



Aalborg Universitet

AALBORG UNIVERSITY
DENMARK

Catalytic hydrothermal conversion of LignoBoost Kraft lignin for the production of bio-oil and aromatic chemicals

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

Published in:

Proceedings of the 2014 International Chemical Recovery Conference, Tampere (Finland)

Publication date:
2014

Document Version
Early version, also known as pre-print

[Link to publication from Aalborg University](#)

Citation for published version (APA):

Maschietti, M., Nguyen, T. D. H., Belkheiri, T., Åmand, L-E., Theliander, H., Vamling, L., ... Andersson, S-I. (2014). Catalytic hydrothermal conversion of LignoBoost Kraft lignin for the production of bio-oil and aromatic chemicals. In M. Nieminen, & P. Lampinen (Eds.), Proceedings of the 2014 International Chemical Recovery Conference, Tampere (Finland) (Vol. 2, pp. 252-261). Finnish Recovery Boiler Committee, 2014 .

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- ? Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- ? You may not further distribute the material or use it for any profit-making activity or commercial gain
- ? You may freely distribute the URL identifying the publication in the public portal ?

Take down policy

If you believe that this document breaches copyright please contact us at vbn@aub.aau.dk providing details, and we will remove access to the work immediately and investigate your claim.

Catalytic Hydrothermal Conversion of LignoBoost Kraft Lignin for the Production of Bio-oil and Aromatic Chemicals

Marco Maschietti^{a,d*}, Thi Dieu Huyen Nguyen^a, Tallal Belkheiri^b, Lars-Erik Åmand^b, Hans Theliander^a, Lennart Vamling^b, Lars Olausson^c, Sven-Ingvar Andersson^a

^aChalmers University of Technology, Department of Chemical and Biological Engineering, Kemigården 4, SE-412 96 Gothenburg, Sweden;

^bChalmers University of Technology, Department of Energy and Environment, SE-412 96 Gothenburg, Sweden;

^cMetso Power AB, Box 8734, SE-402 75 Gothenburg, Sweden

^dPresent address: Aalborg University Esbjerg, Department of Biotechnology, Chemistry and Environmental Engineering, Niels Bohrs Vej 8, 6700 Esbjerg, Denmark

*Corresponding and presenting author (marco@bio.aau.dk)

ABSTRACT

The feasibility of the conversion of lignin into bio-oil and value-added chemicals was demonstrated operating in near-critical water, using ZrO_2/K_2CO_3 as catalytic system and phenol as char suppressing agent. The process was run using a small pilot unit operating in continuous (1 kg/h). The mass fractions of lignin and phenol in the feed slurry were approximately 5.5 % and 4.0 %, respectively, whereas that of K_2CO_3 was varied in the range 0.4 % - 2.2 %. The reactor temperature was also subjected to variation (290 °C – 370 °C). The reaction led to an aqueous phase, dissolving water soluble organics (WSO) in it, a bio-oil and char. The yields (on a phenol-free product basis and on a dry lignin basis) of bio-oil, WSO and char were in the ranges 69 % - 86 %, 5 % - 11 % and 16 % - 22 %, respectively. The main 1-ring aromatic compounds detected in the products were anisoles, alkylphenols, guaiacols and catechols, with alkyl side chains of methyl, ethyl, and propyl type. The bio-oil showed higher heat value (32 MJ/kg) with respect to the lignin feed, and lower sulphur content.

INTRODUCTION

The increase of the price of fossil fuels, their depletion, environmental issues connected with their extensive use and the increasing demand of energy and carbon-based materials have been drawing the attention on developing new process routes based on renewable sources and with a lower negative impact on the environment. In this context, the utilisation of lignocellulosic biomass is particularly promising since it does not directly compete with food supplies [1]. Among lignocellulosic feed stocks, lignin extracted in pulping processes has the potential of developing as a relevant raw material for the production of chemicals and bio-oil in industrial quantities. The overall amount of lignin extracted in pulping operations around the world is estimated to be over 70 million tons per year. Most of this lignin is burned as part of the treatment of the spent pulping liquors for recovery of energy and of the pulping chemicals, with less than 2 % actually recovered for utilisation as chemical product. In particular, in the Kraft pulping process the share of the lignin recovered for chemical use is even lower, when compared to other chemical pulping processes (e.g. sulphite pulping). However, since the energy efficiency in modern Kraft pulp mills has been increasing, the possibility of recovering large amounts of Kraft lignin to be used as raw material outside the pulp mill has nowadays been taken into increasing consideration [2]. In this context, a new efficient process (the LignoBoost process) for extraction of lignin at high purity level was introduced and has recently gained commercial status. Thus, in years to come a huge amount of LignoBoost Kraft lignin is expected to be available for valorisation [3,4].

The aromatic monomeric units constituting lignin suggest this polymer could become a resource for the industrial production of value-added chemicals and transportation fuel additives, if converted into basic phenolic compounds [5,6]. Among possible processes for the conversion of lignin into smaller aromatic units, the hydrothermal liquefaction in near critical water (NCW) is a very promising one, due to the relatively mild temperatures (250 °C - 350 °C), which allow the aromatic structures to be retained, and the peculiar properties of NCW that make it a unique solvent for carrying out chemical reactions. For example, NCW is capable of dissolving both low polarity compounds and salts, has a strong tendency to ionize, thus being a source of H^+ and OH^- which can act as catalyst in many reactions, and its density is highly tuneable with relatively small pressure and temperature variations [7,8,9].

Previous studies on lignin conversion in NCW, albeit promising, have shown that one of the major drawbacks of the process is the tendency of the smaller fragments, produced in the breakage of the polymer, to give secondary re-polymerisation reactions, yielding to high amount of solid residues [10]. In this regard, the use of phenol as co-solvent and agent capable of limiting the re-polymerisation reactions was found to be beneficial, thus allowing to increase the yield in liquid products and to decrease the amount of solid residues [11]. Also, the use of alkali catalysts (e.g. K_2CO_3) was found to be beneficial by several investigators in increasing the yield of liquid products [10]. As far as the selection of the catalytic system is concerned, good results in terms of bio-oil production were obtained by using $ZrO_2 + K_2CO_3$ by Hammerschmidt et al. [12] and Toor et al. [13], on various biomasses different from lignin, and by our research group on lignin [14,15].

The present work reports the main results obtained so far by our research group on the conversion of LignoBoost Kraft lignin into bio-oil and phenolic chemicals, using $ZrO_2 + K_2CO_3$ as catalytic system and phenol as co-solvent and char suppressing agent. The experiments were carried out on a small pilot unit operated in continuous mode with a feed flow rate of 1 kg/h. A discussion on the effect of the concentration of the homogeneous catalyst (i.e. K_2CO_3) and on the reaction temperature is presented.

MATERIALS AND METHODS

Materials

Lignin used in all experiments was from softwood and it was obtained in the LignoBoost demonstration plant located in Bäckhammar (Sweden). The moisture content of this lignin was 32.6 %. The mass average molar mass was 3900 g/mol, with a molar mass dispersity equal to 5.6. The carbon, hydrogen, sulphur and ash mass fractions (on a dry lignin basis) were 65.6 %, 5.7 %, 1.85 % and 0.8 %, respectively. Oxygen was approximately 26 % (by difference). The mass fraction of aliphatic and aromatic groups was equal to 78 % and 22 %, respectively. The Higher Heat Value (HHV) was 27.7 MJ/kg (on a dry lignin basis). Potassium carbonate ($K_2CO_3 \geq 99.5$ %) and phenol (crystallized, ≥ 99.5 %) were from Scharlau. The heterogeneous catalyst, made of zirconia pellets, was from Harshaw Chemie BV (length: 3 mm; diameter: 3 mm; BET surface area 48 m²/g). Further detail on the above-mentioned materials, together with the description of all the chemicals used in the analytical procedure, is available in previous publications on this subject [14, 15].

Apparatus and Procedure

A schematic diagram of the small pilot unit which was used to carry out the hydrothermal experiments is provided in Fig. 1. The unit was developed at Chalmers University of Technology and it is located there. The lignin slurry used to carry out the experimental runs was prepared dispersing lignin particles in deionised water, K_2CO_3 (varied in the range 0.4 % - 2.2 %) and phenol (approximately 4 %). The slurry was kept stirred at 40 °C in the feed tank and continuously fed to the reactor at 1 kg/h by means of a high-pressure pump. The feed was preheated to 80 °C in an electric heater and then mixed with a recirculation stream of hot reaction products, provided by a high-pressure high-temperature recirculation pump. The recycle to feed ratio was kept at approximately 10, with the exception of a single run at the highest reaction temperature (i.e. 370 °C) where this value was at 2. Operating with a high recycle to feed ratio allowed the feed to be rapidly heated up to a temperature close to the reaction temperature and mixed with the reaction products before entering the reactor and coming into contact with the solid catalyst. A further heater was installed before the reactor inlet, with the function of adjusting the temperature at the desired reaction value (varied in the range 290 °C – 370 °C). The reactor pressure was kept at 25 MPa in all runs. The reaction mixture came into contact with the solid catalyst while flowing upward in the 500 cm³ fixed bed reactor (height 171 mm; internal diameter 61 mm), equipped with an electrical heating jacket. The free volume of the reactor charged with the catalyst was 294 cm³. The residence time in the reactor was in the range (10 – 13) min, depending on the reaction temperature which affects the density of the reacting mixture. The reaction products were cooled down and depressurised to ambient condition by means of two pressure control valves. These valves were installed in parallel so that they could be switched over from one to the other when the valve in operation became congested by solid particles. This set up allowed keeping the plant in continuous operation successfully for several hours.

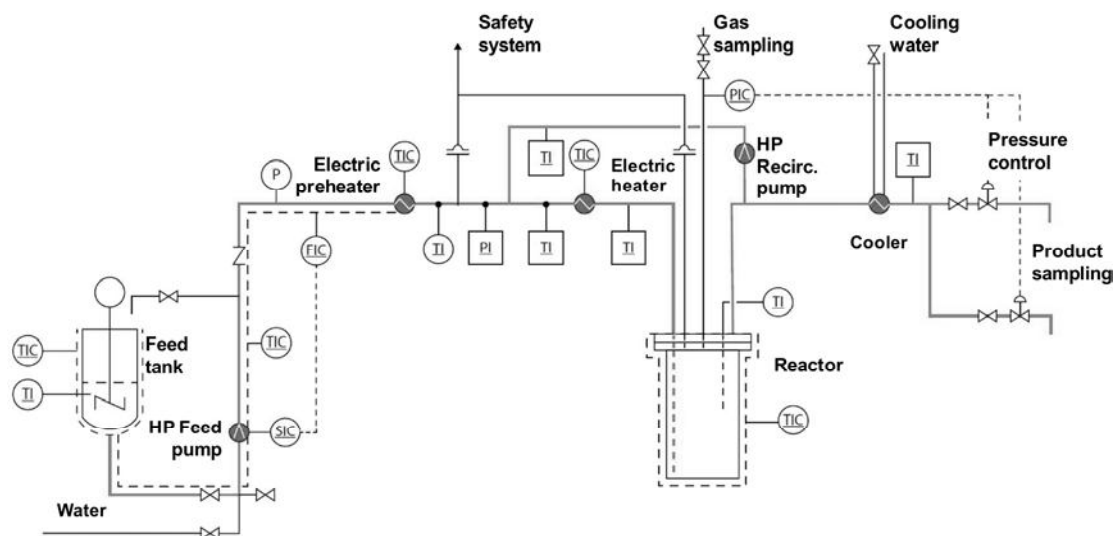


Fig. 1 Schematic diagram of the pilot plant used for carrying out the experiments.

After depressurisation, the products were continuously collected in sampling bottles, which were replaced every approximately 45 minutes. The products consisted of an aqueous phase and a bio-oil (lignin oil). Gas production was very low, as it was qualitatively verified by means of a gas sampling bag placed downstream the sampling bottle, on the output line exiting the cap of the bottle. After the shut down operations of each run, the reactor was disassembled, a portion of the catalyst was sampled and the char deposited on it was burned off for quantitation purpose. Auxiliary lines allowed the cleaning of the apparatus in between the runs. Further detail on the apparatus and procedure is provided in one of the previous publications of our group [14].

Experimental Conditions

Table I summarises the operating parameters selected for the runs presented in this work. The experimental conditions are centred on the run with K_2CO_3 in the feed at 1.6 % (mass fraction) and the reactor temperature at 350 °C. These two independent parameters were varied one at a time, in the ranges 0.4 % - 2.2 % and 290 °C – 370 °C. On the other hand, the pH of the feed (pH_f) is a parameter which depends on the amount of K_2CO_3 . As shown in Table I, it resulted to be in the range 7.9 – 9.3. Phenol mass fraction was fixed at approximately 4 % in all runs. Lignin mass fraction was fixed at approximately 5.5 % in all runs, except a single run (i.e. Run 9) with no lignin in the feed which was carried to demonstrate that the phenolic products obtained in the other runs actually derived from lignin decomposition and conversion. In the execution of the experimental runs, the observation was made that during the start up the liquid products showed a progressive darkening and pH reduction, reaching stable visual appearance and stable pH (± 0.1) after approximately two hours from the start. Also, the operating parameters of the plant kept constant after approximately two hours. In line with these observations, the system was assumed at steady-state after two hours from the start and was kept in steady functioning for additional 2-3 hours.

Table I Operating parameters of the experimental runs. Reactor pressure was kept at 25 MPa in all runs. Composition data are reported as mass fractions.

	1	2	3	4	5	6	7	8	9
Lignin (dry)	5.6	5.5	5.5	5.4	5.5	5.5	5.5	5.5	0
Phenol	4.1	4.1	4.1	4.0	4.1	4.1	4.1	4.1	4.7
K_2CO_3	0.4	1.0	1.6	2.2	1.6	1.6	1.6	1.6	1.9
T (°C)	350	350	350	350	290	310	330	370	350
pH_f	7.9	8.8	9.1	9.3	9.1	9.1	9.1	9.1	9.5

Analytical Methods

Fig. 2 shows a schematic representation of the analytical methods that were applied on the reaction products. At first, they were separated by means of centrifugation, operating at 492 rad/s, 25 °C, for 3 hours. The centrifugation gave a fairly transparent aqueous phase, with a colour ranging from light yellowish to dark green, and black lignin oil. The oil was heavier than the aqueous phase. Because of its high viscosity, it was dissolved in tetrahydrofuran (THF) in order to allow its complete recovery and exact quantitation. The solution of oil in THF was also used to measure the water content of the oil, by means of Karl Fischer titration, and the amount of THF-insoluble suspended solids in the oil, by means of filtration. On the other hand, for the samples that were subjected to other analysis requiring dry oil, THF was evaporated in a rotary vacuum evaporator. The temperature of the evaporator was kept below 35 °C to avoid possible secondary reactions. The dry oil samples were subjected to elemental analysis (C, H, N, S, K and ash) and HHV determination (Sveriges Tekniska Forskningsinstitut, SP, Borås, Sweden). In addition, the dry oil samples were subjected to extraction in diethyl ether (DEE) and the DEE-extracts were analysed by means of Gas Chromatography (GC) coupled with Mass Spectrometry (GCMS), in order to quantitate and characterise the lighter fraction of the oil. As far as the aqueous phase is concerned, the samples obtained by centrifugation (pH in the range 7.1 – 8.5) were analysed for Total Carbon (TC) and Total Organic Carbon (TOC) determination (SP, Borås, Sweden). On the other hand, other samples were used for the characterisation of the water soluble organics (WSO) by means of GCMS analysis. At first, these samples were subjected to acidification to pH below 2 in order to ensure the neutralisation of the organic acids and favour their subsequent extraction with DEE. The acidification step gave rise to further clarification of the aqueous phase, with a separation of small amounts of two additional liquid phases and the liberation of a small amount of gas. In most of the runs, the amount of gas liberated was in line with the expected formation of carbon dioxide from carbonates during the acidification. The two additional liquid phases consisted of a light organic phase at the top and heavy oil at the bottom. Because of their very small amount, these two phases were neglected in subsequent analysis. The acidified aqueous phase was extracted with DEE and the extracts were then subjected to GCMS analysis. The main extracted WSO were identified on the basis of the NIST/EPA/NIH Mass Spectral Database 2011 and quantitated using an internal standard (IST). Syringol was selected as IST, since it is not an aromatic unit of softwood lignin, it was not produced in the reaction, being nevertheless similar to the reaction products.

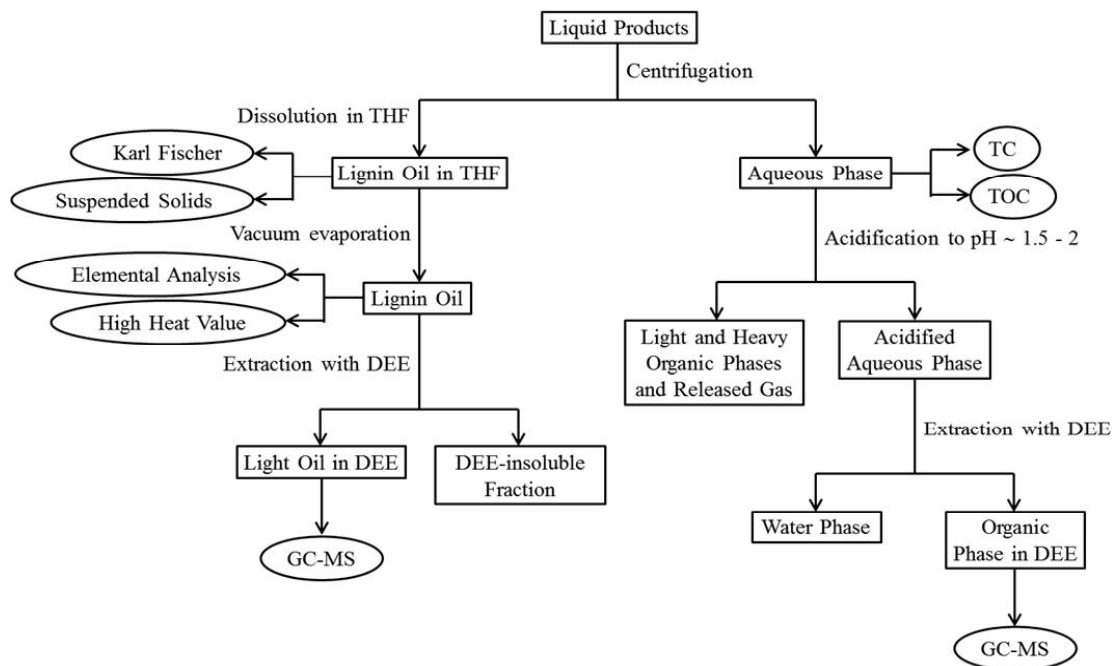


Fig. 2 Block diagram representing the analytical methods applied on the reaction products.

RESULTS AND DISCUSSION

Carbon Balance and Process Yields

On the basis of the analytical results reported in the following sections, the carbon balance was calculated for the experimental runs which were carried out. In all runs, the sum of the mass of carbon exiting the system and carbon accumulated in the system (e.g. char deposited on the catalyst) was found to be in the range 95 % - 103 % of the mass of carbon entering the system. This result indicates that the analytical protocols that were developed guaranteed an excellent closure of the carbon balances. Further detail on the calculation procedure is provided elsewhere [14].

The process yields were calculated taking into account three different product fractions: the oil, the water soluble organics (WSO) and char. The mass yield of each fraction was calculated on water-free phenol-free basis, on the basis of dry lignin fed to the reactor. Indicating with the subscript *i* the generic fraction, the mass yield was thus defined as:

$$Y_i = \frac{m_i(1 - w_i)(1 - p_i)}{m_l(1 - w_l)}$$

where m_i is the mass of the generic product fraction produced in the reaction in a given time interval at steady state; m_l is the mass of (wet) lignin fed to the reactor in the same time interval; w_i and p_i are the mass fractions of water and phenol in the generic product fraction; w_l is the mass fraction of water in the lignin used in the feed. Table II shows the values of the yields obtained in the experiments for the different product fractions. In the run without lignin in the feed, as expected, no oil and char were formed.

At all conditions under investigations, lignin was converted to a large extent into bio-oil (from 69 % to 86 %). The data show that, in the ranges under investigation, temperature has a stronger effect than K_2CO_3 mass fraction in determining the yields of the different class of products. More specifically, the yield of oil decreases with the reaction temperature from 86 % to 69 %; the decrease of oil is compensated by an increase of the water soluble organics recovered in the aqueous phase (from 5 % to 11 %) and by an increase of char (from 16 % to 22 %).

Table II. Yields of oil, water soluble organics and char produced in the reaction.

	T = 350 °C with K_2CO_3 (%) at:				K_2CO_3 (%) = 1.6 % with T (°C) at:				
	0.4	1.0	1.6	2.2	290	310	330	350	370
OIL (%)	70.2	69.4	72.2	70.9	85.8	87.7	78.3	72.2	68.5
WSO (%)	8.7	8.9	9.7	10.8	4.9	6.1	7.9	9.7	11.3
CHAR (%)	20.6	17.8	20.7	17.2	16.1	16.5	17.2	20.7	22.0

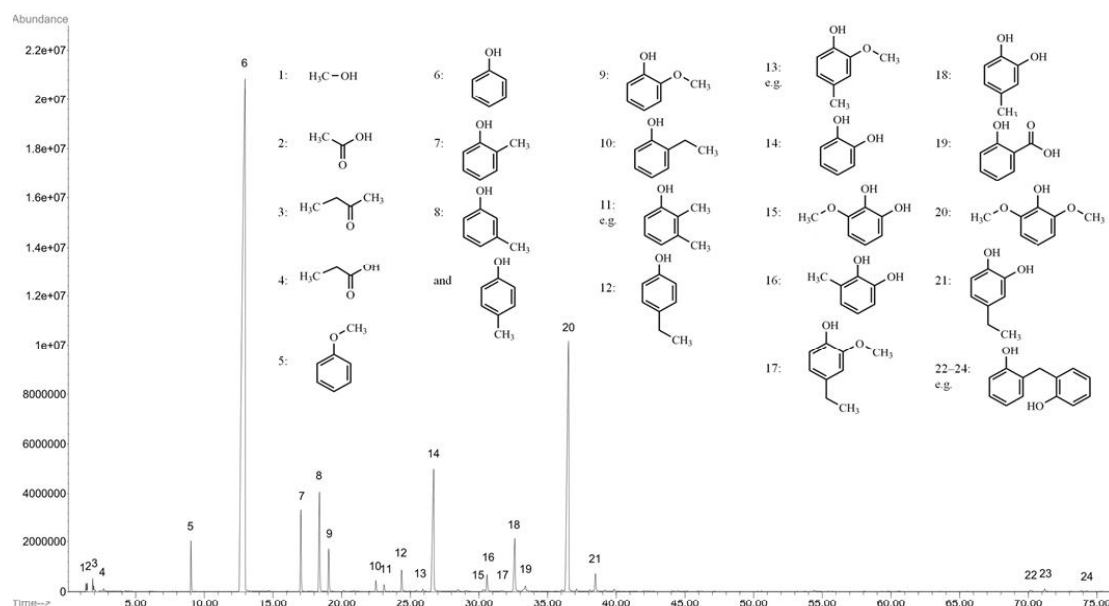
Characteristics of the Aqueous Phase

The GCMS analysis on the aqueous phase produced in run 9 (no lignin in the feed) showed the same concentration of phenol loaded in the feed, together with traces of impurities which are compatible with the impurity profile of phenol used as reagent in the experiments. Also, the pH of the aqueous phase exiting the reactor was the same as the aqueous feed. Therefore, no reactions were observed when the reactor was fed with water, phenol and K_2CO_3 (i.e. no lignin). On the other hand, in the runs with lignin in the feed a large variety of water soluble organics were identified in the aqueous phase. The reaction led to an acidification of the aqueous phase, as can be seen from Table III. This table also reports TC and TOC of the aqueous phase. These values correspond to mass fractions of organics below 3 %, as imposed by the limited solubility of phenolic compounds in water. A typical Total Ion Current Chromatogram (TICC) of the DEE-extract of the aqueous phase produced in the reaction, when lignin was fed to the system, is shown in Fig. 3. Beside phenol (i.e. peak 6), many 1-ring aromatic compounds were detected. They were mainly phenolics, such as alkylphenols (e.g. cresols, peaks 7 and 8), guaiacols (e.g. peaks 9 and 13) and catechols (e.g. peaks 14, 16, 18 and 21).

Table III. pH, TC and TOC of the aqueous phase produced in the reaction.

	T = 350 °C with K ₂ CO ₃ (%) at:				K ₂ CO ₃ (%) = 1.6 % with T (°C) at:				
	0.4	1.0	1.6	2.2	290	310	330	350	370
pHa	7.1	7.4	8.0	8.2	8.5	8.2	8.2	8.0	7.9
TOC (g/L)	27	26	27	27	25	26	25	27	26
TC (g/L)	28	27	29	30	27	28	27	29	28

One methoxybenzene (non-phenolic aromatic compound) was also detected (i.e. anisole, peak 5), together with a small amount of phenolic dimers with structure C6-C1-C6 (peaks 22-24) and a few small oxygenated organic compounds (peaks 1-4). The alkyl side chains of the aromatic compounds found in the aqueous phase were always methyl or ethyl type. With regard to the trends in WSO distribution in response to the variation of the process parameters (i.e. K₂CO₃ mass fraction and temperature), the main observation was a decrease of guaiacols and an increase of catechols as K₂CO₃ or reaction temperature were increased. In addition, the increase in temperature remarkably increased the mass fraction of alkylphenols in the aqueous phase and led to a decrease of phenolic dimers. Temperature variations had also an influence on the distribution of minor compounds, not belonging to the major classes previously mentioned. For example, the mass fraction of vanillin decreased for reaction temperatures increasing from 290 °C to 330 °C; at higher temperatures, vanillin was not detected.

**Fig. 3** Typical Total Ion Current Chromatogram (TICC) of the DEE-extract of the aqueous phase. Peak 20 (syringol) is the internal standard.

Characteristics of the Oil

The amount of lignin oil produced in the process was approximately 5 % - 7 % of the total output of the reactor, consisting most of the output of the diluted aqueous phase. As discussed above, the oil was the major lignin-derived product fraction, with yields in the range 69 % - 86 %. As can be seen from Table IV, the mass fraction of water in the oil obtained by means of centrifugation was between 10 % - 20 % in all runs. The amount of solid particles in the oil, which resulted to be insoluble in THF and which were retained on filters with nominal maximum pore size in the range 10 - 16 μm , is also reported in Table IV.

Table IV. Flow rate of oil to total output flow rate (Oil to Total ratio), water content of the oil after centrifugation (w_{OIL} , mass fraction), THF-insoluble Suspended Solids of the oil (on a dry oil basis).

	T = 350 °C with K ₂ CO ₃ (%) at:				K ₂ CO ₃ (%) = 1.6 % with T (°C) at:				
	0.4	1.0	1.6	2.2	290	310	330	350	370
Oil to Total (%)	5.2	5.1	5.3	5.6	6.6	6.0	5.8	5.3	4.9
w_{OIL}	12.7	12.4	14.1	18.4	19.2	10.9	15.2	14.1	13.3
THF-SS	0.1	1.9	22.8	22.9	23.8	25.4	8.6	22.8	13.2

The mass fraction of THF-insoluble suspended solids (THF-SS) was very low in the two runs with lower amount of K₂CO₃, whereas it was in the range 8 % - 25 % in the other runs, although a clear trend could not be highlighted. The elemental analysis of the oil showed that the oil was partially deoxygenated with respect to the starting lignin. The carbon mass fraction increased from the value of the starting lignin (i.e. 65.6 %) to values in the range 70 % - 76 %, with a degree of carbonisation of the oil increasing with the reaction temperature. Oxygen decreased from 26 % down to values in the range 15 % - 21 %, with the lower values reached at the higher temperatures or at the higher concentrations of K₂CO₃. Consistently with these trends, the HHV of the oil was found to be moderately higher than the HHV of the starting lignin (31 MJ/kg – 33 MJ/kg vs 27.7 MJ/kg). Interestingly, the sulphur mass fraction in the oil was in the range 0.25 – 0.56 %, which is to say substantially lower than that in the lignin feed (i.e. 1.85 %). Fig. 4 shows the TICC of the DEE-extract of the oil. The fraction extracted in DEE represented approximately 20 % - 30 % (mass basis), being this fraction the lighter one. Part of the phenol (peak 2) used in the feed solubilised in the oil, ending up in constituting about 10 % - 16 % of the light fraction. Many other aromatic compounds deriving from lignin decomposition were detected in the oil. The main classes were anisoles (e.g. peaks 1, 3, 4, 7, 9), alkylphenols (e.g. cresols: peaks 5, 6; ethylphenols: peaks 10, 13; propylphenols: peaks 17, 20), guaiacols (e.g. peaks 8, 15, 21), catechols (e.g. peaks 16, 22), phenolic dimers of both C6-C1-C6 type (e.g. peaks 27, 28, 31) and C6-C2-C6 type (e.g. peaks 29, 30, 32, 33). Most of these compounds are the same as those found in the aqueous phase, with relative distributions between the two phases depending on their hydrophilic or hydrophobic nature. For example, guaiacols were relatively more concentrated in the oil, whereas catechols were relatively more concentrated in the aqueous phase due to the two OH groups in the molecule. In addition, some compounds not found in the aqueous phase were instead found in the oil only, as in the case of many anisoles, aromatic compounds with propyl side chains, phenolic dimers of structure C6-C2-C6 and one polycondensed aromatic structure (e.g. peak 34).

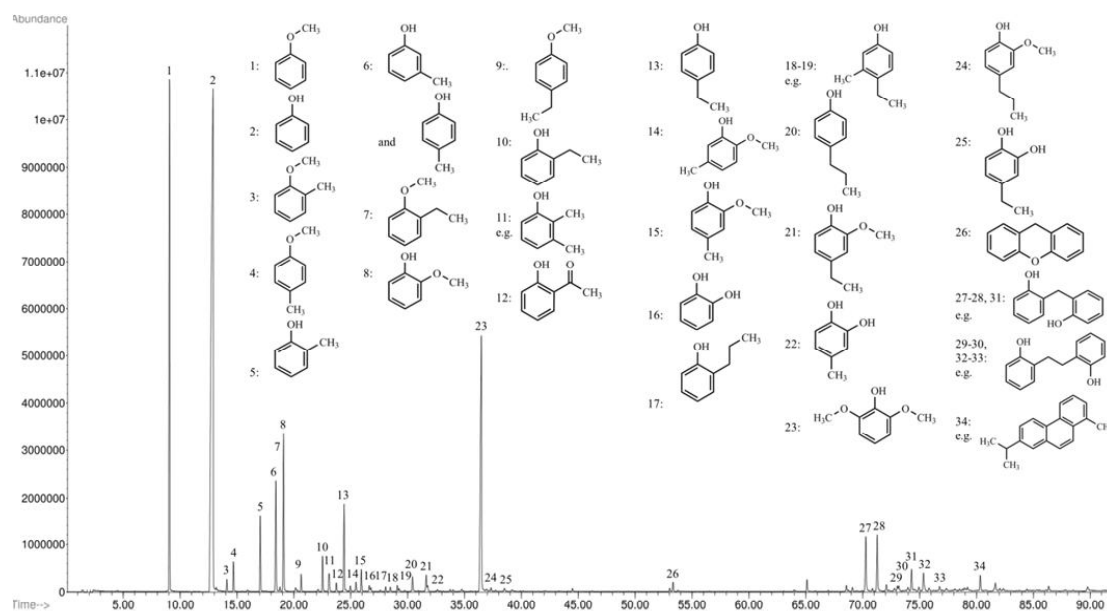


Fig. 4 Typical Total Ion Current Chromatogram (TICC) of the DEE-extract of the oil. Peak 23 (syringol) is the internal standard.

Process Yield of Chemical Classes of Compounds

In order to verify the presence of specific trends in the production of different classes of compounds in the chemical reaction, overall yields (aqueous phase + lignin oil) were calculated. The compounds were grouped in relevant classes, identified as anisoles, alkylphenols, guaiacols, catechols and phenolic dimers. The yield of the generic class i of compounds was defined as:

$$Y_i = \frac{m_{i,WSO} + m_{i,OIL}}{m_i(1 - w_i)}$$

where $m_{i,WSO}$ and $m_{i,OIL}$ stand for the mass of the class i of compounds in the aqueous phase (i.e. among the WSO) and the oil. In addition, the overall yield of 1-ring aromatic compounds (on a phenol-free basis) was calculated in a similar fashion. This term includes anisoles, alkylphenols, guaiacols, catechols and minor 1-ring aromatic compounds not included in the previous classes. Figures 5 and 6 show the obtained trends as a function of the mass fraction of K_2CO_3 and the reaction temperature, respectively. As can be seen, both the increase in the concentration of K_2CO_3 and the increase of the reaction temperature led to an increase in the yield of anisoles, alkylphenols and catechols and to a decrease in guaiacols. In particular, the yield of anisoles showed a high sensitivity to the concentration of K_2CO_3 , whereas the yield of alkylphenols to the reaction temperature. Interestingly, the phenolic dimers were the only class of compounds which responded in opposite ways to K_2CO_3 concentration and temperature. In fact, the higher concentrations of phenolic dimers were seen at the highest K_2CO_3 concentration and at the lowest temperatures under investigation. The overall yield of 1-ring aromatic compounds increased both with K_2CO_3 concentration (from 16.9 % to 27.1 %) and with temperature (from 10 % to 23 %).

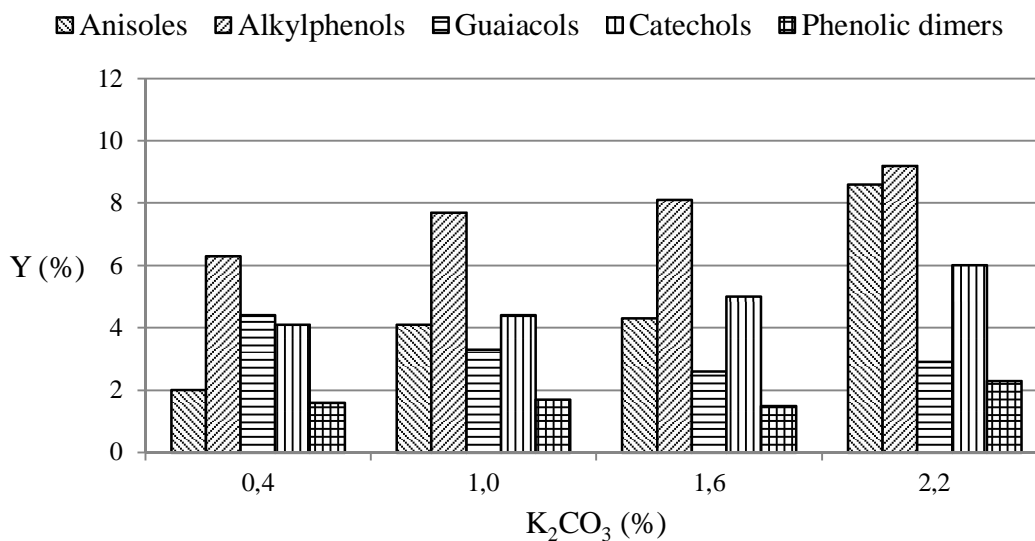


Fig. 5 Overall yields (aqueous phase + oil) of anisoles, alkylphenols, guaiacols, catechols and phenolic dimers as a function of the mass fraction of K_2CO_3 .

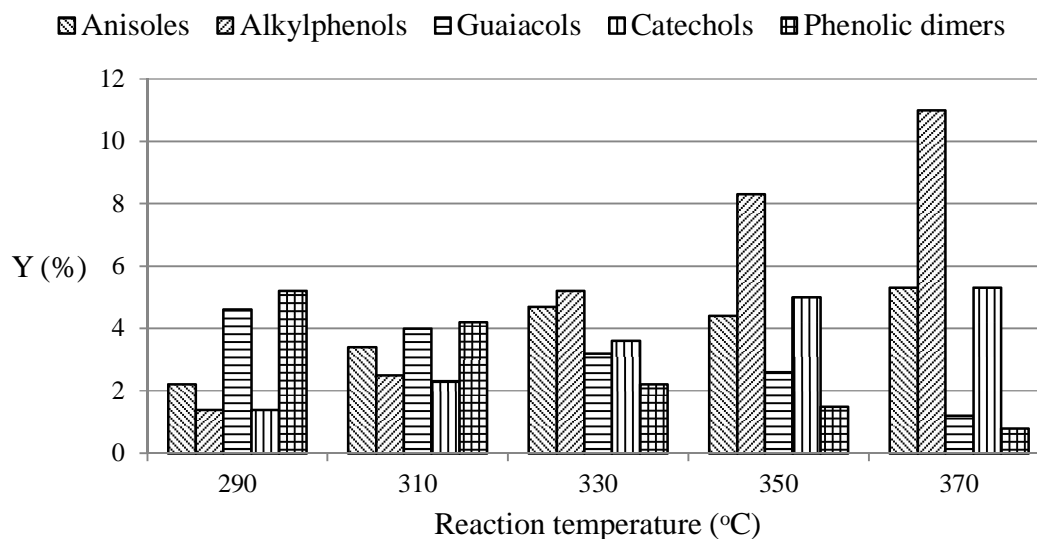


Fig. 6 Overall yields (aqueous phase + oil) of anisoles, alkylphenols, guaiacols, catechols and phenolic dimers as a function of the reaction temperature.

CONCLUSIONS

The feasibility of the conversion of LignoBoost Kraft lignin into bio-oil and small aromatic chemicals was demonstrated, operating with near-critical water as reaction medium, K_2CO_3 and ZrO_2 as catalytic system and phenol as co-solvent and char suppressing agent. The technical feasibility of the process was proved operating a small pilot unit kept in continuous steady state operation (1 kg/h feed) for 2-3 hours. The reactor was operated at 25 MPa. The effect of the reaction temperature (290 ° - 370 °C) and of the mass fraction of K_2CO_3 (0.4 % to 2.2 %) on the yields of different products fractions and different classes of chemicals were investigated. The lignin feed was converted into bio-oil (from 69 % to 86 %), water soluble organics that ends up in the aqueous phase (from 5 % to 11 %) and char (16 % - 22 %). Higher concentrations of K_2CO_3 and higher temperatures led to an increase in the overall yield (aqueous phase + oil) of 1-ring aromatic compounds derived from lignin decomposition. On the other hand, these conditions also favour an increase of char formation.

ACKNOWLEDGEMENT

This research was funded by Chalmers Energy Initiative – LignoFuel Project, Metso Power AB, The Swedish Energy Agency and Ångpanneförenings Forskningsstiftelse. The authors wish to thank Bengt Erichsen, Carina Olsson, Lena Elisabeth Fogelquist and Tommy Friberg for their technical assistance.

References

1. Singhvi, M.S., Chaudhari, S., and Gokhale, D.V., “Lignocellulose Processing: a Current Challenge”, RSC Advances, 4, pp. 8271-8277(2014).
2. Lora, J., “Industrial Commercial Lignins: Sources, Properties and Applications”, in: Belgacem, M.N., Fandini, A., (Eds.), “Monomers, Polymers and Composites from Renewable Resources”, Elsevier, Great Britain, Chapter 10, pp. 225-241(2008).
3. Theliander, H., “Withdrawing Lignin from Black Liquor by Precipitation, Filtration and Washing”, proceedings from the First Nordic Wood Biorefinery Conference, Stockholm, Sweden, pp. 36-42(2008).
4. Tomani, P., “The LignoBoost process”, Cellulose Chemistry and Technology, 44, pp. 53-58(2010).
5. Pandey, M.P., Kim, C.S., “Lignin Depolymerisation and Conversion: A Review of Thermochemical Methods”, Chemical Engineering and Technology, 34, pp. 29-41(2011).

6. Vigneault, A., Johnson, D.K., Chornet, E., "Base-Catalyzed Depolymerization of Lignin: Separation of Monomers", *Canadian Journal of Chemical Engineering*, 85, pp. 906-916(2007).
7. Carr, A.G., Mammucari, R., Foster, N.R., "A Review of Subcritical Water as a Solvent and its Utilisation for the Processing of Hydrophobic Organic Compounds", *Chemical Engineering Journal* 172, pp. 1-17(2011).
8. Eckert, C.A., Chandler, K., "Tuning Fluid Solvents for Chemical Reactions", *The Journal of Supercritical Fluids*, 13, pp. 187-195(1998).
9. Brunner, G., "Near Critical and Supercritical Water. Part I. Hydrolytic and Hydrothermal Processes", *The Journal of Supercritical Fluids*, 47, pp. 373-381(2009).
10. Azadi, P., Inderwildi, O.R., Farnood, R., King, D.A., "Liquid Fuels, Hydrogen and Chemicals from Lignin: A Critical Review", *Renewable and Sustainable Energy Reviews* 21, pp. 506-523(2013).
11. Fang, Z., Sato, T., Smith Jr., R.L., Inomata, H., Arai, K., Kozinski, J.A., "Reaction Chemistry and Phase Behavior of Lignin in High-Temperature and Supercritical Water", *Bioresource Technology*, 99, pp. 3424-3430(2008).
12. Hammerschmidt, A., Boukis, N., Hauer, E., Galla, U., Dinjus, E., Hitzmann, B., Larsen, T., Nygaard, S.D., "Catalytic Conversion of Waste Biomass by Hydrothermal Treatment", *Fuel*, 90, pp. 555-562(2011).
13. Toor, S.S., Rosendahl, L., Nielsen, M.P., Glasius, M., Rudolf, A., Iversen, S.B., "Continuous Production of Bio-Oil by Catalytic Liquefaction from Wet Distiller's Grain with Solubles (WDGS) from Bio-Ethanol Production", *Biomass and Bioenergy* 36, pp. 327-332(2012).
14. Nguyen, T.D.H., Maschietti, M., Belkheiri, T., Åmand, L.-E., Theliander, H., Vamling, L., Olausson, L., Andersson, S.-I., "Catalytic Depolymerisation and Conversion of Kraft Lignin into Liquid Products using Near-Critical Water", *The Journal of Supercritical Fluids*, 86, pp. 67-75(2014).
15. Nguyen, T.D.H., Maschietti, M., Åmand, L.-E., Theliander, H., Vamling, L., Olausson, L., Andersson, S.-I., "Effect of Temperature on the Catalytic Conversion of Kraft Lignin using Near-Critical Water", submitted to *Bioresource Technology*.