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Conjugated processes of black liquor mineral and organic components conversion in supercritical water

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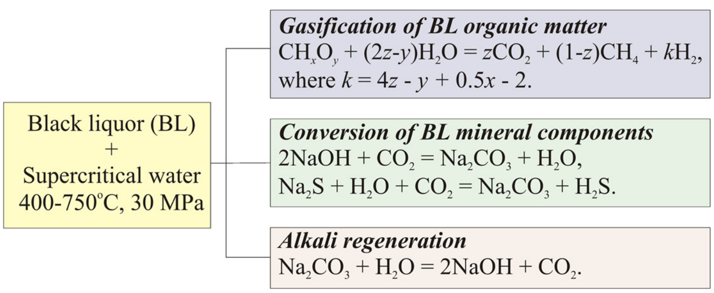
GRAPHICAL ABSTRACT



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ABSTRACT

The conversion of black liquor (BL) in supercritical water (SCW) at a pressure of 30 MPa and different temperatures ranged from 400 to 750 °C was studied using a tubular reactor made of stainless steel. It follows from the mass spectrometric analysis that at 600 °C the gasification degree of BL organic matter is α = 65% wt., while when increasing the temperature to 750 °C, α > 100% due to water decomposition. It was revealed that the conversion of the main mineral components of BL (NaOH and Na_2S) to Na_2CO_3 results from their interaction with the products of SCW gasification of BL organic matter. As was detected, solid products of SCW conversion of BL contain elemental sulfur. It is shown that regeneration of alkali is effectively realized by pumping SCW through the layer of Na_2CO_3 powder that results from removal of CO_2, generated through reaction of $Na_2CO_3 + H_2O \rightarrow 2NaOH + CO_2$.

1. Introduction

Kraft pulping provides 90% of the world pulp production [1]. As a result of this process a waste solution is formed, namely the black liquor (BL), whose annual world production amounts to 200 mln tons [2]. The content of organic and mineral substances in the dry mass of BL is at the level of 65–70 and 30–35% wt., respectively [3]. Black liquor's organic matter includes alkaline lignin, monosaccharides decomposition products, phenols, fatty and resin acids, and sulfur-containing organic substances [3]. The composition of BL mineral components includes mainly sodium carbonate, sulfate, thiosulfate, sulfide, hydroxide, and chloride [1,3]. The conventional method of black liquor regeneration (Tomlinson process) consists of the following stages: evaporation of water under vacuum, combustion of its organic components at 1000–1100 °C, and causticization of Na_2CO_3, formed during the reaction of NaOH with carbon dioxide, with slaked lime at 95 °C [1,3]. However, this process is characterized by low efficiency due to the need to evaporate a large amount of water (its content in BL exceeds 70% wt.), as well as sintering of alkali, and emission of sulfur-containing substances (H_2S, SO_2, methyl mercaptan, dimethyl sulfide, etc.) and

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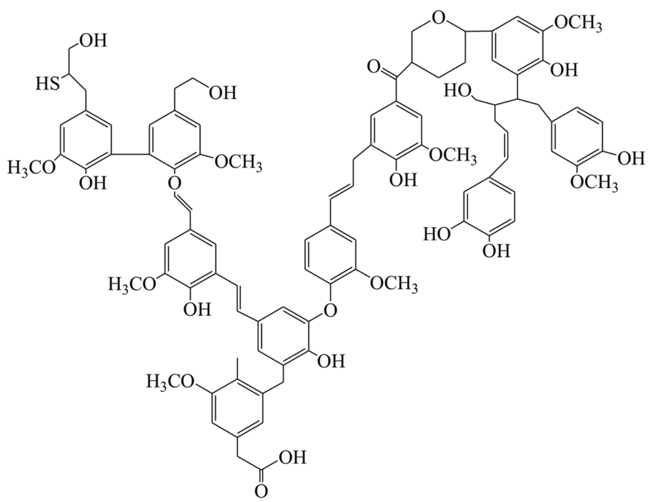

Fig. 1. The assumed structure of the sulfate lignin fragment according to [11].

nitrogen oxides into the atmosphere [1,4,5].

Gasification of pulp and paper industry waste in supercritical water ($T > 374\,^{\circ}C$, $P > 22.1$ MPa) has a number of advantages compared to conventional technologies. First, gases and non-polar organic substances dissolve in supercritical water (SCW) that improves mass transfer and, as a result, increases the conversion rate. Secondly, there is no need for evaporation of water, which becomes a reaction medium and an active chemical reagent [6–10]. Third, SCW conversion is done in closed-loop system that improves environmental performance of the process.

High content of phenolic structural fragments in sulfate lignin (Fig. 1) determines the fact that the main products of its depolymerization in sub- and supercritical water are alkyl derivatives of phenols and polyphenols [12–15]. Jiang et al. [12], when studying SCW conversion of lignin in an autoclave (375 °C, 22.1 MPa, reaction time 10–60 min), revealed that the main components of liquid products are derivatives of 2-methoxyphenol, 1,2-dihydroxybenzene, and 2,6-dimethoxyphenol. It is shown that the yield of the carbonized residue decreases with increasing holding time from 10 to 30 min, and then increases due to depolymerization of lignin at the initial stage of the process and subsequent polymerization of its conversion products.

Nguyen et al. [15] studied conversion of the sulfate lignin in the liquid water flow at 350 °C and 25 MPa in the presence of the ZrO_2 catalyst. The solution containing 5.5% lignin, 0.4–2.2% potassium carbonate, and 4.1% phenol was fed into the reactor at a rate of 1 kg/h. It is shown that the total yield of phenols increases from 17 to 27% (based on dry matter of lignin) along with an increase in the concentration of K_2CO_3. According to [16,17], the addition of phenol suppresses recombination of forming radical fragments and promotes the decomposition of lignin with the formation of low-molecular substances.

Sricharoenchaikul [18] studied SCW gasification of black liquor in a quartz capillary (375–650 °C, 22–40 MPa, BL concentration 10–20% wt., reaction time 5–120 s). The maximum yield of combustible gases (H_2, CH_4, C_2H_x, and C_4H_y) was observed at the maximum temperature and dilution level of black liquor with water; the carbon removal degree from BL was 84.8%. It is shown that the increase in the concentration of BL leads to an increase in the yield of CO. Hawangchu et al. [19] studied the influence of Na_2CO_3 on the composition of SCW products of lignin and black liquor conversion in quartz capillary (400–600 °C, 25–40 MPa, reaction time 600 s). The maximum yield of gas products (CO_2, H_2, CH_4, and CO) was recorded at the maximum conversion temperature. It is stated that the increase in pressure leads to a decrease in the yield of H_2 and CH_4. The authors of [19] explained this effect by the superposition of two processes: increasing the rate of gas-phase reactions and reducing the rate of decomposition of organic matter with increasing water density. Carboxylic acids, ethers, hydrocarbons, chlorine-, nitrogen-, and sulfur-containing organic substances were detected as part of the liquid conversion products obtained at $T \leq 500\,^{\circ}C$. According to Hawangchu et al. [19], the addition of Na_2CO_3 contributes to an increase in the yield of CO due to the replacement of hydrogen with sodium in carboxyl and phenol groups that eventually leads to a shift in the equilibrium of the water gas shift reaction.

Rönnlund et al. [20] conducted SCW conversion of pulp and paper production waste in a horizontally arranged tubular flow reactor (500–650 °C, 25 MPa, residence time 90–300 s) with additives of KOH, K_2CO_3, NaOH, and black liquor. The main components of liquid products obtained at 500 °C are alkyl derivatives of phenols, while obtained at 650 °C – polyaromatic hydrocarbons. It is shown that the efficiency of H_2 generation in SCW gasification in the presence of additives increases in the following sequence: KOH $<$ NaOH $\approx$ BL $<$ K_2CO_3. The authors of [20] explained this by the catalytic effect of the resulting potassium formiate on the water gas shift reaction.

The results of a study of SCW gasification of alkaline black liquor in a horizontally arranged tubular flow reactor (400–600 °C, 25 MPa, residence time 4.9–13.7 s) show [21] that an increase in temperature and residence time, as well as a decrease in the concentration of the solution increases the efficiency of gasification. The portion of H_2 in the products varies from 40 to 61% mol. The carbon removal degree from lignin at 600 °C was 88.7%. Low portion of CO ($<$ 1.5% mol.) in the products composition is explained by Cao et al. [21] by catalytic effect of alkali on the water gas shift reaction. Note that the maximum carbon removal degree (98.2%) from the alkaline black liquor as a result of SCW gasification was registered by Cao et al. [22] at a temperature of 750 °C, pressure 25 MPa, reaction time 50 min, and BL concentration 2.5% wt.

From the literature data it follows that the conversion of BL mineral components is practically not investigated, and this despite the fact that the conversion of organic and mineral components of BL are interdependent. In this work, the conjugate processes of SCW conversion of organic and mineral components of black liquor at $T \leq 750\,^{\circ}C$ were studied for the first time, and the possibility of alkali regeneration without the use of additional chemical reagents was shown.

2. Experiments

2.1. Experimental procedure

The experiments were conducted using a tubular reactor (volume 10 cm^3, internal diameter 10 mm, length 127 mm), fabricated of stainless steel AISI 321H. The schematic diagram of the experimental setup is shown in Fig. 2. The supercritical water was supplied to reactor

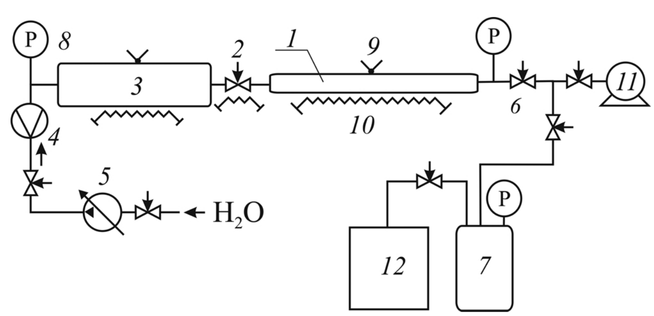

Fig. 2. The schematic diagram of the experimental setup: *1*– reactor; *2* – heated control valve; *3* – heat exchanger; *4* – differential flow meter; *5* – high pressure plunger pump; *6* – control valves; *7* – product collector; *8* – membrane strain gauge; *9* – thermocouple; *10* – resistive heater; *11* – forevacuum pump; *12* – mass spectrometric unit diagnostics.