylated phenols and phenolic dimers besides of xanthene. This is due to their formation is the result of the capping agent effect of phenol, phenol react with “reactive lignin fragments” formed from depolymerization of lignin by water at subcritical conditions and thus form more stable fragments and prevents repolymerization to high Mw structures (THF insolubles).

The higher levels of phenol also yields a decrease of guaiacols in the bio-oil fraction indicating the shift from “subcritical water pathway” to the phenol capping mechanism pathway outlined in Scheme 4.

As to anisole, presents a decrease tendency with increase of phenol, fact that not corresponds to the idea of that it comes from phenol presence and further studies is needed for clarification of this reaction pathway.

Variation of the phenol content give thus different product mixtures, fact that demonstrates the important role of phenol in the subcritical depolymerization conversion process of LignoBoost Kraft lignin.



Graphic 9.: GC-MS bio-oil phase results of phenol series.

For a better understanding of the error in this GC-MS analytical method of small organic compounds standard deviation were calculated for all detected compounds using equation 13. In Table 14 an average of the standard deviation of all detected compounds is presented and as can be seen in Table 15.

Table 15.: Bio-oil standard deviation of phenol series.

	σ
Run 51	0.0120348
Run 50	0.1026010
Run 53	0.0192396
Run 54	0.0113602
Run 55	0.0081593

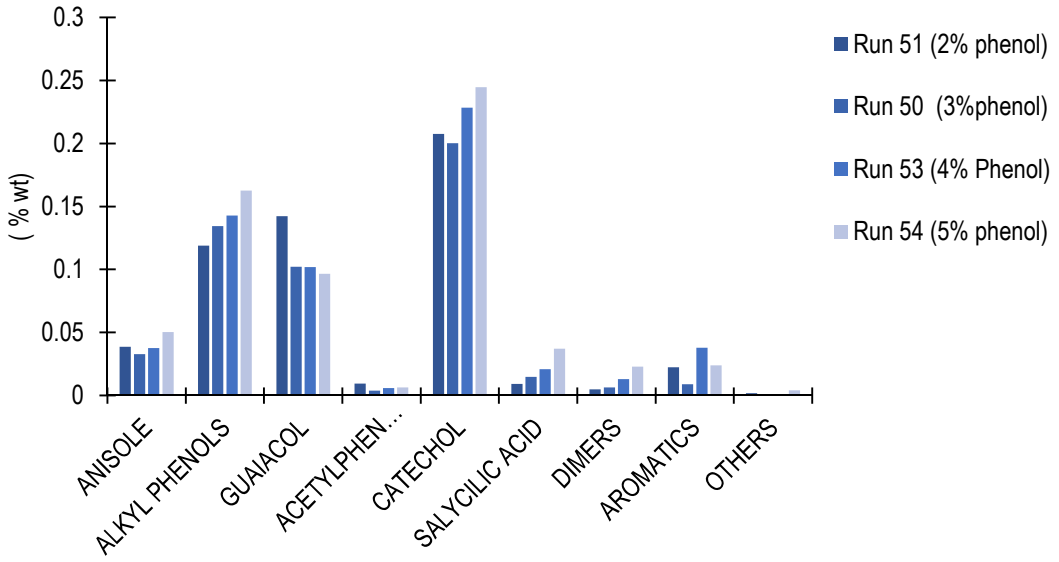
4.2.2. Aqueous phase analysis with GC-MS

The water phase from the subcritical depolymerization of lignin was also analysed for extractable organic compounds using DEE as a solvent. It can be seen in Graphic 8 that the presence of both alkyl phenols and phenolic dimers are increased with presence of more phenol and the opposite in case of guaiacols and catechols, which are clearly decreasing with augment of phenol presence (Graphic 8).

Catechols are mainly detected in the water phase due to the hydrophilic nature of this compound, almost all catechols are transported to the water phase and it was not possible to detect a trend of this compound class in the bio-oil GC-MS analysis.

No dominating levels of anisoles was found in the water phase and this is also due to the hydrophobic properties of this compound (i.e. no hydroxyl group) and trends of anisole can only be seen in the bio-oil phase.

Generally, the detected components in the water phase follow the same trend detected in the results of the GC-MS analysis of bio oil, these results only facilitate the estimation of the yield of catechol.



Graphic 8.: GC-MS aqueous phase results of phenol series.

In addition, an average of the standard deviation of every analysed compound in the different runs were calculated with equation 13. As can be seen the analysis is very accurate with lower standard deviation versus the bio-oil measurements (Table 16).

Table 16.: Mean value of aqueous phase standard deviation of phenol series.

	σ
Run 51	0.0052643
Run 50	0.0037025
Run 53	0.0009050
Run 54	0.0005998
Run 55	0.0039748

4.2.3. Total yield of organic compounds in the bio-oil and WSO fraction

To provide a better overview of the total yield of released organic compounds from in the bio-oil and WSO fraction, the GC-MS mass fraction yields were calculated on the basis of dry lignin excluding phenol see Table 17.

By removing phenol, it can be seen that in batches with low phenol content (2-4% Phenol, run 50, 51 and 53) the percentage of monomers from dry lignin bases is roughly stable. Regarding to batch 54 (5% phenol) presents a higher monomer yield compared to the others. This indicate that phenol presence avoiding repolymerization, acting as a capping agent as it was seen in chapter 4.2.4.

For the total monomeric yield calculations results from GC-MS both from the aqueous phase and the oil phase were used, removing the phenolic dimers compounds, resin acids, xanthene, huge aromatic molecules and others.

Table 17.: Total yields of monomers released during subcritical depolymerization of LignoBoost Kraft lignin.[a]

	Run 51	**Run 50**	**Run 53**	**Run 54**
Phenol content	2%	3%	4%	5%
Dry lignin (g)	143.83	148.49	146.71	100.46
Monomer wt. aq. Phase (wt. %)	0.55	0.50	0.58	0.62
Monomer wt. oil Phase (wt. %)	12.78	14.27	12.44	11.85
Monomer total (g)	28.65	31.07	33.41	25.11
Monomer yield (wt. %)	19.92	20.92	22.77	24.99

[a] calculated on dry lignin basis without phenol.

4.3. Solvent extraction study of aqueous phase of GC-MS

The common extraction procedure it was using diethyl ether (DEE), but it is known that is not an environmental friendly solvent and other options have to be tested. Besides, the switch of solvent it will provide the opportunity to see the extractive behaviour of various polar and nonpolar organic structures in the aqueous phase. Methyl-tert-butyl ether (MTBE) is the solvent used to test in the extraction procedure. This solvent study was executed using an old aqueous phase stored for 6 months and the results was only used for see the different extracting properties of the solvents DEE and MTBE.

DEE is a colourless liquid of ether class with the formula $(C_2H_5)_2O$ used as solvent in laboratories and which is one of the compounds belonging to the Hazardous Substances List [30]. This compound is

extremely flammable and since ether is heavier than air it can collect low to the ground and the vapour may travel considerable distances to ignition sources [31]. Otherwise, MTBE is an organic compound used as a gasoline additive manufactured via the chemical reaction of methanol and isobutylene with formula $C_5H_{12}O$. This compound is not presently considered a major harmful pollutant and it could be a suitable substitute in solvent extractions instead of DEE [32].

A way to see the difference between both compounds is through the Solvent Polarity Index (P) [33]. A number that gives the polarity character of the compound, the higher is solvent polarity index more polarity character presents the compound and a table with different polarity index it can be found in APPENDIX 4.

4.3.1. GC-MS results of DEE and MTBE extraction

DEE and MTBE extraction were carried out with two replicates and two different preparations to establish accurate results. In the graphics below, there are the results of the average of both different analysis. Phenol have been excluded from this data representation in Graphic 10 and 11. The new compounds detected that doesn't belong to any class or which haven't been detected in the two different extraction methods have been classified as "Others".

The main compounds detected in old aqueous phase are alkylphenols, catechols and guaiacols at the same level that was seen in phenol series with fresh aqueous phase analysis with low phenol content. Quantitatively, yield is slightly higher in MTBE extraction than in DEE extraction. However, very similar levels are found indicating a possible switch to MTBE in the future analysis of the aqueous phase.

Regarding to compounds detected classified as others, it has been found 1,2,3-Trimethoxybenzene and 2,5-Dimethoxybenzyl alcohol in the DEE extraction. Compounds found only in MTBE extraction were Benzene (1,1 dimethylethoxy) and 1,3 Diethoxybenzene.

A compound found in all analysis and which it was not detected before in a fresh aqueous phase analysis is hydrocoumarin, this could be adjudicated to the fact that aqueous phase used was stored for 6 months and this compound has been formed during the storage.

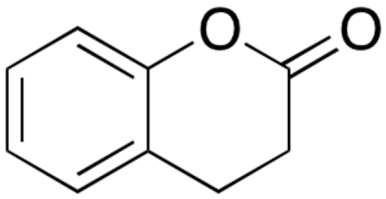
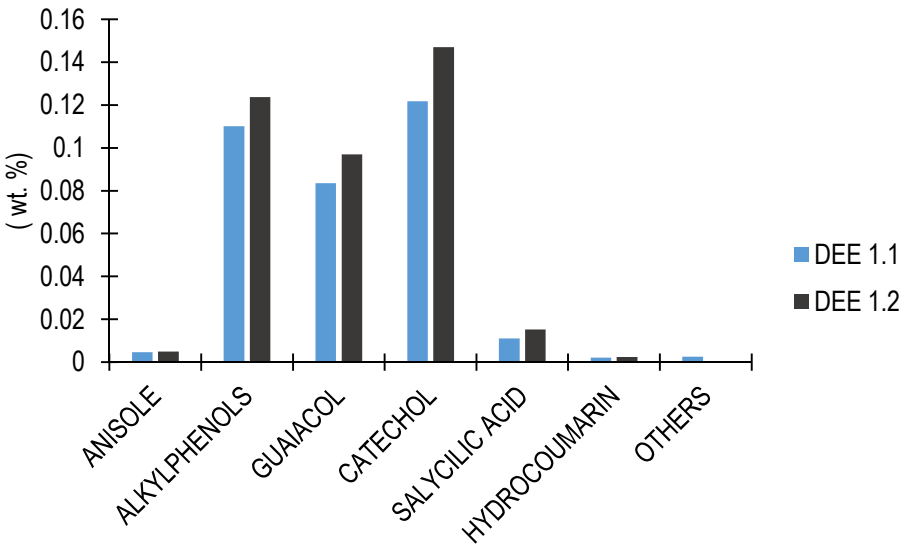
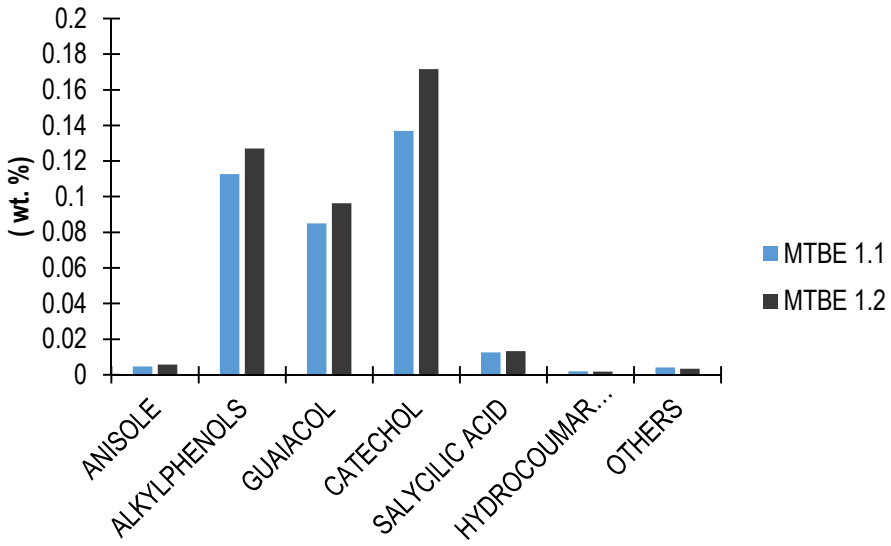


Figure 11.: Hydrocoumarin molecular structure.



Graphic 10.: GC-MS results of DEE extraction replicas.



Graphic 11.: GC-MS results of MTBE extraction replicas.

The standard deviation between two replicas it has been calculated following the equation 13 and it is presented in the tables below:

Table 18.: Standard deviation of the results in DEE extraction test.

	σ
ANISOLE	2.17E-04
ALKYLPHENOLS	9.62E-03
GUAIACOL	9.48E-03
CATECHOL	1.78E-02
SALYCILIC ACID	2.95E-03
HYDROCOUMARIN	2.36E-04

Table 19.: Standard deviation of the results in MTBE extraction test.

	σ
ANISOLE	6.65E-04
ALKYLPHENOLS	1.02E-02
GUAIACOL	7.98E-03
CATECHOL	2.45E-02
SALYCILIC ACID	4.65E-04
HYDROCOUMARIN	1.58E-04
OTHERS	4.91E-04

5. Conclusion

- The presence of phenol is needed, 4% phenol is still the optimum choice. 2% and 3% phenol worked, but the bio-oil produced appear to be “very viscous”. Important information of reaction pathways of the capping effects of phenol was established.
- Catalyst change is possible from potassium to sodium catalyst. No decrease in bio-oil yield and lower formation of THF insolubles was detected.
- Aqueous phase extracted with MTBE shows almost the same results as with DEE, concluding that a change of a solvent extraction is possible.

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NOMENCLATURE

A Area []

DEE Diethyl ether

GC-MS Gas chromatography mass spectrometry.

GPC Gas permeation chromatography

h hours

HHV higher heating value [MJ/kg]

KF Karl Fischer

m mass [g]

Mw Molecular weight [kDa]

ºC Celsius degrees

P Index Polarity [-]

SS Suspended solids

TC Total Carbon [ppm]

THF Tetrahydrofuran

TIC Total Inorganic Carbon [ppm]

TOC Total Organic Carbon [ppm]

σ Standard deviation [-]

APPENDIX

I. APPENDIX 1

Refrence test 100% KOH/K_2CO_3		
	Mass (g)	**Mass fraction (wt.%)**
Water	2660.732	88.6%
Lignin(dry)	164.968	5.5%
K_2CO_3	48	1.6%
Phenol	120	4.0%
KOH	9	0.3%
Total	3003	100.0%

II. APPENDIX 2

	PhOH (wt.%)	**Catalyst specie**	**TC (ppm)**	**TOC (ppm)**	**TIC (ppm)**
Run 51	2	KOH/K_2CO_3	18525	16600	1925
Run 50	3	KOH/K_2CO_3	21912.5	19437.5	2475
Run 53	4	KOH/K_2CO_3	24810	23430	1380
Run 54	5	KOH/K_2CO_3	28475	26900	1575
Run 56	4	$NaOH/Na_2CO_3$	26450	25125	1325
Run 57	4	90% $NaOH/Na_2CO_3$ 10% KOH/K_2CO_3	26575	26500	75
Run 58	4	80% $NaOH/Na_2CO_3$ 20% KOH/K_2CO_3	-	-	-

III. APPENDIX 3

	Oil sample (g)	THF (added) (g)	Total Crude Oil + THF (g)	Karl Fisher on THF w %	Water Average %	Mass water in sample (g)	Mass water in THF (g)	Mass water in Oil (g)	Water Mass Fraction in the Oil on THF free basis (%)
Run 51 2% phenol	2.07	15.10	17.17	0.03	0.43	0.074	0.005	0.069	3.34
Run 51 2% phenol	2.21	14.56	16.78	0.03	0.34	0.056	0.004	0.052	2.34
Run 50 3% phenol	2.22	14.99	17.21	0.03	0.22	0.038	0.004	0.033	1.51
Run 50 3% phenol	2.24	14.90	17.14	0.03	0.25	0.042	0.004	0.038	1.68
Run 53 4% phenol	2.02	13.18	15.20	0.03	0.26	0.039	0.004	0.035	1.73
Run 53 4% phenol	2.30	15.17	17.47	0.03	0.16	0.028	0.005	0.023	1.02
Run 54 5% phenol	2.26	14.04	16.30	0.03	0.26	0.042	0.004	0.038	1.69
Run 54 5% phenol	2.45	13.87	16.32	0.03	0.25	0.041	0.004	0.037	1.49
Run 56 100% Sodium	2.38	12.90	15.27	0.03	1.06	0.161	0.004	0.157	6.61
Run 56 100% Sodium	2.13	14.24	16.37	0.03	0.91	0.149	0.004	0.145	6.79

IV. APPENDIX 4

Solvent	Solvent Polarity Index, *P*
Hexane	0.1
Carbon tetrachloride	1.56
Isopropyl ether	1.83
Toluene	2.4
Methyl-*t*-butyl ether	2.4
Chloroform	2.7
Diethyl ether	2.8
Dichloromethane	3.1
Isopropanol	3.92
Tetrahydrofuran	4.0
Ethyl Acetate	4.4
Methanol	5.1
Acetone	5.1
Dioxane	5.27
Acetonitrile	5.8
Water	10.2