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# Catalytic depolymerisation and conversion of Kraft lignin into liquid products using near-critical water

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## ABSTRACT

A high-pressure pilot plant was developed to study the conversion of LignoBoost Kraft lignin into bio-oil and chemicals in near-critical water (350 °C, 25 MPa). The conversion takes place in a continuous fixed-bed catalytic reactor (500 $cm^3$) filled with $ZrO_2$ pellets. Lignin (mass fraction of approximately 5.5%) is dispersed in an aqueous solution containing $K_2CO_3$ (from 0.4% to 2.2%) and phenol (approximately 4.1%). The feed flow rate is 1 kg/h (reactor residence time 11 min) and the reaction mixture is recirculated internally at a rate of approximately 10 kg/h. The products consist of an aqueous phase, containing phenolic chemicals, and a bio-oil, showing an increased heat value (32 MJ/kg) with respect to the lignin feed. The 1-ring aromatic compounds produced in the process are mainly anisoles, alkylphenols, guaiacols and catechols: their overall yield increases from 17% to 27% (dry lignin basis) as $K_2CO_3$ is increased.

## 1. Introduction

After cellulose, lignin is the second most abundant natural organic polymer found on earth, being the first among those composed of aromatic units (phenylpropane monomer units). A vast amount of lignin is extracted from wood in the Kraft pulping process and thereby ends up in the black liquor. Today this liquor is concentrated by means of evaporation and used as fuel in the production of heat and power for the pulping process itself. So far only a small proportion of the lignin (approx. 1%) has been used as a raw material in the production of materials and chemicals with a higher value than fuel. A new process called “LignoBoost” has recently been developed with the aim of extracting part of the lignin in the black liquor at a high purity level, thus exploiting the energy surplus of Kraft pulp mills. The LignoBoost process has recently gained commercial status; therefore, in years to come, a huge amount of LignoBoost Kraft lignin is expected to be available for valorisation [1,2].

Lignin is an amorphous biopolymer whose primary aromatic units are linked together randomly by different types of ether (C—O—C) and carbon–carbon (C—C) bonds [3]. Its chemical structure suggests that this biopolymer could be a good source of liquid fuel additive and commercially important chemicals, phenolics in particular, if it could be broken down into smaller molecular units that retain the oxy-aromatic nature [4,5]. In the quest to reach this goal, several processes for depolymerisation and conversion of different types of lignin have been investigated for decades, such as pyrolysis, which uses thermal treatment in the absence of air, hydrogenolysis, which is a thermal process in the presence of gaseous hydrogen or of a hydrogen-donating solvent, and oxidative cracking, which occurs in the presence of oxidising agents such as hydrogen peroxide [5].

More recently, it has been demonstrated that lignin can be depolymerised and converted into smaller molecular units in supercritical water. This process was, for example, carried out by Saisu et al. [6] at 400 °C without using a catalyst: they found that the yield of monomeric phenolic compounds was lower than expected. This was probably due to the re-polymerisation of monomers, resulting in the formation of char. Many authors [6–8] have however found that adding phenol to the reacting system decreases the formation of char. The effect of phenol in particular was studied in detail by Fang et al. [8], who decomposed lignin in supercritical water at temperatures between 400 °C and 600 °C in a micro-reactor. More specifically, according to these authors, phenol allows the system to become homogeneous at the reaction conditions and prevents the re-polymerisation reactions, which lead to char being

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formed. The fact that the addition of phenol was found able to prevent the formation of char is also very much in line with the results obtained by Aida et al. [9], who carried out the depolymerisation of coal in phenol–water mixtures at 400 °C.

One promising alternative for processes in supercritical water is the catalytic conversion in near-critical water, where the bonds of the lignin network are cleaved at mild temperatures (i.e. 280–370 °C), thus allowing the aromatic nature of the building block molecules to be retained to a greater extent. In this regard, some authors have focused on lignin depolymerisation and conversion in near-critical water using strong bases as a catalyst [10–13], but high yields of heavy fractions and char are reported. In another research work, Karagöz et al. [14] compared the effect of different base solutions (i.e. $K_2CO_3$, KOH, NaOH and $Na_2CO_3$) in the hydrothermal treatment of wood biomass at 280 °C; they reported $K_2CO_3$ as being the most efficient catalyst in increasing the liquid-product yield and decreasing the solid residue. In a following work on the same topic, Karagöz et al. [15] observed that an increase in the concentration of $K_2CO_3$ leads to a decrease in char formation and an increase in liquid-product yield, together with an increase in catechol and a decrease of guaiacol in the water-soluble products. These results on the effect of $K_2CO_3$ are in line with those reported by Bhaskar et al. [16] pertaining to the same process applied to different wood biomasses.

Moreover, Andersen [17,18] disclosed a process whereby an organic material is converted into small molecular units operating in water at temperatures from 270 °C to 380 °C, pressures from 15.2 MPa to 27.4 MPa and in the presence of the catalyst $ZrO_2$. In these patents, the important role of $ZrO_2$ in reducing the formation of char is emphasised. Furthermore, Hammerschmidt et al. [19] and Toor et al. [20] carried out the catalytic conversion of different types of sludge waste streams from food industry and machinery work [19] or distiller's grain with solubles [20], operating in near-critical water (>300 °C, 25 MPa) in the presence of both $K_2CO_3$ and $ZrO_2$ catalysts. These works show not only the feasibility of the conversion of different slurries of organic substances using this catalytic system but also good results in terms of oil yield. Since these applications are very different compared to conversion of pure lignin, it is of interest to test the feasibility of a process based on $ZrO_2 + K_2CO_3$ on this peculiar biomass. Furthermore, the previous attempts of converting lignin in near-critical or supercritical water were carried out on small laboratory batch units and they typically led to high amount of solid residues, if phenol was not added to the reacting system. A high production of solid residues may lead to serious operational problems in the development of the process to a continuous mode of operation on a large scale.

Therefore, the objective of the present work is to study the feasibility of a continuous process for converting LignoBoost Kraft lignin into transportation bio-fuels and aromatic chemicals in near-critical water (350 °C, 25 MPa), using $ZrO_2$ and $K_2CO_3$ as the catalysts and phenol as the co-solvent. The set-up of the plant and the development of the analytical procedure of the reaction products are described in details. In addition, preliminary results focusing on the effect of the $K_2CO_3$ mass fraction are presented and discussed.

## 2. Materials and methods

### 2.1. Materials

The Kraft lignin used as the feed material in this work is from softwood and is produced in the LignoBoost demonstration plant in Bäckhammar (Sweden). The heterogeneous catalyst used in the reactor is made of zirconia ($ZrO_2$) pellets (Harshaw Chemie BV, length: 3 mm, diameter: 3 mm, BET surface area 48 $m^2$/g). The potassium carbonate ($K_2CO_3$, ≥99.5%) used as the homogeneous co-catalyst and the phenol (crystallised, ≥99.5%) used as the co-solvent are from Scharlau, as is the 1 mol/L hydrochloric acid (HCl) used in the analytical procedure of the aqueous phase. Sigma–Aldrich is the source of the following: anisole (≥99.65%), phenol (≥99.5%), o-cresol (≥99%), m-cresol (99%), p-cresol (≥99.0%), guaiacol (≥98.0%), catechol (≥99%) and syringol (≥98.5%), used as analytical standards, Hydranal-Composite 5 and methanol (puriss. p.a. ≥ 99.8%), used for Karl Fischer titration, tetrahydrofuran (THF, ≥99.9%) and diethyl ether (DEE, ≥99.9%), used as solvents in the analytical protocol. All chemicals were used as provided, without further purification.

### 2.2. Apparatus and procedure

A schematic diagram of the laboratory plant used is shown in Fig. 1. Prior to the start of the experimental run the system is heated up and pressurised to operating conditions, keeping a continuous flow of deionised (DI) water. During the run the feed, composed of lignin, $K_2CO_3$, phenol and DI water, is continuously pumped by a high-pressure diaphragm pump (Lewa) at a flow rate of 1 kg/h, measured by a mass flow-metre (Endress and Hauser, Promass). The lignin slurry is prepared by crushing lignin manually before dispersing it in a solution of $K_2CO_3$ in DI water. The actual dispersion procedure is performed using an Ultra Turrax disperser (IKA WERK T 45/N), operating at room temperature for approx. 5 min. The feed is made by mixing the prepared lignin slurry with phenol; it is stored in a 10 L feed tank equipped with an impeller, where it is kept at 40 °C. Prior to entering the reactor, the feed is heated to 80 °C in the electric preheater and is mixed with the recirculation stream of reaction products provided by the high-temperature high-pressure recirculation pump. The recycle to feed ratio is kept at approximately 10, and is estimated by measuring temperatures before and after the mixing point and then applying an energy balance. The recirculation allows the fresh feed to be heated rapidly and mixed before coming into contact with the heterogeneous catalyst in the reactor. There is a second electric heater installed in the inlet line of the reactor. The reaction mixture comes into contact with the solid catalyst whilst flowing upwards in the 500 $cm^3$ fixed-bed reactor (Parr 4575; height: 171 mm, internal diameter: 61 mm), which is composed of Inconel 600 in the high-temperature parts and equipped with an electrical heating jacket. The free volume of the reactor charged with the catalyst is 294 $cm^3$. At reaction conditions (350 °C, 25 MPa), the density of water is 625 kg/$m^3$ (NIST data base) and the reactor residence time ($\tau$) is approximately 11 min.

The reaction products are cooled down and depressurised to ambient conditions. Two pressure control valves are used for controlling the system pressure and for depressurising the reaction products. These valves are in parallel so that they can be switched over from one to the other in case the valve in operation becomes congested by solid particles. The liquid products are collected continuously in sampling bottles for analysis. Each sampling bottle is used to collect the liquid products corresponding to approximately 45 min of operation. The pH of the liquid products of each sampling bottle is measured through a pH-metre (Jenway, 370) equipped with a glass electrode (Jenway, 924005), using a 2-point calibration with standard buffer solutions. Gas samples were not taken in the runs that were carried out since no significant amount of gas was collected in a gas sampling bag (Tedlar sample bag, SKC, USA) placed downstream of the sampling bottle, on the output line exiting the cap of the bottle. Auxiliary lines for cleaning the apparatus in between the runs and safety systems are also installed.

The observation was made that the visual appearance of the products in the sampling bottles changes progressively during the start-up period and shows a progressive darkening: the exception was a single run without lignin in the feed (see Section 2.3), in which the products consisted of a homogeneous liquid phase showing a