The effect of temperature on the catalytic conversion of Kraft lignin using near-critical water

Bioresource Technology (ISSN: 0960-8524)

Citation for the published paper:
Nguyen, T. ; Maschietti, M. ; Åmand, L. et al. (2014) "The effect of temperature on the catalytic conversion of Kraft lignin using near-critical water". Bioresource Technology, vol. 170 pp. 196-203.

http://dx.doi.org/10.1016/j.biortech.2014.06.051

Bioresource Technology 170 (2014) 196–203

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

The effect of temperature on the catalytic conversion of Kraft lignin using near-critical water

Thi Dieu Huyen Nguyen [a], Marco Maschietti [a,1], Lars-Erik Åmand [b], Lennart Vamling [b], Lars Olausson [c], Sven-Ingvar Andersson [a], Hans Theliander [a,*]

[a] Chalmers University of Technology, Department of Chemical and Biological Engineering, SE-412 96 Gothenburg, Sweden
[b] Chalmers University of Technology, Department of Energy and Environment, SE-412 96 Gothenburg, Sweden
[c] Valmet Power AB, Box 8734, SE-402 75 Gothenburg, Sweden

HIGHLIGHTS

- The conversion of lignin in near-critical water was investigated at 290–370 °C.
- ZrO_2/K_2CO_3 was used as catalytic system and phenol as char suppressing agent.
- The lignin-oil has higher HHV and lower contents of oxygen and sulphur than lignin.
- The main 1-ring aromatics are anisoles, alkylphenols, guaiacols and catechols.
- The yield of 1-ring aromatics increases remarkably with an increase in temperature.

ARTICLE INFO

Article history:
Received 2 April 2014
Received in revised form 5 June 2014
Accepted 6 June 2014
Available online 21 June 2014

Keywords:
Lignin
LignoBoost
Catalytic conversion
Bio-oil
Near-critical water

ABSTRACT

The catalytic conversion of suspended LignoBoost Kraft lignin was performed in near-critical water using ZrO_2/K_2CO_3 as the catalytic system and phenol as the co-solvent and char suppressing agent. The reaction temperature was varied from 290 to 370 °C and its effect on the process was investigated in a continuous flow (1 kg/h). The yields of water-soluble organics (WSO), bio-oil and char (dry lignin basis) were in the ranges of 5–11%, 69–87% and 16–22%, respectively. The bio-oil, being partially deoxygenated, exhibited higher carbon content and heat value, but lower sulphur content than lignin. The main 1-ring aromatics (in WSO and diethylether-soluble bio-oil) were anisoles, alkylphenols, catechols and guaiacols. The results show that increasing temperature increases the yield of 1-ring aromatics remarkably, while it increases the formation of char moderately. An increase in the yields of anisoles, alkylphenols and catechols, together with a decrease in the yield of guaiacols, was also observed.

1. Introduction

Natural gas, fossil-oil, and coal are non-renewable resources that are used for the production of fuels and chemicals. The depletion of these resources, together with the increase of anthropogenic greenhouse gas emissions deriving from their extensive use, has inspired scientists and researchers to find alternatives which are renewable. In such a scenario, biomass has been gaining increasing importance in addressing these issues. In this context, the utilisation of lignocellulosic biomass is very promising since it does not compete directly with food supplies (Singhvi et al., 2014). Wood, which consists of approximately 40–50% cellulose, 20–30% hemicellulose and 20–30% lignin on mass basis, is the most common lignocellulosic material available. Today, about 50% of the wood consumed on a global scale is used as fuel for the production of heat and power. The remaining 50% is mostly used for the production of timber-framed constructions and various paper products (Fengel and Wegener, 1989; Gellerstedt, 2009). The dominant methods used for the production of paper pulp are a variety of chemical pulping processes, such as Kraft pulping (generating Kraft lignin), sulphite pulping (generating lignosulphonate) and soda pulping (generating soda lignin). The aim of chemical pulping is to dissolve and remove lignin to liberate wood fibres, although some hemicelluloses are also degraded in the process (Brännvall, 2009). Nowadays, most of the lignin (almost 99%)

---

[*] Corresponding author. Tel.: +46 31 772 2992; fax: +46 31 772 2995.
E-mail address: hanst@chalmers.se (H. Theliander).

[1] Current address: Aalborg University Esbjerg, Department of Biotechnology, Chemistry and Environmental Engineering, 6700 Esbjerg, Denmark.

http://dx.doi.org/10.1016/j.biortech.2014.06.051
0960-8524/© 2014 Published by Elsevier Ltd.

extracted by these methods is used as internal fuel in the pulping process itself, thereby recovering energy. The pulp mills have become more energy efficient than in the past and now have an energy surplus, which can be expressed as a lignin surplus. In the modern Kraft pulping process (the dominant chemical pulping process) in particular, there is a remarkable lignin surplus that can be exploited (Lora, 2008). Furthermore, a new efficient process, namely the "LignoBoost" process, for extracting lignin at high levels of purity has been introduced and that has recently gained commercial status. Thus, in years to come, a huge amount of LignoBoost Kraft lignin is expected to be available for valorisation (Theliander, 2008; Tomani, 2010).

Lignin is an amorphous, three-dimensional, aromatic polymer that acts as binding material in the cell walls and between the cells. In addition, the hydrophobic character of lignin hinders water from penetrating the cell walls. Lignin is derived from the polymerisation of three phenylpropane monomers, namely *p*-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol, which connect randomly with ether (C–O–C) bonds (i.e. β-O-4, 4-O-5 and 1-O-4) and carbon–carbon (C–C) bonds (i.e. 5-5, β-5, β-β and β-1) (Henriksson, 2009). Due to its aromatic nature and its abundant availability, this material could become a resource for the industrial production of value-added chemicals and transportation fuel additives if converted into basic phenolic compounds (Pandey and Kim, 2011; Vigneault et al., 2007).

Among the possible processes for the conversion of lignin into smaller aromatic units, hydrothermal liquefaction in near-critical water (NCW) is a very promising one due to the relatively mild temperatures employed, which allows the aromatic structures to be retained, and the fact that NCW is a unique solvent for carrying out chemical reactions. Water is generally considered to be in the near-critical region at temperatures between 250 and 350 °C and pressures high enough to be in the liquid state. In the near-critical region, water behaves as a low polarity compound, showing the capability of dissolving most of the nonpolar or low polar organic compounds present. At the same time, the dielectric constant, albeit reduced, is still high enough to allow water to dissolve salts. Also, NCW has a strong tendency to ionise because of the increase in the ionic product with temperature, thus being a source of (H^+) and (OH^-) in many reactions. Furthermore, the density of water in this region is highly tuneable, with relatively small variations in pressure and temperature (Carr et al., 2011; Eckert and Chandler, 1998; Brunner, 2009).

Previous studies of lignin conversion in NCW have shown that one of the major drawbacks of the process is the tendency of the smaller fragments, produced by the breakage of ether bonds, to give secondary re-polymerisation reactions, yielding to high amount of solid residues (Azadi et al., 2013). It has been found that re-polymerisation reactions can be limited if phenol is used as a co-solvent, which increases the yield of the liquid products and decreases the amount of solid residues formed (Fang et al., 2008; Okuda et al., 2004). According to these authors, phenol favours the formation of a homogeneous phase at reaction conditions and entraps the active fragments derived from lignin depolymerisation, thus preventing the formation of heavier compounds. Also, several investigators have found the use of alkali catalysts (e.g. K_2CO_3) to be beneficial in increasing the yield of liquid products in the conversion of wood biomass (Bhaskar et al., 2008; Karagöz et al., 2005, 2006). Moreover, Andersen (1989, 1990) presented a process operating in water at temperatures in the range of 270–380 °C, pressures in the range of 15.2–27.4 MPa, in which an organic material is converted into small molecular units in the presence of the catalyst ZrO_2. In these patents, it was reported that ZrO_2 played an important role in char limitation, even though no detailed information regarding the mechanism was given. Watanabe et al. (2003) reported that ZrO_2 acts as a basic catalyst in supercritical water. Roberts et al. (2010a) showed that alkali catalysts, including K_2CO_3, affect the reaction pathways in the cleavage of aryl–alkyl bonds of benzyl phenyl ether, which was selected as a model compound for lignin depolymerisation. In another study related to lignin depolymerisation, Roberts et al. (2010b) proposed a synergic positive effect of ZrO_2 and K_2CO_3 in near and supercritical water in the cleavage of aryl-aryl ether bonds of diphenyl ether and in the suppression of side reactions. Moreover, good results in terms of bio-oil production have been obtained by using ZrO_2 and K_2CO_3 on biomasses different from lignin (Hammerschmidt et al., 2011; Toor et al., 2012) as well as on lignin (Nguyen et al., 2014). In the work of Nguyen et al. (2014) in particular, the feasibility of the continuous conversion of Kraft Lignin into bio-oil and phenolic chemicals was demonstrated in a small pilot unit, where the reaction in NCW was carried out at 25 MPa and 350 °C, using ZrO_2 and K_2CO_3 as the catalytic system and phenol as the co-solvent. The influence of the concentration of K_2CO_3 was studied; the yields of 1-ring aromatic compounds that increased from 17% to 27% as the mass fraction of K_2CO_3 was increased from 0.4% to 2.2%, together with a relatively low amount of char (about 20%) were obtained. Among the other process parameters that play a key role, the reaction temperature is surely one of the most important, due to its effect on the reaction kinetics, chemical equilibrium and properties of NCW. For instance, a large variation in the yields of different product fractions in the lignin conversion in NCW was observed by several investigators (Beauchet et al., 2012; Lavoie et al., 2011; Pińkowska et al., 2012; Yong and Matsumura, 2013).

In the present study, the conversion of LignoBoost Kraft lignin in NCW was carried out at reaction temperatures varying from 290 to 370 °C, while all the other parameters were kept at the same values used previously (Nguyen et al., 2014).

2. Methods

2.1. Materials

The Kraft lignin used in this work came from softwood and was produced in the LignoBoost demonstration plant in Bäckhammar, Sweden. The characterisation methods and analytical results related to this lignin are reported in the previous work of Nguyen et al. (2014). In summary, its moisture content was 32.6% and the carbon, hydrogen, sulphur and ash contents were 65.6%, 5.7%, 1.85% and 0.8%, respectively. Oxygen comprised approximately 26% (calculated value), the Higher Heat Value (HHV) was 27.7 MJ/kg and the mass fraction of aromatic and aliphatic groups was 78% and 22%, respectively. The mass average molar-mass (Mw) of this lignin was 3900 g/mol, with a molar-mass dispersity of 5.6. The feed slurry, which was prepared prior to each experimental run, was composed of deionised (DI) water, lignin, potassium carbonate (K_2CO_3) and phenol. The mass fraction of the solutes was as follows: lignin 5.5% (dry basis), phenol 4.1% and K_2CO_3 1.6%. The resulting feed pH was 9.1. The zirconia (ZrO_2) pellets (length: 3 mm, diameter: 3 mm, BET surface area 48 m^2/g) used as the heterogeneous catalyst came from Harshaw Chemie BV. Further details regarding the preparation of the feed slurry, together with the specifications of the chemicals used in the analytical procedures, are reported in Nguyen et al. (2014). In addition to these chemicals, the analytical standards from Sigma–Aldrich were used in this work: anisole (⩾99.65%), phenol (⩾99.5%), *o*-cresol (⩾99%), *m*-cresol (99%), *p*-cresol (⩾99.0%), guaiacol (⩾98.0%), catechol (⩾99%), syringol (⩾98.5%), 4-methylguaiacol (⩾98%), hydrocoumarin (99%) and 4-hydroxybenzaldehyde (98%). All chemicals were used without further purification.

2.2. Apparatus and procedure

Fig. 1 is a schematic flow sheet of the conversion process used in this work. During the experimental runs, the feed slurry was pumped continuously at a flow rate of 1 kg/h from a 10 L stirred tank, which was kept at 40 °C. Prior to entering the reactor, the feed was preheated to 80 °C and then mixed with the recirculation stream of reaction products. A high-pressure high-temperature pump was used for recirculation. The recycle-to-feed ratio was set at approximately 10, with the exception of the run at the highest reaction temperature (i.e. 370 °C), where this value was set at 2, because operational problems prevented it from being kept at higher values. The mixture then passed through another heater that adjusted its temperature to the reaction temperature which, in this series of tests, was varied from 290 and 370 °C. The reaction pressure was fixed at 25 MPa in all runs. The reaction mixture was in contact with the solid catalyst while flowing upwards in the 500 cm^3 fixed-bed reactor that was equipped with an electrically heated jacket. The free volume of the reactor charged with the catalysts was 294 cm^3, which gave a reaction residence time (τ) in the range of 10–13 min, depending on the temperature of the reactor. The reaction products were cooled down and depressurised to ambient conditions through two pressure control valves installed in parallel.

The liquid products were collected continuously in sampling bottles, whilst gas production was not significant. The same behaviour was also observed in previous experimental runs carried out at 350 °C for various K_2CO_3 concentrations (Nguyen et al., 2014). In all of the runs it was observed that, after approximately 2 h from the start, the operating parameters of the plant, the pH of the aqueous phase and the visual appearance of the products in the sampling bottles were all steady. The plant was run for an additional time in the range of 2–3 h once the steady state was reached before shut-down operations began. The plant was cleaned, the reactor disassembled and the char deposited on the catalyst measured after the end of each experimental run.

Several liquid product samples were taken during the steady-state operation. These product samples consisted of two distinct liquid phases: aqueous and oil. They were separated by using a centrifugation operating at 492 rad/s for 3 h and at 25 °C. Centrifugation gave a fairly transparent aqueous phase and a heavier oil phase of high viscosity (lignin-oil). All of the aqueous samples were mixed into one single aqueous sample in order to obtain a larger single sample for the analytical procedures; the same was done with the oil samples. These samples thus represent the average values during the steady-state period. The high viscosity of the oil meant that it had to be dissolved in tetrahydrofuran (THF) to achieve complete recovery. THF was then evaporated in a rotary vacuum evaporator at temperatures never exceeding 35 °C. Details of the equipment, pH measurements and procedure for quantitating the char deposited on the catalyst are provided in the previous work of Nguyen et al. (2014).

2.3. Analytical methods

A block diagram showing the various steps of the analytical methods applied to the liquid products is shown in Fig. 2. For each experimental run, a sample of aqueous phase obtained after centrifugation was withdrawn and used for Total Carbon (TC) and Total Organic Carbon (TOC) analyses, which were carried out at Statens Provningsanstalt, Sveriges Tekniska Forskningsinstitut (SP, Borås, Sweden). Another sample was first subjected to acidification to a pH in the range of 1.5–2.0 and then to extraction with diethyl ether (DEE), using a solvent-to-feed ratio (S/F) equal to 1. The acidification led to further clarification of the aqueous phase but gave rise to small amounts of additional liquid phases: some heavier black drops at the bottom and a lighter yellowish phase at the top, both of which were separated from the aqueous phase. These additional phases were, however, not analysed because the amounts were very small at all reaction temperatures. The gas that was released from the solution during the acidification, on the other hand, was quantified gravimetrically. Its amount was found to be about the same as the amount of carbon dioxide expected to be formed from the carbonates added as K_2CO_3. An internal standard (IST) was added to the acidified aqueous phase, prior to the extraction with DEE. The DEE-extract was analysed using Gas Chromatography (GC, Agilent 7890A) coupled with Mass Spectrometry (MS, Agilent 5975C). The main compounds were identified through the NIST MS Search Program (version 2.0) operating on the NIST/EPA/NIH Mass Spectral Database 2011 (NIST 11) and confirmation using analytical standards was carried out in selected cases. In addition, the compounds identified were quantitated on the basis of the IST. Syringol was selected as the IST since it is not a unit present in softwood lignin; it is not produced in the reaction but is very similar to the reaction products.

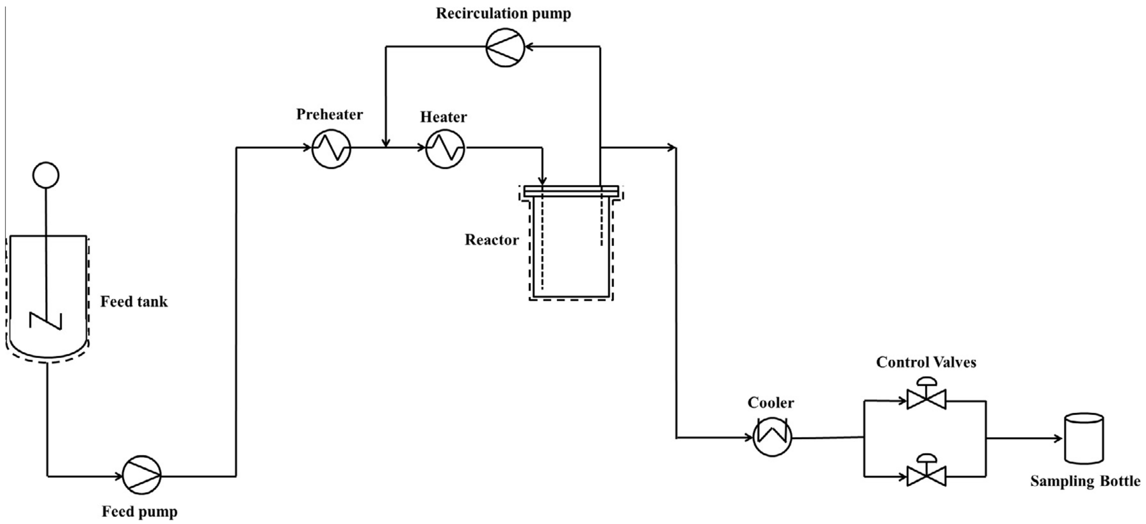

Fig. 1. Schematic flow sheet of the conversion process in near-critical water.

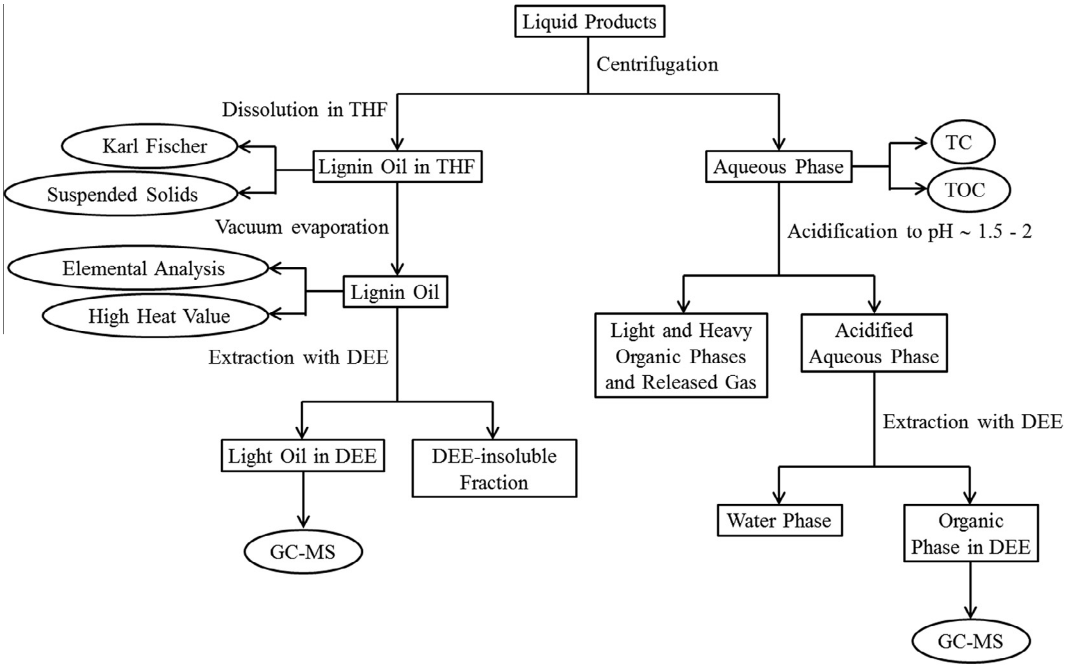

Fig. 2. Block diagram of the analytical methods used for the liquid products.

For each experimental run, a few samples of lignin-oil obtained after centrifugation were withdrawn prior to THF removal. These samples were subjected to Karl Fischer titration in order to determine their water content, and to a filtration process to determine the amount of THF-insoluble Suspended Solids (SS). The filtration was carried out in two steps, using Duran glass filters P2 (nominal maximum pore size 40–100 μm) in the first and P4 (nominal maximum pore size 10–16 μm) in the second. In this way, both the amount of solids retained and a rough indication of their size distribution could be determined. In addition, a sample of lignin-oil was withdrawn after the evaporation of THF and analysed at SP in order to determine the elemental composition and HHV. Furthermore, an additional sample of THF-free lignin-oil was withdrawn, extracted with DEE (S/F approximately 34/1) and mixed with a known amount of IST. The DEE-soluble fraction was analysed through GC–MS and the main compounds were identified and quantified. Further details on the analytical procedures can be found in Nguyen et al. (2014).

3. Results and discussion

The total carbon balance is calculated based on the results presented below, i.e. including phenol and inorganic carbon. In these calculations the carbon content of char is assumed to be the same as that of dry lignin. It is found that the sum of output and accumulated carbon accounts for between 97 and 103% of the carbon input. On the whole, these results show that a very reliable carbon balance was obtained in all runs.

3.1. The liquid products after centrifugation

After centrifugation, the liquid products were composed of two distinct phases: one aqueous and the other oil. The visual appearance of the former was dark yellowish and the latter black. The steady-state characteristics that refer to both phases are provided in Table 1, along with the TC and TOC of the aqueous phase.

As can be seen, the fraction of oil in the exit product stream decreases from 6.6% to 4.9% as the reaction temperature increases from 290 to 370 °C. Also, the reaction leads to a decrease in pH, from 9.1 (pH of the feed slurry) to values decreasing from 8.5 to 7.9 (pH of the aqueous phase after centrifugation), as the reaction temperature increases. The concentration of organic carbon in the aqueous phase is between 25 and 27 g/L. Since the density of the aqueous phase is approximately 1000 kg/m^3, this also means that the organic carbon mass fraction in the aqueous phase is in the range of 2.5–2.7%. The TC values are slightly higher than the TOC.

Table 1
Steady-state output data of the experimental runs at different reaction temperatures.

Steady-state output data	290 °C	310 °C	330 °C	350 °C	370 °C
Oil/total[a] (%)	6.6	6.0	5.8	5.3	4.9
pH$_a$[b]	8.5	8.2	8.2	8.0	7.9
TC[b] (g/L)	27	28	27	29	28
TOC[b] (g/L)	25	26	25	27	26

[a] Oil/total is the ratio of the output mass flow rate of oil and the sum of the output mass flow rate of oil and aqueous phase.

[b] pH$_a$, TC and TOC indicate pH, total carbon and total organic carbon in aqueous phase after centrifugation.

3.2. Aqueous phase

Table 2 reports the mass fraction of the compounds identified by GC–MS of the DEE-extract of the acidified aqueous phase, together with total values including, and excluding, phenol. Besides phenol, which is used in feed, the main compounds detected are alkylphenols (e.g. cresols), guaiacols (i.e. guaiacol and alkylguaiacols) and catechols (i.e. catechol and alkylcatechols). Other phenolic compounds detected are 3-methoxycatechol, salicylic acid, 4-hydroxybenzaldehyde, dimethylbenzenediol, vanillin, acetovanillone and three phenolic dimers with structure C6–C1–C6. Alkyl side groups of aromatic rings are of methyl or ethyl type only. Moreover, three non-phenolic aromatic compounds are found (i.e. anisole, 2-coumaranone and hydrocoumarin), together with small amounts of methanol, acetic acid, 2-butanone and propanoic acid. It was assumed that the phenolic compounds derived from the original lignin or from the reaction between phenol and lignin

Table 2
Mass fraction (%) of compounds identified by GC–MS in the acidified aqueous phase. LOD: limit of detection.

	Compound	290 °C	310 °C	330 °C	350 °C	370 °C
1	Methanol	0.002	0.003	0.003	0.004	0.003
2	Acetic acid	0.005	0.005	0.006	0.006	0.007
3	2-Butanone	0.004	0.007	0.006	0.004	0.006
4	Propanoic acid	0.002	0.002	0.002	0.002	0.003
5	Anisole	0.014	0.021	0.031	0.001	0.030
6	Phenol	1.806	1.714	1.639	1.964	1.702
7	*o*-Cresol	0.006	0.016	0.037	0.067	0.109
8	*m*/*p*-Cresol[a]	0.010	0.026	0.057	0.099	0.134
9	Guaiacol	0.123	0.104	0.068	0.054	0.022
10	2-Ethylphenol	0.002	0.004	0.007	0.010	0.013
11	Dimethylphenol	0.001	0.001	0.003	0.005	0.010
12	4-Ethylphenol	0.006	0.010	0.014	0.020	0.023
13	4-Methylguaiacol	0.002	0.003	0.003	0.003	0.001
14	Catechol	0.065	0.101	0.148	0.193	0.191
15	2-Coumaranone	0.004	0.003	0.002	<LOD	0.001
16	3-Methoxycatechol	0.003	0.002	0.002	0.006	0.001
17	3-Methylcatechol	0.001	0.002	0.006	0.013	0.019
18	4-Ethylguaiacol	0.001	0.001	0.001	<LOD	0.001
19	4-Methylcatechol	0.004	0.014	0.035	0.051	0.054
20	Salicylic acid	0.004	0.006	0.008	0.002	0.004
21	Syringol[b]	–	–	–	–	–
22	4-Hydroxybenzaldehyde	0.003	0.002	0.002	0.001	0.002
23	Hydrocoumarin	0.001	0.001	0.001	0.003	0.002
24	4-Ethylcatechol	0.002	0.005	0.011	0.016	0.014
25	Vanillin	0.004	0.002	0.001	<LOD	<LOD
26	Dimethylbenzenediol	<LOD	0.001	0.002	0.002	0.002
27	Acetovanillone	0.002	0.001	0.001	<LOD	<LOD
28–30	Phenolic dimers (C6–C1–C6)	0.016	0.015	0.007	0.006	0.001
Total mass fraction including phenol		2.093	2.072	2.103	2.532	2.355
Total mass fraction excluding phenol		0.287	0.358	0.464	0.568	0.653

[a] *p*-Cresol and *m*-Cresol elute together.
[b] Internal standard.

decomposition products (Okuda et al., 2004). Also, we have previously demonstrated that they derive from the chemical conversion of lignin in near-critical water (350 °C, 25 MPa) using the same catalytic system (ZrO_2/K_2CO_3) and in the presence of phenol as co-solvent (Nguyen et al., 2014).

Regarding the variation in composition resulting from the reaction temperature, the mass fractions of catechols and alkylphenols increase as the reaction temperature increases, whereas those of guaiacols and phenolic dimers decrease (see Table 3). The mass fractions of vanillin and acetovanillone also decrease with increasing reaction temperature even though the amounts detected are small; these two compounds are not detected in the two runs at the higher temperatures (i.e. 350 and 370 °C) (see Table 2). In the range of temperature under investigation, the same qualitative trends regarding guaiacol and catechol are reported in the literature that refer to different types of lignin and different conversion processes in NCW (Lavoie et al., 2011; Beauchet et al., 2012; Pińkowska et al., 2012). In summary, the total mass fraction of water-soluble organic compounds (excluding phenol) in the aqueous phase clearly increases as the reaction temperature increases (see Table 2).

3.3. Lignin-oil

The oil phase in the products decreases from 6.6% to 4.9% (with respect to the total liquid output) as the reaction temperature increases from 290 to 370 °C (see Table 1). The oil was separated from the aqueous phase by means of centrifugation and its water content was measured; it was also measured after THF was removed by means of vacuum evaporation at a temperature not exceeding 35 °C. As shown in Table 4, a relatively large reduction in the water content in each run (from 49% to 88%) was achieved by removing the solvent.

Table 3
Mass fractions (%) of the main classes of compounds of the acidified aqueous phase and the DEE-soluble fraction of the lignin-oil. Data referring the oil are reported on a dry lignin-oil basis (i.e. THF-free and water-free basis).

	Class	290 °C	310 °C	330 °C	350 °C	370 °C
Aqueous phase	Phenol	1.81	1.71	1.64	1.96	1.70
	Alkylphenols	0.03	0.06	0.12	0.20	0.29
	Guaiacols	0.13	0.11	0.07	0.06	0.02
	Catechols	0.07	0.12	0.20	0.27	0.28
	Phenolic dimers	0.02	0.02	0.01	0.01	0.00
Lignin-oil	Anisoles	2.04	3.09	4.72	5.33	6.17
	Phenol	11.51	9.77	12.44	12.80	11.35
	Alkylphenols	0.95	1.61	3.60	5.83	7.75
	Guaiacols	2.55	2.26	2.16	2.00	1.02
	Catechols	0.14	0.25	0.19	0.42	0.62
	Phenolic dimers	5.08	4.08	2.27	1.84	1.03

Table 4
Water content and THF-insoluble suspended solids in the lignin-oil. The water mass fraction (%) in the lignin-oil is given before and after vacuum evaporation to remove THF. The suspended solids, retained on filters P2 and P4, are given as mass fraction (%) on a dry lignin-oil basis.

	290 °C	310 °C	330 °C	350 °C	370 °C
Water content before evaporation	19.2	10.9	15.2	14.1	13.3
Water content after evaporation	9.8	1.3	2.4	2.0	2.1
Suspended solids on P2	21.2	14.0	0.3	0.6	1.9
Suspended solids on P4	2.6	11.4	8.3	22.2	11.3
Total suspended solids	23.8	25.4	8.6	22.8	13.2

Table 5
Elemental composition (as mass fraction) and HHV of the lignin-oil obtained from the conversion of LignoBoost Kraft lignin in near-critical water. Data are reported on water-free oil; oxygen is calculated by difference.

Elemental composition (%)	290 °C	310 °C	330 °C	350 °C	370 °C
C	70.0	72.6	73.9	74.9	76.0
H	6.5	6.4	6.1	6.6	6.8
N	–	<0.1	<0.1	<0.1	<0.1
S	0.41	0.51	0.56	0.38	0.25
Cl	<0.01	<0.01	<0.01	<0.01	<0.01
Ash	2.4	2.0	2.4	2.8	1.8
O	21	18	17	15	15
Na	0.0110	0.0070	0.0100	0.0100	0.0057
K	1.5	1.4	1.7	1.6	1.4
HHV (MJ/kg)	31.66	31.12	31.03	31.90	32.73

Table 4 also reports the THF-insoluble SS in the lignin-oil. The SS values referring to the mass of the retained solids on the filters P2 and P4 are reported as mass fraction on a dry lignin-oil basis (i.e. THF-free and water-free basis). The total mass of the retained solids (P2 and P4) is also given. Although there is no clear trend of the total amount of SS, the data clearly show that, whereas the fraction of SS with larger size (i.e. retained on filter P2) is high at the lower temperatures (290 and 310 °C), it is quite low from 330 °C upwards. However, fine particles predominate above 330 °C. A minimum value of SS was obtained at 330 °C (8.6%), the reason for which is not known.

Following evaporation an elemental analysis was made on each oil sample, and the ash content and heat value were measured. These results are reported on a dry lignin-oil basis in Table 5. The oil obviously has a higher content of carbon compared to dry lignin and has been partially deoxygenated; its carbon content also increases with the reaction temperature. On average, the heat value of the dry lignin-oil is 14% higher than that of dry lignin. Also, the sulphur content is reduced, on average, from 1.85% to 0.42%.

Table 6 reports the mass fractions of compounds in the DEE-soluble fraction of lignin-oil samples as well as the total values including, and excluding, phenol. The DEE-soluble fraction of lignin-oil that is identified by GC–MS is in the range of 21–29% of the total oil, and contains a large amount of 1-ring aromatic compounds. As reaction temperature increases from 290 to 370 °C, phenol increases from 10% to 13% (on dry lignin-oil basis), anisoles increase from 2% to 6%, alkylphenols increase from 1% to 8%, catechols increase from 0.1% to 0.6% but guaiacols, on the other hand,

Table 6
Mass fraction (%) of compounds identified by GC–MS in the DEE-soluble fraction of the lignin-oil. Data based on dry lignin-oil are reported. LOD: limit of detection.

	Compound	290 °C	310 °C	330 °C	350 °C	370 °C
1	Anisole	1.964	2.897	4.173	4.414	4.966
2	Phenol	11.505	9.772	12.436	12.797	11.351
3	2-Methylanisole	0.011	0.032	0.098	0.173	0.273
4	4-Methylanisole	0.023	0.074	0.242	0.409	0.570
5	*o*-Cresol	0.101	0.222	0.662	1.158	1.823
6	*p*/*m*-Cresol[a]	0.187	0.413	1.167	1.923	2.533
7	2-Ethylanisole	0.007	0.018	0.047	0.094	0.128
8	Guaiacol	2.226	1.820	1.586	1.344	0.611
9	4-Ethylanisole	0.031	0.066	0.156	0.238	0.232
10	2-Ethylphenol	0.100	0.163	0.321	0.511	0.637
11	Dimethylphenol	0.137	0.165	0.253	0.402	0.605
12	2-Acetylphenol	0.080	0.093	0.104	0.156	0.114
13	4-Ethylphenol	0.315	0.473	0.848	1.200	1.278
14	5-Methylguaiacol	0.018	0.047	0.105	0.146	0.103
15	4-Methylguaiacol	0.118	0.167	0.230	0.253	0.145
16	Catechol	0.096	0.115	0.097	0.181	0.212
17	2-Propylphenol	0.014	0.024	0.049	0.088	0.126
18–19	Ethylcresols	0.022	0.045	0.119	0.259	0.409
20	4-Propylphenol	0.077	0.109	0.181	0.288	0.341
21	4-Ethylguaiacol	0.155	0.180	0.193	0.204	0.120
22	4-Methylcatechol	0.017	0.059	0.039	0.122	0.219
23	Syringol[b]	–	–	–	–	–
24	4-Propylguaiacol	0.031	0.041	0.048	0.050	0.038
25	4-Ethylcatechol	0.026	0.078	0.051	0.113	0.191
26	9H-Xanthene	0.129	0.195	0.103	0.100	0.346
27–28, 31	Phenolic dimers (C6–C1–C6)	3.973	3.254	1.760	1.357	0.665
29–30, 32–33	Phenolic dimers (C6–C2–C6)	1.104	0.822	0.513	0.485	0.366
34	Isopropyl-methyl-phenanthrene	0.073	0.127	0.182	0.242	0.264
Total mass fraction including phenol		22.54	21.47	25.76	28.71	28.67
Total mass fraction excluding phenol		11.04	11.70	13.33	15.91	17.32

[a] *p*-Cresol and *m*-Cresol elute together.

[b] Internal standard.

decrease from 3% to 1%. A large amount of phenolic dimers are also found (decreasing from 5% to 1%) with a C6–C1–C6 or C6–C2–C6 structure. Most of the compounds in the DEE-soluble fraction of lignin-oil are the same as in the aqueous phase, but the relative concentration differs depending on their hydrophilic or hydrophobic nature. Catechol, for example, is relatively more abundant in the aqueous phase, whereas anisole is relatively more abundant in the oil. In addition, some compounds not found in the aqueous phase are identified in the DEE-soluble fraction of lignin-oil, as in the case of alkylanisoles, 1-ring aromatic compounds with propyl side groups, ethylcresols, acetylphenol, and two 3-ring compounds. The total mass fraction of DEE-soluble compounds in lignin-oil increases as the reaction temperature increases; with regard to specific classes of compounds, the amount of anisoles, alkylphenols, and catechols increases whilst that of guaiacols decreases (see Table 3). These trends are also found for the water-soluble compounds in the aqueous phase.

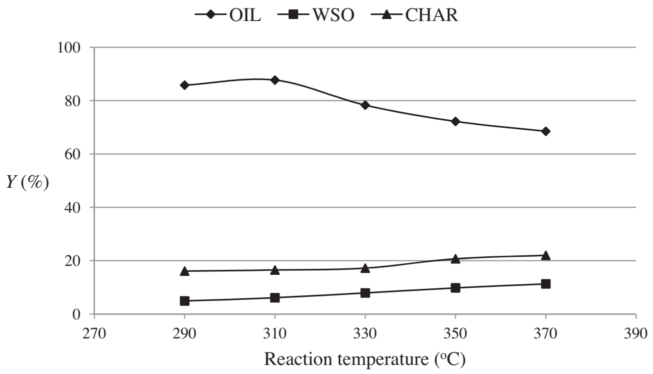

Fig. 3. Yields (*Y*) of oil (OIL), water-soluble organics in the acidified aqueous phase (WSO) and char (CHAR) as a function of the reaction temperature. Yields are defined on phenol-free dry reaction products on a dry lignin basis.

3.4. Product yields and carbon balances

Product yields are calculated taking three different products into consideration: dry lignin-oil (*OIL*), water-soluble organics in the acidified aqueous phase (*WSO*) and char (*CHAR*). The corresponding yields (*Y*) are defined here as the mass of phenol-free products relative to the mass of dry lignin fed to the system (see Fig. 3). The calculations are made assuming that the average rate of char formation during the entire run (i.e. start-up, steady-state and cooling down) is equal to the rate of formation at steady-state. The yield of the main classes of 1-ring aromatic compounds is also calculated, taking into account the quantities found in both the aqueous and the oil phase (see Fig. 4).

As can be seen in Fig. 3, the yield of dry lignin-oil is around 85–88% at the two lower reaction temperatures (290 and 310 °C), but decreases down to 69% as the reaction temperature increases (up to 370 °C). On the other hand, both the char and the water-soluble organics increase with an increase in reaction temperature. More specifically, Y_{CHAR} increases from 16% to 22% and Y_{WSO} increases from 5% to 11% as the reaction temperature increases from 290 to 370 °C.

Besides analysing the yields of the different product fractions, it is also interesting to examine the overall yield (aqueous phase and lignin-oil) of specific classes of 1-ring aromatic compounds and phenolic dimers (see Fig. 4a). The overall yield increases remarkably as the reaction temperature increases (290–370 °C), varying from 10% to 23%. In particular, a larger relative increase is found for alkylphenols (from 14 to 110 g/kg); anisoles and catechols increase moderately, whilst the maximum yield of guaiacols is

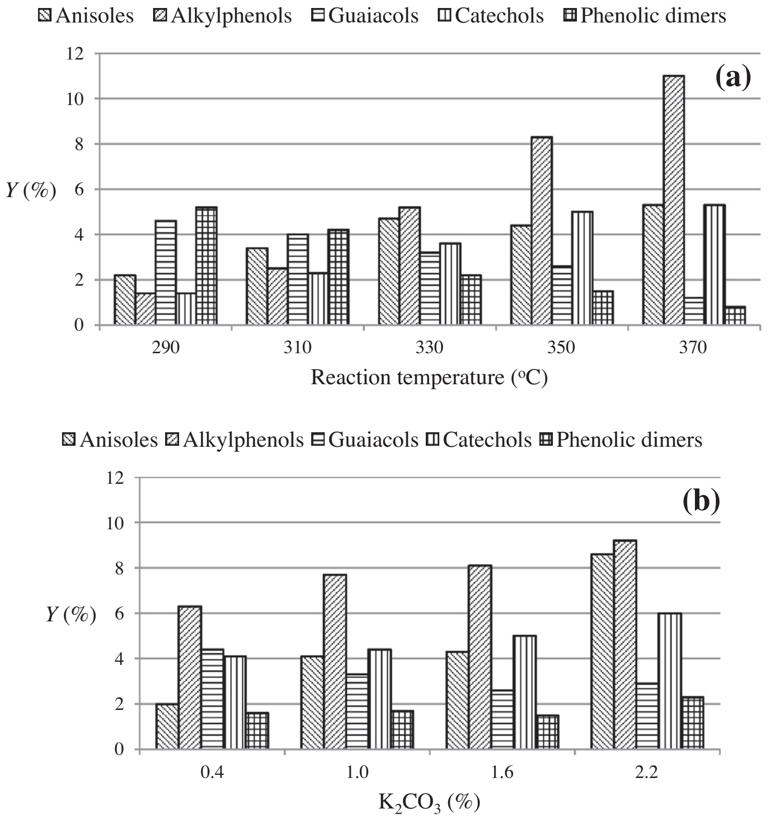

Fig. 4. Yields (*Y*) of different classes of aromatic compounds (in water-soluble organics and DEE-soluble lignin-oil) as a function of (a) the reaction temperature (at K_2CO_3 mass fraction of 1.6% and (b) K_2CO_3 mass fraction (at the reaction temperature of 350 °C). Yields are on a dry lignin basis.

found at the lowest reaction temperature (290 °C). The comparison with the yields obtained when varying the mass fraction of K_2CO_3 (Nguyen et al., 2014), reported in Fig. 4b, shows some interesting features. The increase of the K_2CO_3 mass fraction and the reaction temperature have the same effect on the yields of all the product fractions (i.e. the amount of anisoles, alkylphenols and catechols increases but that of guaiacols decreases), with the exception of the phenolic dimers. More specifically, the yield of the phenolic dimers increases with the K_2CO_3 mass fraction (see Fig. 4b), whereas it decreases with increasing the reaction temperature. In addition, it is observed that the reaction temperature has a relatively large effect on alkylphenols, whereas K_2CO_3 has a relatively large effect on anisoles.

Approximate mass balances of phenol were also carried out in order to provide an insight of the role of phenol in the reaction. The output flow rate of phenol was estimated taking into account the amount of phenol in the DEE-extracts of the acidified aqueous phase and the amount of phenol in the DEE-soluble fraction of the oil. Considering both the experimental runs of this work and those previously published (Nguyen et al., 2014), it was found that the phenol consumption is in the range of 35–49% of the phenol input. These values may represent an overestimation of the real phenol consumption, since there could be some phenol in the residual fractions not extracted with DEE. However, these values support the hypothesis that part of the phenol fed to the reactor reacts with the active fragments deriving from lignin.

The elemental analysis of the oil samples was used to calculate the ratio of potassium ending up in the wet oil to potassium that enters the system. It was found that this value is in the range of 6.5–9.2%, with no clear trend with respect to the reaction temperature. This range coincides approximately to that found when the reactor was operated at 350 °C, varying the mass fraction of K_2CO_3 (Nguyen et al., 2014). On the whole, in the ranges of the operating variables that were tested, the amount of potassium in the oil is quite constant at values in the range of approximately 7% to 9%.

4. Conclusions

The products obtained from the conversion of LignoBoost Kraft lignin in NCW consist of water-soluble organics (WSO), lignin-oil and char. As the reaction temperature increases (290–370 °C), the yield of WSO increases (5–11%), lignin-oil decreases (87–69%) and char increases (16–22%). The lignin-oil, being partially deoxygenated, has higher carbon content and HHV; and lower sulphur content than lignin. The main 1-ring aromatics (in WSO and DEE-soluble lignin-oil) are anisoles, alkylphenols, guaiacols and catechols. The yield of 1-ring aromatics increases remarkably with an increase in temperature. In addition, the yield of alkylphenols is very sensitive to the temperature.

Acknowledgements

We are grateful to Chalmers Energy Initiative – LignoFuel Project, Valmet Power AB, The Swedish Energy Agency and the research foundation Ångpanneförenings Forskningsstiftelse for their financial support.

Our thanks go to Bengt Erichsen, Carina Olsson, Lena Elisabeth Fogelquist and Tommy Friberg for their technical assistance.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.biortech.2014.06.051.

References

Andersen, K., 1989. Gasification process. DE 3806732 A1.
Andersen, K., 1990. Gasification process. EP 0402405 B1.
Azadi, P., Inderwildi, O.R., Farnood, R., King, D.A., 2013. Liquid fuels, hydrogen and chemicals from lignin: a critical review. Renew. Sustain. Energy Rev. 21, 506–523.
Bhaskar, T., Sera, A., Muto, A., Sakata, Y., 2008. Hydrothermal upgrading of wood biomass: influence of the addition of K_2CO_3 and cellulose/lignin ratio. Fuel 87, 2236–2242.
Beauchet, R., Monteil-Rivera, F., Lavoie, J.-M., 2012. Conversion of lignin to aromatic-based chemicals (L-chems) and biofuels (L-fuels). Bioresour. Technol. 121, 328–334.
Brännvall, E., 2009. Overview of pulp and paper processes. In: Ek, M., Gellerstedt, G., Henriksson, G. (Eds.), Pulp and Paper Chemistry and Technology, vol. 2, Pulping Chemistry and Technology. Walter de Gruyter, Berlin, Germany.
Brunner, G., 2009. Near critical and supercritical water. Part I. Hydrolytic and hydrothermal processes. J. Supercrit. Fluids 47, 373–381.
Carr, A.G., Mammucari, R., Foster, N.R., 2011. A review of subcritical water as a solvent and its utilisation for the processing of hydrophobic organic compounds. Chem. Eng. J. 172, 1–17.
Eckert, C.A., Chandler, K., 1998. Tuning fluid solvents for chemical reactions. J. Supercrit. Fluids 13, 187–195.
Fang, Z., Sato, T., Smith Jr., R.L., Inomata, H., Arai, K., Kozinski, J.A., 2008. Reaction chemistry and phase behavior of lignin in high-temperature and supercritical water. Bioresour. Technol. 99, 3424–3430.
Fengel, D., Wegener, G., 1989. Wood: Chemistry, Ultrastructure, Reactions. Walter de Gruyter, Berlin, New York.
Gellerstedt, G., 2009. The worldwide wood resource. In: Ek, M., Gellerstedt, G., Henriksson, G. (Eds.), Pulp and Paper Chemistry and Technology, vol. 1, Wood Chemistry and Wood Biotechnology. Walter de Gruyter, Berlin, Germany.
Hammerschmidt, A., Boukis, N., Hauer, E., Galla, U., Dinjus, E., Hitzmann, B., Larsen, T., Nygaard, S.D., 2011. Catalytic conversion of waste biomass by hydrothermal treatment. Fuel 90, 555–562.
Henriksson, G., 2009. Lignin. In: Ek, M., Gellerstedt, G., Henriksson, G. (Eds.), Pulp and Paper Chemistry and Technology, vol. 1, Wood Chemistry and Wood Biotechnology. Walter de Gruyter, Berlin, Germany.
Karagöz, S., Bhaskar, T., Muto, A., Sakata, Y., Oshiki, T., Kishimoto, T., 2005. Low-temperature catalytic hydrothermal treatment of wood biomass: analysis of liquid products. Chem. Eng. J. 108, 127–137.
Karagöz, S., Bhaskar, T., Muto, A., Sakata, Y., 2006. Hydrothermal upgrading of biomass: effect of K_2CO_3 concentration and biomass/water ratio on products distribution. Bioresour. Technol. 97, 90–98.
Lora, J., 2008. Industrial commercial lignins: sources, properties and applications. In: Belgacem, M.N., Gandini, A. (Eds.), Monomers, Polymers and Composites from Renewable Resources. Elsevier, Great Britain.
Lavoie, J.-M., Baré, W., Bilodeau, M., 2011. Depolymerization of steam-treated lignin for the production of green chemicals. Bioresour. Technol. 102, 4917–4920.
Nguyen, T.D.H., Maschietti, M., Belkheiri, T., Åmand, L.-E., Theliander, H., Vamling, L., Olausson, L., Andersson, S.-I., 2014. Catalytic depolymerisation and conversion of Kraft lignin into liquid products using near-critical water. J. Supercrit. Fluids 86, 67–75.
Okuda, K., Umetsu, M., Takami, S., Adschiri, T., 2004. Disassembly of lignin and chemical recovery-rapid depolymerization of lignin without char formation in water–phenol mixtures. Fuel Process. Technol. 85, 803–813.
Pandey, M.P., Kim, C.S., 2011. Lignin depolymerisation and conversion: a review of thermochemical methods. Chem. Eng. Technol. 34, 29–41.
Pińkowska, H., Wolak, P., Złocińska, A., 2012. Hydrothermal decomposition of alkali lignin in sub- and supercritical water. Chem. Eng. J. 187, 410–414.
Roberts, V., Fendt, S., Lemonidou, A.A., Li, X., Lercher, J.A., 2010a. Influence of alkali carbonates on benzyl phenyl ether cleavage pathways in superheated water. Appl. Catal. B 95, 71–77.
Roberts, V.M., Knapp, R.T., Li, X., Lercher, J.A., 2010b. Selective hydrolysis of diphenyl ether in supercritical water catalyzed by alkaline carbonates. ChemCatChem 2, 1407–1410.
Singhvi, M.S., Chaudhari, S., Gokhale, D.V., 2014. Lignocellulose processing: a current challenge. RSC Adv. 4, 7271–8277.
Theliander, H., 2008. Withdrawing lignin from black liquor by precipitation, filtration and washing. In: 1st Nordic Wood Biorefinery Conference, pp. 36–42.
Tomani, P., 2010. The LignoBoost process. Cell. Chem. Technol. 44, 53–58.
Toor, S.S., Rosendahl, L., Nielsen, M.P., Glasius, M., Rudolf, A., Iversen, S.B., 2012. Continuous production of bio-oil by catalytic liquefaction from wet distiller's grain with solubles (WDGS) from bio-ethanol production. Biomass Bioenergy 36, 327–332.
Vigneault, A., Johnson, D.K., Chornet, E., 2007. Base-catalyzed depolymerization of lignin: separation of monomers. Can. J. Chem. Eng. 85, 906–916.
Watanabe, M., Osada, M., Inomata, H., Arai, K., Kruse, A., 2003. Acidity and basicity of metal oxide catalysts for formaldehyde reaction in supercritical water at 673 K. Appl. Catal. A Gen. 245, 333–341.
Yong, T.L.-K., Matsumura, Y., 2013. Kinetic analysis of lignin hydrothermal conversion in sub- and supercritical water. Ind. Eng. Chem. Res. 52, 5626–5639.