



Contents lists available at ScienceDirect

Biomass and Bioenergy

journal homepage: <http://www.elsevier.com/locate/biombioe>

Research paper

## Hydrothermal treatment of black liquor for energy and phenolic platform molecules recovery in a pulp mill

Marion Huet <sup>a</sup>, Anne Roubaud <sup>a,\*</sup>, Christine Chirat <sup>b</sup>, Dominique Lachenal <sup>b</sup>

<sup>a</sup> CEA Grenoble, LITEN, Laboratoire des Technologies Biomasse, 17 rue des martyrs, 38054 Grenoble, France

<sup>b</sup> LGP2 - Grenoble INP - Pagora, 461 rue de la Papeterie, CS 10065, 38402 Saint-Martin-d'Hères, France

### ARTICLE INFO

#### Article history:

Received 12 August 2015

Received in revised form

15 March 2016

Accepted 17 March 2016

Available online xxx

#### Keywords:

Biorefinery

Black liquor

Energy recovery

Hydrothermal treatment

Platform molecules production

Sodium recovery

### ABSTRACT

The aim of this study was to study the conversion of black liquor under hydrothermal conditions and its integration in a pulp mill. Three sulfur-free black liquors produced from caustic soda cooking of pre-hydrolyzed softwood, prehydrolyzed hardwood and non prehydrolyzed hardwood chips were converted. Experiments were performed in a batch reactor, for temperature between 250 °C and 310 °C, and for holding time between 5 and 120 min. Three phases were formed: an aqueous phase containing monomeric phenolic compounds and the sodium cations, a biocrude containing most of the carbon, and a small amount of gas. The combustion of the biocrude could allow an energy recovery for the mill of up to 70%. The main monomeric compounds identified in aqueous phase were phenol, catechol, guaiacol and syringol, with a total yield up to 28 g kg<sup>-1</sup> of dry BL, at 250 °C. Among them, guaiacol was the major product. Sodium recovery was 97 %, slightly better than typical kraft recovery value, and compatible with causticizing. Finally, results obtained with a kraft softwood lignin were compared to those obtained with softwood black liquor. Results show that biocrude yields were greater with black liquor, whereas platform molecules production was higher with lignin. Presence of carbohydrates derivatives in black liquor is identified as a major parameter for biocrude production as it would favor bonding between phenolic species.

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### 1. Introduction

Biorefineries integrate processes and technologies for an efficient biomass conversion into materials, platform chemicals, fuels and energy. Economic and environmental viability of the future wood-based biorefineries depends on conversion of each component of the wood, i.e. cellulose, hemicellulose and lignin, into value-added compounds. Softwood kraft pulp mills are already working as a biorefinery, since they produce a material (cellulosic fibers), some chemicals (tall oil and turpentine) and the energy needed for running the mill. During this process, the main part of the lignin and a significant amount of the hemicelluloses are degraded and dissolved during the cooking step, producing black liquor. This liquor is then concentrated by evaporation and burned in the recovery boiler of the mill [1]. This process allows the recovery of up to 65.4% of the energy content of black liquor and 96.6% of its Na [1].

The energy yield of the mill is significantly decreased by the evaporation step: taking into account the energy needed for evaporating the black liquor, energy efficiency is below 40%. However, black liquor combustion produces more energy than the energetic needs of the mill. Those mills are self sufficient in terms of energy, and, in many cases, are net electricity producers.

Studies have been done recently in order to valorize some other components of the wood chips and make the cellulosic pulp mill an even better wood based biorefinery. For instance, the extraction of the wood hemicelluloses by autohydrolysis (high temperature steam or water treatment) allows the recovery of sugars for the chemical industry [2,3]. Autohydrolysed wood chips are easier to delignify than untreated wood chips [4] allowing the use of soda cooking instead of kraft to produce the cellulosic fibers. As lignin of wood is only used for energy production, a more interesting treatment of black liquor is required.

Black liquor is a complex mixture of numerous molecules, including inorganic species (residual chemical reagents) and organic species of various molecular weight. It is mainly composed of alkali lignin, lignin fragments, sodium salts of carbohydrate

\* Corresponding author. LITEN/DTBH/LTCB, CEA Grenoble, 17 rue des Martyrs, 38054 Grenoble Cedex 9, France.

E-mail address: [anne.roubaud@cea.fr](mailto:anne.roubaud@cea.fr) (A. Roubaud).

degradation products (saccharinic acids and other carboxylic acids), sodium salt of sugar oligomers [1]. Lignin in black liquor is different from lignin in wood. In particular, the percentage of C–O–C linkages between the propyl phenol units of lignin has been significantly decreased during cooking, making it more difficult to depolymerize than original lignin.

On the other hand, a lot of studies are done in order to depolymerize lignin into small phenolic molecules: oxidative depolymerization, ionic liquid catalyzed depolymerization, heterogeneously catalyzed depolymerization, enzymatic depolymerization and thermal deconstruction were applied [5]. However, these technologies present several drawbacks. For instance, lignin needs to be pure. Moreover, the use of metal catalyst is an environmental concern if no recycling is done.

Hydrothermal liquefaction (HTL) is a process taking place in an aqueous medium under subcritical conditions. This process allows to convert various kind of wet organic resources into a biocrude. The biocrude is a kind of “green” petroleum, with a higher heating value of 20–35 MJ kg<sup>-1</sup>, a high viscosity and a lower oxygen content than the initial matter. A small quantity of gas is produced, mainly CO<sub>2</sub>. The remaining carbon is in the aqueous phase under the form of small organic molecules and carbonates.

Hydrothermal liquefaction offers ecological benefits since no pollutant solvent is needed. Indeed, water behaves both as reactant and solvent [6]. Its dielectric constant decreases from 80 at ambient conditions to 14 at 350 °C and 20 MPa, leading to an increased solubility of organic compounds and a decreased solubility of alkali salts. Moreover, under these conditions, the ionic product of water is a hundred times higher (10<sup>-12</sup> compared to 10<sup>-14</sup> at ambient conditions). Acid or base catalyzed reactions, such as hydrolysis, are thus enhanced.

Depolymerization of lignin by subcritical fluids has been reported frequently in literature [7–9]. However, water is often preferred as it is a cheap and environmental solvent. Beauchet et al. [10] demonstrated that based-catalyzed hydrothermal liquefaction of lignin with sodium hydroxide is efficient to depolymerize kraft lignin with a monomer yield of up to 84 g kg<sup>-1</sup> at 315 °C. Main products of the monomer fraction are phenolic compounds as phenol [10,11], cresol [11], catechol [10–12], guaiacol [12,13] and syringol [14,12]. Nevertheless, in these studies, several points have not been considered: recycling of the base catalyst (NaOH), recycling of water and valorization of the remaining part of the lignin.

Moreover, lignins used in these studies are pure. In fact, this lignin has been extracted from wood via an alkaline process, precipitated, dried and purified. The pure lignin is solubilized back into a caustic soda solution to be liquefied. In a sustainable bio-refinery process, black liquor should be directly converted in order to avoid those steps. However there is few information available about direct hydrothermal liquefaction of black liquor and these studies have not quantified platform molecules production [15–17] and focused on the production of an energetic biocrude [16,17].

In this work, we propose to convert directly black liquor coming from the pulp washing step of the pulping process. The idea here is to avoid any evaporation step and benefit from the initial sodium concentration of black liquor. This black liquor is a sulfur free one as it is produced by a soda cooking and not a sulfate cooking (kraft process). The aim of this paper is to examine if an hydrothermal treatment of black liquor could be of any interest regarding production of platform molecules, sodium recovery and energy recovery for the mill. Moreover, the impact of wood type and prehydrolysis before delignification will be studied. Finally, the behavior of black liquor will be compared to pure alkali lignin one.

## 2. Materials and method

### 2.1. Materials

Sulfur free weak black liquors were supplied by our project partner Grenoble-INP Pagora (Grenoble, France). The black liquor was obtained by a caustic soda cooking of mixed softwood chips (pine 75 %, spruce 15 % and douglas fir 10 %) and mixed hardwood chips (poplar 35 %, beech 20 %, oak 15 %, chestnut tree 15 % and eucalyptus 15 %) provided by the Saint Gaudens Fiber Excellence pulp mill in France. Alkaline cooking was performed under conditions similar to those used in the industry: temperature was raised to 175 °C in 95 min and maintained for 45 min. Temperature was decreased to 50 °C in 50 min. Effective alkali was 20 % (as NaOH on dry wood weight corresponding to a solution of 56.8 g L<sup>-1</sup>) and the liquor-to-wood mass ratio was 3.5:1.

Properties of the black liquor used are summarized in Table 1.

Softwood kraft lignin was obtained as powder from Sigma–Aldrich France Co. (ref 370959, CAS 8068-05-1) and solubilized at 10 g L<sup>-1</sup> in a mixture of deionized water and NaOH at 100 mmol · L<sup>-1</sup> (pH = 13).

### 2.2. Hydrothermal liquefaction procedure

Black liquor was directly introduced in the 0.6L batch reactor (Parr mini 4560 in stainless steel grade 316) with an initial nitrogen pressure of about 1.1 MPa. Stirring was kept at 8.3 Hz. Then, the reactor was heated at a rate of 6 K min<sup>-1</sup>. Maximum temperature (T<sub>max</sub>) was reached in about 30–40 min. Temperature remained stable (±0.2 °C) during the holding time. Then, the reactor was cooled down (see Fig. 1 for experimental temperature time profile) and the gas analysis was performed about 1 h later. The aqueous phase and raw biocrude phases were collected, separated by Buchner filtration and analyzed.

### 2.3. Analysis

Molar gas composition was determined with a μGC (Micro-Gas Chromatography) Varian CP-4900. Temperature, initial and final pressure were measured in the reactor and then gas production was calculated via the equation of ideal gas law.

Total carbon concentrations (TC) and inorganic carbon concentrations in the liquid phase (IC, i.e. ions CO<sub>3</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup>) were analyzed with a TOC-L meter (Shimadzu VCSH). Total organic carbon concentration (TOC, in g · L<sup>-1</sup>) was calculated by the difference between TC and IC.

Sodium concentration in the liquid phase was analyzed by ion chromatography (Dionex ICS-3000/Dionex Ionpac CS16).

Identification of small phenolic species was performed on the ethylacetate extract of the liquid phase by GC–MS (Perkin Elmer Clarus 500/Clarus 600S). Carrier gas was He (1.0 cm<sup>3</sup> min<sup>-1</sup>). The oven temperature was held at 45 °C for 10 min, increased up to 230 °C at 6 K min<sup>-1</sup> and finally held at 230 °C for 9 min.

Concentration of phenol, catechol, guaiacol and syringol were measured through HPLC (thermofisher TCC-100) equipped with a column C18 (hypersil gold, 150 × 4.6 mm). Analyses were performed under the following conditions: eluant CH<sub>3</sub>CN/H<sub>2</sub>O, flow rate 1.0 cm<sup>3</sup> min<sup>-1</sup>, temperature of oven 40 °C, UV detector (200 nm), gradient flow (linear variation of CH<sub>3</sub>CN: from 5 % to 10 % in the first 10 min, 20 % at 20 min, 30 % at 22 min and 5 % at 24 min, steady until 26 min).

Molecular weight of organic species in aqueous phase was measured by gel permeation chromatography (GPC). Aqueous phase was evaporated at 105 °C and resolubilized in LiCl/DMAc with a concentration of 2 g L<sup>-1</sup> (LiCl in DMAc at 0.5%). A viscotek

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