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Hydrothermal Liquefaction of Softwood: Selective Chemical Production Under Oxidative Conditions

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ABSTRACT

This work was conducted to determine the effect of oxygen on hydrothermal liquefaction of softwood for the production of valuable chemicals. Softwood was subjected to liquefaction in the presence and absence of either 1.6 g/L sodium carbonate or 5 bar oxygen gas. The oxygen supplementation diverted sugars from dehydration towards oxidation resulting in fourfold elevated yields of organic acids. Dissolved sugars and furans showed maxima in narrow temperature regions of 170–190 °C and 210–230 °C while the yields (weight percentage based on dry wood) of organic acids, phenolic substances, and bio-oil reached their respective maxima of 10.4%, 3.5% and 7.4% at 230–270 °C. These results of oxidative hydrothermal liquefaction advance sustainable production of chemicals from renewable lignocellulose.

KEYWORDS: Lignocellulose, oxidation, aqueous, renewable, treatment, sustainable

INTRODUCTION

Co-streams from industrial processing of wood must be better utilized to replace fossil resources in the large-scale production of energy and commodity chemicals. Torrefaction, gasification, and carbonization in aqueous-phase have been studied in recent years as sustainable biomass conversion processes.¹⁻³ Hydrothermal liquefaction (HTL) likewise avoids the energy-intensive drying of moist feedstock and instead of removing water uses it as a reactive solvent. HTL hydrolyses wood first into soluble products that undergo further condensation, cyclization, and polymerization reactions forming organic solvent soluble bio-oil.⁴

Alkaline catalysts have been shown to enhance the performance of HTL, as bio-oil yields of 17–52% (based on wood dry weight) have been roughly twofold higher than those obtained without catalyst at 280–300 °C.⁵⁻⁷ The amounts of alkaline chemicals in these studies were up to 41% of wood dry weight, but according to the green chemistry principles minimum chemical usage and environmentally friendly solvents should be pursued in industrial processes. Besides chemical catalysts, reductive gases such as hydrogen or carbon monoxide give higher yields of bio-oil.⁴ However, low-value side products carbon dioxide and water are generated under reductive conditions.

The production of bio-oil has been pursued to substitute fossil fuel,⁸ but many alternative uses exist for the intermediate products that could be produced at lower temperatures. Lignin-derived phenolics can be converted to aromatic chemicals by hydrogenation,⁹ sugars

may serve as carbon source for fermentation or catalytic production of hydrogen,^{10,11} and short-chain carboxylic acids may be isolated as valuable products.¹² Moreover, in contrast to alkaline reductive conditions, HTL in the presence of oxygen can be beneficial for the production of intermediate products since hydrothermal treatment releases more liquid products than pyrolysis does.¹³ It is also known that alkaline oxidative treatments are effective in depolymerization of pulping black liquors in the partial wet oxidation process.¹⁴

Previous oxidative hydrothermal treatments have used either hydrogen peroxide or Fenton's reagent as the oxidant, and aimed at rendering the solid fraction accessible for enzymatic hydrolysis,¹⁵ oxidizing isolated lignin,¹⁶ or limited to only following the decomposition of organic matter.¹⁷ To our best knowledge, the use of molecular oxygen in HTL was proposed for the first time in a recent conference paper.¹⁸ In the present study we extend that investigation with a goal to determine the effect of oxygen on the production of various intermediate products from HTL of softwood under mild conditions. Identification of the products and their generation sequence will shed light on the oxidative liquefaction process and its industrial implementation.

EXPERIMENTAL SECTION

Materials

The raw material used in this work was pine wood processing waste with fine particle size. The moisture content of this softwood feedstock was 55.4% by weight, and the dry matter comprised $28.2\% \pm 0.1\%$ of lignin and $70.6\% \pm 2.6\%$ of polysaccharides that consisted of

64.8% glucose, 24.5% mannose and arabinose, 6.6% xylose, and 4.1% galactose. The elemental composition of the feedstock is comparable to that of Finnish pine wood sawdust containing 51.0% C, 5.99% H, 0.08% N, 42.8% O, and 0.08% ash.¹⁹

Hydrothermal treatments in the pressure reactor

HTL reactions were performed by heating softwood (14 g) with deionized water (62.5 g) in an autoclave reactor to a pre-defined maximum temperature of 130–270 °C and after 30 min isothermal stage cooling rapidly to room temperature. The isothermal residence time in the batch reactor was chosen based on published data.¹⁷ The average heating rates to reach the isothermal stage were 5.6, 5.2, and 4.6 °C/min at corresponding temperatures of 130, 200, and 270 °C. Examples of the heating and cooling curves of the pressure reactor are shown in Fig. S3 in the SI. In the case of oxidative treatments, oxygen was supplied into the reactor 5 °C before reaching the set temperature. The reactor configuration was the same as previously described.¹⁴ A total of 28 HTL treatments in the presence or absence of 5 bar partial pressure of oxygen (AGA, Finland 99.99% purity) and 1.6 g/L of sodium carbonate (Merck, 99% purity) were conducted (Table 1). Following the treatment, the solid and liquid phases were separated by filtration, and the solid fraction washed with 10 mL of water. The liquid fractions were combined and subjected to a series of analyses. The solid fraction was dried in a convection oven at 105 °C to constant weight, and the dissolved amount of wood was determined from the mass balance.

Table 1: Operating conditions in HTL of softwood at a liquid to solid ratio of 11. Isothermal heating for 30 min at various temperatures was conducted in the presence or absence of sodium carbonate or molecular oxygen.

Entry no:	Temperature (°C)	Sodium carbonate (g/100 g dry wood)	p O ₂ (bar)
1	130	-	-
2	150	-	-
3	170	-	-
4	190	-	-
5	210	-	-
6	230	-	-
7	250	-	-
8	270	-	-
9	130	-	5
10	150	-	5
11	170	-	5
12	190	-	5
13	210	-	5
14	230	-	5
15	250	-	5
16	270	-	5
17	130	1.8	-
18	150	1.8	-
19	170	1.8	-
20	190	1.8	-
21	210	1.8	-
22	230	1.8	-
23	130	1.8	5
24	150	1.8	5
25	170	1.8	5
26	190	1.7	5
27	210	1.8	5
28	230	2.2	5

Analytical procedures

The composition of the starting material was determined following the two-stage sulfuric acid hydrolysis procedure.²⁰ The softwood was first milled to pass a 0.2 mm sieve, and 300 mg of the powder was hydrolyzed with 3 mL of 72 w-% sulfuric acid at 30 °C for one hour. For the second hydrolysis stage, the sulfuric acid concentration was diluted to 4 w-% with deionized water, and the capped glass bottles cooked for one hour in an autoclave at 121 °C. After cooling to room temperature, the acid-insoluble lignin was separated from the hydrolysate by filtration on a Whatman GF/F glass fibre membrane, washed with deionized water, and dried at 105 °C to constant weight. Acid-soluble lignin was determined from the hydrolysate by measuring the absorbance at 205 nm ($\epsilon=210$ L/g/cm). An aliquot of the hydrolysate was neutralized with calcium carbonate and analyzed for monosaccharides with high-performance liquid chromatography (HPLC). The system comprised a Micro-Guard De-Ash pre-column (Bio-Rad, USA) and an SPO810 column (Shodex) coupled to a refractive index detector (Shimadzu). Deionized water delivered at a flow rate of 0.7 mL/min was used to elute the column at 60 °C. Monosaccharides were identified and quantified based on their retention times and peak areas relative to external standard calibration constructed for D-xylose, D-glucose, D-galactose, L-arabinose, and D-mannose. Sugar recovery standards subjected to the acid hydrolysis were used to correct for sugar degradation. The composition analysis was carried out in duplicate.

The combined liquid fraction from HTL was analyzed for total organic carbon (TOC), chemical oxygen demand (COD), pH, and organic acids as previously described.¹⁴ Soluble

sugars were analyzed with HPLC after dilute acid hydrolysis.²¹ The concentration of furfural, 5-hydroxymethyl furfural (HMF), and ethyl acetate soluble material was determined by extraction of 1 mL of the liquid fraction three times with 3 mL of ethyl acetate in screw-cork glass tubes at room temperature. The combined organic fraction was sampled for HPLC analysis. The remaining extract was evaporated to dryness in a convection oven at 50 °C for the gravimetric determination of ethyl acetate soluble material. Furfural, HMF, and phenolic substances were analyzed using the previously described HPLC system (Sipponen et al., 2014). The mobile phase comprised of (A) water:formic acid (99.9:0.1 v/v) and (B) acetonitrile:formic acid (99.9:0.1 v/v) delivered at a flow rate of 0.5 mL/min. The gradient elution program started with 15 min isocratic step at 91% A, followed by a linear reduction of A to 83% at 28 min and further to 20% at 45 min. The column temperature was 50 °C, and UV detection at 280 nm was used to quantify the compounds against external standard calibration. Water-soluble phenolic compounds were additionally determined relative to guaiacol standards from duplicate samples according to the colorimetric Folin-Ciocalteu assay.²²

RESULTS AND DISCUSSION

Softwood was subjected to liquefaction at various temperatures from 130 to 270 °C either in water suspension only, or with sodium carbonate to alter the prevailing pH during the treatment. These two type of treatments were additionally carried out under 5 bar oxygen pressure. The liquid fractions were collected and analyzed to elucidate the effect of oxygen

as well as alternating processing conditions on the production of soluble chemicals from wood.

Effect of oxygen and temperature on liquefaction of wood

The extent of dissolution increased with increasing temperature, reaching 62% of wood dry material after the treatment at 270 °C (Fig. 1a). These dissolution values were based on the recovery of the solid fraction and are only slightly higher compared to 56–58% conversions previously reported in HTL of pine and cypress wood at 280 °C.^{5,23} Generally, either acidic or alkaline conditions are required to achieve marked dissolution of wood in water under subcritical conditions. Compared to the other treatments, less wood dissolved when sodium carbonate and molecular oxygen were used in combination especially at temperatures below 200 °C (Fig. 1a). The underlying reason, in this case, might be linked to pH since the presence of oxygen caused acidification which helped to neutralize the alkalinity of sodium carbonate (Fig. 1b). The initial stages of liquefaction can be seen from the total organic carbon (TOC) and chemical oxygen demand (COD) concentrations which increased when the treatment temperature was raised (Fig. 1c–d). The incorporation of oxygen into the autocatalytic and sodium carbonate treatments gave a marked 2–4 -fold increase in the TOC and COD concentrations. Distinct maxima were observed at 190 °C for the TOC and COD of the oxidative autocatalytic treatment. Thereafter decreasing TOC and COD could be explained by the release of carbon dioxide and partially oxidized soluble products with a lower degree of polymerization. Some support for this postulation came from the size exclusion chromatography which showed lower weight average molar mass from the

oxidative treatments until 190 °C (Fig. 2a). In order to elucidate the role of oxygen in the liquefaction process, the chemical compositions of the product liquors were determined more in detail.

Figure 1. HTL of wood: (a) dissolution of wood and (b) pH (c) total organic carbon (TOC) and (d) chemical oxygen demand (COD) of the liquid fractions obtained in autocatalytic and sodium carbonate containing (1.6 g/L) hydrothermal treatments as a function of temperature and in the presence or absence of 5 bar oxygen atmosphere.

Chemical production in oxidative liquefaction of wood

It is well known that the complex liquefaction reactions involve two main events: hydrolysis of wood polymers and further degradation and polymerization reactions. Hydrolysis of hemicellulose generates sugars and acetic acid, while an array of phenolic decomposition products arises from lignin. Secondary degradation reactions give potential intermediate products for further upgrading and isolation. Under the subcritical reaction conditions of the present work, these secondary reactions involve mainly dehydration, polymerization, and oxidation. The latter occurs through free radical mechanism forming organic ($R\cdot$) and hydroperoxyl ($ROO\cdot$) radicals, which then decompose into lighter carboxylic acids that undergo further rate-limiting oxidation into carbon dioxide.²⁴

Figure 2. Properties and yields (g from 100 g dry wood) of water-soluble products released in HTL of softwood: (a) weight average molar mass of the liquid fractions (b) water-soluble sugars (c) furans (furfural and HMF) (d) short chain organic acids (e) total phenolics (f) ethyl acetate-soluble material. Autocatalytic and sodium carbonate containing (1.6 g/L)

HTL was carried out as a function of temperature and in the presence or absence of 5 bar oxygen atmosphere. Markers are similar in all figures. Error bars in (b) and (e) indicate average deviation from the mean value of duplicate determinations.

Dissolution of wood carbohydrates

Hydrolytic cleavage and dissolution of hemicellulose occurred during the first stages of HTL at 130–190 °C. In addition to the abovementioned reduction in molar mass, this event caused accumulation of soluble sugars (Fig. 2b). HPLC analysis confirmed dissolution of galactoglucomannan and arabinoglucuronoxylan, which are known softwood hemicelluloses.²⁵ The total sugar yield from softwood was maximized at 170 °C with the autocatalytic treatment, but the maximum glucose yield was detected at higher temperatures between 190–230 °C (Fig. S1 in the SI). This observation suggests that hydrolytic dissolution of hemicellulose was predominant over that of cellulose at temperatures up to approximately 180 °C. Oxygen supplied into the reaction system appeared to attack cellulose, facilitating its dissolution at high severities when the treatment temperature exceeded 200 °C either in the autocatalytic treatment or the one with sodium carbonate (Fig. S1 in the SI). The maximum yield of glucose relative to the total sugars released was at most 19%. When compared to the content of non-glucan carbohydrates in the softwood raw material, and thus excluding cellulose and some glucose in softwood hemicelluloses, the maximum yield of total sugars was 62%. This value is in accordance with previous sugar recovery yields from hardwood and wheat straw hemicelluloses in hydrothermal processing.^{25,26}

Production of furans from dissolved sugars

The drastically decreasing sugar yields at severities above the optimum conditions result from complex sugar degradation reactions.²⁷ The first step in this reaction series involves acid-catalyzed dehydration of monosaccharides yielding furfural and HMF from pentoses and hexoses, respectively. The highest yield of furans was 6.0% (based on wood dry weight) following the autocatalytic treatment at 210 °C (Fig. 2c). As previously observed, summing up the sugars and furans cannot close the carbohydrate mass balance because furans undergo acid-catalyzed polymerization simultaneously with their formation from sugars.²⁶ Supplementation of oxygen into the autocatalytic liquefaction decreased the furan concentrations and shifted the maximum yield into a higher temperature region (Fig. 2c). With sodium carbonate present, the yields of furans were notably lower compared to those from the autocatalytic treatments even if calculated on the relative basis of dissolved sugars. Rather than solely being an outcome of the final pH of the liquid phase, the effective reaction time at acidic conditions is a more plausible explanation for this observation. In addition to dehydration of hexoses, degradation of organic acids also yields HMF, which in addition to furfural forms resinous polymers previously termed humins, pseudo-lignin, and polyfurans.^{27,28} While the identification of these complex and partially insoluble carbonaceous polymers is difficult, the detection of organic acids such as formic acid, acetic acid, and glycolic acid is important because these are potential value-added products of the wood liquefaction process.

Remarkable impact of oxygen on organic acid production

It is of key interest that the formation of organic acids increased markedly when oxygen was used in HTL (Fig. 2d). Formic acid, acetic acid, and chromatographically unresolved glycolic acid and lactic acid were the main organic acids detected (Fig. S2 in the SI). The formation of organic acids increased linearly with the treatment temperature when both sodium carbonate and oxygen were present in the liquefaction reaction. In this case, as much as 10.4% of organic acids were obtained from the wood dry matter at 230 °C. This yield is higher than the one obtained at the similar temperature of 230 °C without sodium carbonate. However, it is clear that either in the absence or presence of sodium carbonate the organic acid yields from the oxidative treatments were 3–4 -fold higher than the corresponding ones obtained without oxygen. Because of the low sodium carbonate loadings used (2% based on wood dry weight), the production of acids did not result from alkaline degradation of sugars.²⁹ Instead, the results in Fig. 2d suggest that oxygen diverted the decomposition of sugars towards the oxidative generation of organic acids and blocked the route towards dehydration into furans. The mechanism of oxidative HTL was not investigated in the present study, and this could be elucidated by more detailed experiments using model compounds and elemental analysis. In addition to acting on sugars, oxygen may catalyze the side-chain cleavage of lignin with concomitant release of formic acid and acetic acid. Previously, yields of organic acids from isolated softwood lignin have been 0.20–0.45 g/g-lignin using hydrogen peroxide as an oxidant.¹⁶ The usage of molecular oxygen would be favorable over that of hydrogen peroxide which is acidic and cannot be easily recycled. While the exact contribution of lignin to the yield of organic acids cannot

be concluded from the present data, the major class of products expected to arise from lignin is the phenolic decomposition compounds.

Dissolution of lignin from wood

The dissolution of lignin was followed by analysis of water-soluble phenolics determined with the colorimetric Folin-Ciocalteu method. Regardless of sodium carbonate or oxygen, the yields of total phenolics increased linearly (overall $R^2=0.82$) as a function of HTL temperature (Fig. 2e). The maximum yield of total phenolics was 3.5% based on dry wood, but it is noted that this method underestimated the yield of lignin-derived oligomeric or polymeric fragments as it only measures the free phenolic groups relative to the guaiacol standards used. Furthermore, no common lignin-derived phenolic compounds such as vanillin were detected in the HPLC analysis of the HTL liquors (data not shown). This lack of monophenolic compounds and the low molar mass of the liquors suggests the presence of lignin oligomers which may have formed upon re-polymerization reactions of lignin. These type of reactions have been previously described for hydrothermal pretreatment of wood.^{25,30} One explanation for the lack of oxidized monophenolic degradation products is the pH that remained neutral or slightly acidic after all treatments as contrasted to the alkaline oxidative conditions used in analytical degradation of lignin.²⁶ Additionally, the gas phase of the reactor appears to influence the type of products arising from lignin. For instance, a range of monophenols was detected in the bio-oil after HTL of a mixture of softwood and hardwood under hydrogen pressure and at temperatures 250–350 °C.³¹ In any case, according to a recent review paper the solubilized lignin-derived phenolic products pose several alternative oxidative upgrading routes.³²

Formation of bio-oil in hydrothermal liquefaction

The final interesting product type from the wood liquefaction process is the bio-oil fraction which was isolated from the product liquor by extraction with ethyl acetate. Above 170 °C, the yields of bio-oil from the autocatalytic liquefactions exceeded those obtained with sodium carbonate present. The highest yield of bio-oil from wood dry matter was 7.3% following the autocatalytic HTL under oxygen at 230 °C. With increasing temperature, similar yields were obtained without oxygen at 250–270 °C. Unlike with organic acids, the presence of oxygen did not notably affect the generation of bio-oil during the HTL process. The achieved bio-oil yields from wood dry matter are comparable to the literature values of 8–9%.^{5,33} Earlier studies have obtained generally much higher yield of bio-oil from alkaline HTL compared to the ones without the catalyst. One explanation for this difference may be that the present study used very low sodium carbonate loadings of 2% (as per dry wood) at temperatures not exceeding 230 °C, whereas others have used alkaline chemical loadings that were more than five times as much as in the current study at temperatures above 280 °C.^{5–7} Furans are known to undergo acid catalyzed polymerization.³⁴ Under the conditions of the present study, the bio-oil fraction probably consisted of mixtures of lignin fragments and polymers formed from furans.

Maximum product yields and corresponding process conditions

The major products of the HTL of wood are sugars, furans, short-chain organic acids, phenolic lignin fragments, bio-oil, biochar, and gaseous products. The optimum conditions

for the formation of the dissolved products are summarized in Table 2. From this data, it can be observed that the selection of suitable conditions is important for the generation of the desired products. The yield of sugars is maximized at 170 °C, whereas other products required higher process severity. Oxygen and sodium carbonate enhanced the generation of organic acids, and the maximum yield of obtained at 230 °C might be improved further by increased reaction time, temperature, partial pressure of oxygen or sodium carbonate loading. Finally, the highest amounts of soluble lignin and bio-oil can be produced simultaneously by autocatalytic HTL at high temperatures.

Table 2: The operating conditions that maximize the generation of major products in HTL of softwood at a liquid to solid ratio of 11. Isothermal heating for 30 min at various temperatures was conducted in the presence or absence of sodium carbonate or molecular oxygen.

Product type	Maximum yield (g/100 g dry wood)	Temperature (°C)	Sodium carbonate (g/100 g dry wood)	p O ₂ (bar)
Sugars	15.4	170	-	0–5
Furans	6.0	210	-	-
Organic acids	10.4	≥ 230	≥ 2	5
Lignin oligomers	3.5	250	-	-
Bio-oil	7.3	230–270	-	0–5

In summary, the HTL of softwood involves several overlapping sequential reactions as depicted in Figure 3. We found that, due to the buffering capacity of wood, the treatments with initial sodium carbonate concentration of 1.6 g/L were effectively taking place in near neutral pH 5–7. Despite the minor impact on pH, the low amount of alkaline chemical

influenced the reactivity of monosaccharides when the treatment was carried out under the oxygen atmosphere. In that case, more organic acids and fewer furans were produced. Reactivity of lignin is known to be also dependent on the reaction pH. Maintaining the pH above the harshly acidic conditions could help to avoid the formation of reactive carbocation intermediates of lignin and the resulting carbonaceous polymers. Though lignin condensation reactions may occur either in acidic or alkaline pH, bases have in general a positive effect in reducing the formation of heavy components.³⁵

Figure 3. Overview of the reaction routes in HTL of softwood. The dashed lines indicate (alkaline) oxidative conditions.

CONCLUSIONS

Hydrothermal liquefaction of softwood was investigated to determine the effect of oxygen on chemical production. The main original finding was that liquefaction in the presence of

molecular oxygen sharply increased the formation of organic acids while having only a limited impact on other products. Correlations of yields to the treatment temperatures indicated that a multi-product process can be reasonable at 230 °C or higher temperature for the production of organic acids, phenolics, and bio-oil. These results facilitate industrial efforts to scale up chemical production from renewable biomass. The use of air as oxidant instead of pure oxygen could be tested in future experiments. Further work is underway to kinetically model and optimize the oxidative liquefaction process.

ASSOCIATED CONTENT

Yields of glucose and short chain carboxylic acids in the autocatalytic and sodium carbonate catalyzed HTL carried out as function of temperature and in the presence or absence of molecular oxygen. Examples of the temperature data of the pressure reactor used in the HTL experiments. This material is available free of charge via the Internet at <http://pubs.acs.org/>

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REFERENCES

- (1) Li, M. F.; Shen, Y.; Sun, J. K.; Bian, J.; Chen, C. Z.; Sun, R. C. Wet Torrefaction of Bamboo in Hydrochloric Acid Solution by Microwave Heating. *ACS Sustain. Chem. Eng.* **2015**, 3 (9), 2022–2029.
- (2) Loppinet-Serani, A.; Reverte, C.; Cansell, F.; Aymonier, C. Supercritical water biomass gasification process as a successful solution to valorize wine distillery wastewaters. *ACS Sustain. Chem. Eng.* **2013**, 1 (1), 110–117.
- (3) Yang, W.; Shimanouchi, T.; Kimura, Y. Characterization of the residue and liquid products produced from husks of nuts from *carya cathayensis* sarg by hydrothermal carbonization. *ACS Sustain. Chem. Eng.* **2015**, 3 (4), 591–598.
- (4) Balat, M. Mechanisms of Thermochemical Biomass Conversion Processes. Part 3: Reactions of Liquefaction. *Energy Sources, Part A Recover. Util. Environ. Eff.* **2008**, 30 (7), 649–659.
- (5) Bhaskar, T.; Sera, A.; Muto, A.; Sakata, Y. Hydrothermal upgrading of wood biomass: Influence of the addition of K₂CO₃ and cellulose/lignin ratio. *Fuel* **2008**, 87 (10–11), 2236–2242.
- (6) Demirbaş, A. Yields of oil products from thermochemical biomass conversion processes. *Energy Convers. Manag.* **1998**, 39 (7), 685–690.
- (7) Zhong, C.; Wei, X. A comparative experimental study on the liquefaction of wood. *Energy* **2004**, 29 (11), 1731–1741.
- (8) Kumar, S.; Lange, J. P.; Rossum, G. V.; Kersten, S. R. A. Liquefaction of Lignocellulose in Fractionated Light Bio-Oil: Proof of Concept and Techno-Economic Assessment. *ACS Sustain. Chem. Eng.* **2015**, 3 (9), 2271–2280.
- (9) Bu, Q.; Lei, H.; Zacher, A. H.; Wang, L.; Ren, S.; Liang, J.; Wei, Y.; Liu, Y.; Tang, J.; Zhang, Q.; et al. A review of catalytic hydrodeoxygenation of lignin-derived phenols from biomass pyrolysis. *Bioresour. Technol.* **2012**, 124, 470–477.
- (10) Wei, Z.; Zeng, G.; Huang, F.; Kosa, M.; Sun, Q.; Meng, X.; Huang, D.; Ragauskas, A. J. Microbial lipid production by oleaginous *Rhodococci* cultured in lignocellulosic autohydrolysates. *Appl. Microbiol. Biotechnol.* **2015**, 99 (17), 7369–7377.
- (11) Huber, G. W.; Cortright, R. D.; Dumesic, J. A. Renewable alkanes by aqueous-phase reforming of biomass-derived oxygenates. *Angew. Chemie - Int. Ed.* **2004**, 43 (12), 1549–1551.
- (12) Kumar, H.; Alén, R. Recovery of aliphatic low-molecular-mass carboxylic acids from hardwood kraft black liquor. *Sep. Purif. Technol.* **2015**, 142, 293–298.
- (13) Mosteiro-Romero, M.; Vogel, F.; Wokaun, A. Liquefaction of wood in hot compressed water Part 1 - experimental results. *Chem. Eng. Sci.* **2014**, 109, 220–235.
- (14) Muddassar, H. R.; Sipponen, M. H.; Melin, K.; De Kokkonen, D.; Pastinen, O.; Golam, S. Effects of Catalysts and pH on Lignin in Partial Wet Oxidation of Wood and Straw Black Liquors. *Ind. Eng. Chem. Res.* **2015**, 54 (32), 7833–7840.
- (15) Jeong, S.-Y.; Lee, J.-W. Sequential Fenton oxidation and hydrothermal treatment to improve the effect of pretreatment and enzymatic hydrolysis on mixed hardwood. *Bioresour. Technol.* **2016**, 200, 121–127.

- (16) Hasegawa, I.; Inoue, Y.; Muranaka, Y.; Yasukawa, T.; Mae, K. Selective production of organic acids and depolymerization of lignin by hydrothermal oxidation with diluted hydrogen peroxide. *Energy and Fuels* **2011**, *25* (2), 791–796.
- (17) Jomaa, S.; Shanableh, A.; Khalil, W.; Trebilco, B. Hydrothermal decomposition and oxidation of the organic component of municipal and industrial waste products. *Adv. Environ. Res.* **2003**, *7* (3), 647–653.
- (18) Özdenkci, K.; Hassan, R. M.; Melin, K.; Sipponen, M. Aqueous Phase Oxidative Treatment of Saw Dust. In *Proceedings of NWBC2015, the 6th Nordic Wood Biorefinery Conference, Helsinki, Finland*; 2015; pp 358–363.
- (19) Wilén, C.; Moilanen, A.; Kurkela, E. Biomass feedstock analyses. *VTT Publications*. 1996, pp 1–39.
- (20) Sluiter, J. B.; Ruiz, R. O.; Scarlata, C. J.; Sluiter, A. D.; Templeton, D. W. Compositional analysis of lignocellulosic feedstocks. 1. Review and description of methods. *J. Agric. Food Chem.* **2010**, *58* (16), 9043–9053.
- (21) Pihlajaniemi, V.; Sipponen, M. H.; Pastinen, O.; Lehtomäki, I.; Laakso, S. Yield optimization and rational function modelling of enzymatic hydrolysis of wheat straw pretreated by NaOH-delignification, autohydrolysis and their combination. *Green Chem.* **2015**, *17*, 1683–1691.
- (22) Waterhouse, A. L. Determination of Total Phenolics. In *Handbook of Food Analytical Chemistry Pigments Colorants Flavors Texture and Bioactive Food Components*; 2002; Vol. II, pp 1–8.
- (23) Karagöz, S.; Bhaskar, T.; Muto, A.; Sakata, Y.; Uddin, M. A. Low-temperature hydrothermal treatment of biomass: Effect of reaction parameters on products and boiling point distributions. *Energy and Fuels* **2004**, *18* (1), 234–241.
- (24) Li, L.; Chen, P.; Gloyna, E. F. Generalized kinetic model for wet oxidation of organic compounds. *AIChE J.* **1991**, *37* (11), 1687–1697.
- (25) Garrote, G.; Domínguez, H.; Parajó, J. C. Hydrothermal processing of lignocellulosic materials. *Holz als Roh- und Werkst.* **1999**, *57* (3), 191–202.
- (26) Sipponen, M. H.; Pihlajaniemi, V.; Sipponen, S.; Pastinen, O.; Laakso, S. Autohydrolysis and aqueous ammonia extraction of wheat straw: effect of treatment severity on yield and structure of hemicellulose and lignin. *Rsc Adv.* **2014**, *4* (44), 23177–23184.
- (27) Dunlop, A. P. Furfural formation and behaviour. *Ind. Eng. Chem.* **1948**, *40* (2), 204–209.
- (28) Weingarten, R.; Cho, J.; Conner, Jr., W. C.; Huber, G. W. Kinetics of furfural production by dehydration of xylose in a biphasic reactor with microwave heating. *Green Chem.* **2010**, *12* (8), 1423.
- (29) de Bruijn, J. M.; Kieboom, A. P. G.; van Bekkum, H. Alkaline degradation of monosaccharides V: Kinetics of the alkaline isomerization and degradation of monosaccharides. *Recl. des Trav. Chim. des Pays-Bas* **2010**, *106* (2), 35–43.
- (30) Li, J.; Henriksson, G.; Gellerstedt, G. Lignin depolymerization/repolymerization and its critical role for delignification of aspen wood by steam explosion. *Bioresour. Technol.* **2007**, *98* (16), 3061–3068.
- (31) Tymchyshyn, M.; Xu, C. C. Liquefaction of bio-mass in hot-compressed water for the production of phenolic compounds. *Bioresour. Technol.* **2010**, *101* (7), 2483–

2490.

- (32) Lange, H.; Decina, S.; Crestini, C. Oxidative upgrade of lignin - Recent routes reviewed. *Eur. Polym. J.* **2013**, *49* (6), 1151–1173.
- (33) Karagöz, S.; Bhaskar, T.; Muto, A.; Sakata, Y. Effect of Rb and Cs carbonates for production of phenols from liquefaction of wood biomass. *Fuel* **2004**, *83* (17-18), 2293–2299.
- (34) Hu, X.; Kadarwati, S.; Wang, S.; Song, Y.; Hasan, M. D. M.; Li, C. Z. Biomass-derived sugars and furans: Which polymerize more during their hydrolysis? *Fuel Process. Technol.* **2015**, *137*, 212–219.
- (35) Kumar, S.; Lange, J. P.; Van Rossum, G.; Kersten, S. R. A. Liquefaction of lignocellulose: Do basic and acidic additives help out? *Chem. Eng. J.* **2015**, *278*, 99–104.

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Hydrothermal Liquefaction of Softwood: Selective Chemical Production Under Oxidative Conditions

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Synopsis:

Molecular oxygen increases the selectivity of sustainable chemical production in the hydrothermal liquefaction of softwood lignocellulose.