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

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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.

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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%)

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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.