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Fractionation and gasification of black liquor derived from kraft pulping

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ABSTRACT

By combining hydrolysis, it was observed that the maximum concentration of xylose + mannose + -galactose (xmg) was 10.7 g/L at a CS of 1.72. The aliphatic acid, aromatic acid and aldehydes were released 29.8, 0.45 and 0.90 g/L from the black liquor at CS of 1.19, 1.72, and 2.19, respectively. In the gasification using bench-scale bubbling fluidized bed (BFB) reactor, high-quality syngas (H_2/CO: 1.47) was obtained from the steam of acid-insoluble lignin (AIL), suitable for conventional energy systems such as gas engines, turbines, and boilers.

Introduction

This study focuses on black liquor, the waste liquor obtained after pulping is completed in the kraft process. Most modern pulp mills burn the spent pulping liquor to recover the cooking chemicals and use the heat value of the extracted organic material. Spent pulping liquor fractionation processes are therefore economically attractive for pulp mills with no chemical recovery system. Such mills are principally calcium bisulfite and straw-based pulp mills, with high concentrations of silica in the pulping liquor that causes scaling [1–3]. The primary organic compounds in black liquor are lignin, polysaccharides, carboxylic acids, and extracts, while the main inorganic substances are sodium hydroxide and sodium sulfide [4–6]. The standard method for separating the individual components of black liquor involves acid hydrolysis using sulfuric acid, which is followed by gravimetric determination of lignin and chromatographic determination of new chemicals. During acid hydrolysis, the high temperature and pressure of the steam facilitate the conversion of acetyl groups on the xylan backbone to acetic acid. This released acetic acid enhances the hydrolysis and dehydration reactions that convert xylan to oligomeric and molecular xylose, and furfural; and hexan to hydroxymethylfurfural (HMF). In addition, lignin molecules are broken down to smaller molecules, such as phenolic compounds, during acid hydrolysis [7]. The yield of decomposed products increases with increased severity factors (i.e. reaction time and temperature). The amount of degradation products and the production of sugar and lignin during acid hydrolysis can be increased by carefully optimizing the reaction conditions. Fig. 1 presents a simplified block diagram representing the process flow of a pulp-mill-based bio-refinery that co-produces pulp with lignin, fermentable sugars, and extracted products from fractionated waste pulping liquor.

The primary objective of this study was to identify the sugars, organic acids, furans, and decomposition products from kraft black liquor hydrolyzed under various combined severity (CS) factors. The secondary objective was to calculate the yield of the precipitated lignin byproduct and to determine its physical

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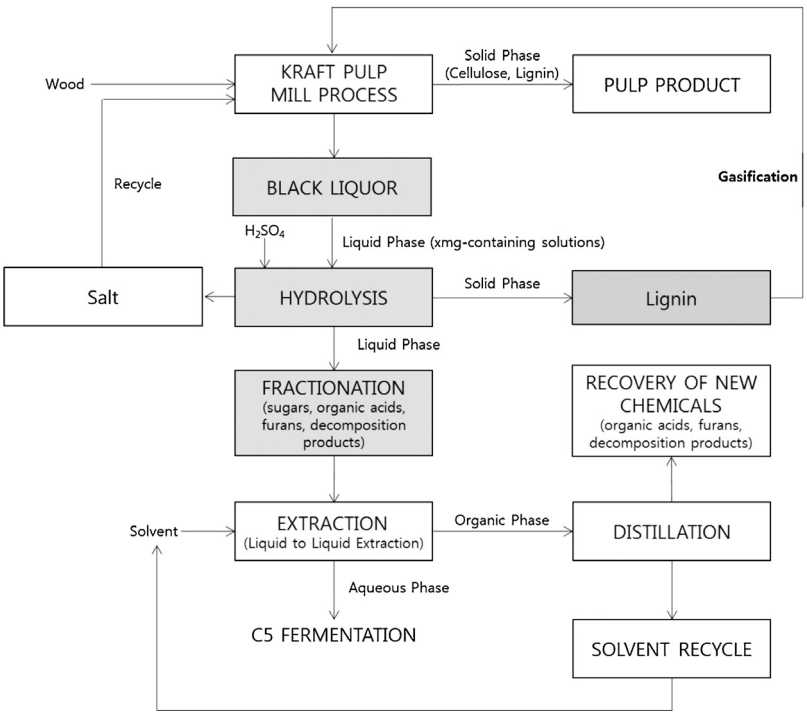

Fig. 1. Flow diagram of black liquor utilization in a bio-refinery plant producing wood pulp, fermentation-derived alcohol, and new chemicals.

characteristics using ultimate and proximate analyses. In addition, air/steam gasification of the byproduct was conducted for investigating the application of lignin as a renewable fuel for current energy systems. A tube furnace and a bubbling fluidized-bed (BFB) reactor were used for the gasification experiments, and the product gas quality was analyzed in terms of the heating value and H_2/CO ratio.

Materials and methods

Raw materials

The kraft black liquor used in this study was supplied by Moorim P&P Co., Ltd. (Ulsan, Korea). The pH of the liquor was 13–14 and it contained most of the original inorganic cooking elements, as well as the dissolved, degraded wood particles. The composition of the black liquor was analyzed according to the NREL Chemical Analysis & Testing Standard Procedures in NREL/TP-510-42623 [8] and TAPPI T222 om-06 [9]. The composition of the black liquor is shown in Table 1.

Combined severity (CS) factor

To simplify the comparison of experimental results, the residence time, fractionation temperature, and pH were combined as the combined severity (CS) factor. Overend and Chornet [10] developed a severity index (R_0) that is widely used for optimizing steam explosion processes. R_0 is a function of the reaction time (t, min) and temperature (T, °C), and is described by the following equation:

$$R_0 = t \times \exp\left[\frac{T-100}{14.75}\right] \quad (1)$$

The effect of pH is incorporated using the CS, as shown in the following equation:

$$CS = \log(R_0) - pH \quad (2)$$

The fractionation conditions used in this study are expressed as CS values in the range −0.78 to 3.96.

Table 1
The chemical composition of acid hydrolyzed black liquor.

Component	g/L
Glucose	0.89
[a]xmg	10.33
Arabinose	0.26
Total carbohydrate	11.47
Acetic acid	10.67
Acid insoluble lignin	263.35
Acid soluble lignin	10.64
Total non-carbohydrate	274.02
Total (Total carbohydrate + Total non-carbohydrate)	285.48

[a] xmg: xylose + mannose + galactose.

Acid hydrolysis of black liquor at 121 °C

The black liquor samples (initial pH = 13) were adjusted to a series having pH values in the range 0.5–3, using 96% (w/v) sulfuric acid. The black liquor was contained in a 1-L media bottle with a 100 mL working volume. The autoclave was heated to a temperature of 121 °C for 40, 60, and 80 min with the corresponding water vapor pressures. The resulting liquid was decanted and a portion was filtered using a Buchner funnel with Advantec No. 2 qualitative filter paper. The liquid hydrolysate was immediately centrifuged at 15000 rpm for 20 min to settle the solid residue. Aliquots of 1 mL were withdrawn from the micro-tube and filtered with a 0.45-μm syringe filter. The composition of the hydrolyzed black liquor was identified by high-performance liquid chromatography (HPLC) and ultra-fast liquid chromatography (UFLC-XR).

Acid hydrolysis of black liquor at temperatures >121 °C

In this study, hydrolysis was conducted at higher temperatures (>121 °C) using simple bomb reactors immersed in an oil bath. The concentrations of the components generated under these high-severity acid hydrolysis conditions were then identified. The