# Generation of Hydrogen, Lignin and Sodium Hydroxide from Pulping Black Liquor by Electrolysis

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Keywords: Hydrogen, lignin, Energy, electrolysis, black liquor

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Article





# Generation of Hydrogen, Lignin and Sodium Hydroxide from Pulping Black Liquor by Electrolysis

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**Abstract:** Black liquor is generated in Kraft pulping of wood or non-wood raw material in pulp mills, and regarded as a renewable resource. The objective of this paper was to develop an effective means to remove the water pollutants by recovery of both lignin and sodium hydroxide from black liquor, based on electrolysis. The treatment of a 1000 mL of black liquor (122 g/L solid contents) consumed 345.6 kJ of electric energy, and led to the generation of 30.7 g of sodium hydroxide, 0.82 g of hydrogen gas and 52.1 g of biomass solids. Therefore, the recovery ratios of elemental sodium and biomass solids are 80.4% and 76%, respectively. Treating black liquor by electrolysis is an environmentally friendly technology that can, in particular, be an alternative process in addressing the environmental issues of pulping waste liquor to the small-scale mills without black liquor recovery.

Keywords: black liquor; electrolysis; energy; lignin; hydrogen

# 1. Introduction

Black liquor is a wastewater that is generated in pulp mills during Kraft pulping of wood or non-wood raw materials [1]. Black liquor contains approximately 25%–41% lignin [2,3] and 18%–23% sodium [4] and other dissolved organics (hemicelluloses, cellulose, extractives, *etc.*), and inorganics. Due to the presence of large amounts of organics, black liquor can be considered as a renewable resource [5]. In a modern pulp mill, black liquor is processed in the so-called black liquor recovery process [6], where the original thin black liquor is concentrated to 65%–75% (wt %) and is then combusted in a recovery boiler so that the organics are recovered in the form of steam and electricity while the sodium salts are converted to sodium carbonate and sodium sulfide. For small scale operations, for example, those typically found in Asia, the conventional black liquor recovery process is not economic; instead black liquor is treated following standard industrial waste water treatment technologies, such as aerobic and/or anaerobic systems.

Another process to treat black liquor is the gasification technology so that syngas, and other gases are produced. Such a technology has been under development for the past three decades [7]. The process of black liquor gasification feeds black liquor with a 65%–75% solid content and limited amount of oxygen/air into the gasifier, so that a series of reactions lead to the conversion of the black liquor into CO, H<sub>2</sub>, CO<sub>2</sub> and sodium carbonate at high temperatures [8]. Biomass syngas containing CO and H<sub>2</sub> can then be used as the base material to synthesize methanol and dimethyl ether (DME) [9,10] or as a fuel for combustion in a gas turbine to generate power [11]. The generated sodium carbonate is converted into sodium hydroxide via alkalization with slaked lime.

Lignin can be used to generate liquid fuels for internal combustion engines [12,13] and to generate other useful materials [14,15]. One way to utilize lignin for the above is to acidify the black

liquor to pH = 2-4 to precipitate the lignin; subsequently, the wet lignin is obtained by filtering the mixture and then further processed [16].

Treating black liquor by combustion and gasification treatments, sodium hydroxide and heat can be recovered; however, lignin is converted into energy and gas pollutants are discharged using these treatments. Treating black liquor by the acidification treatment, recovering the lignin consumes sulfuric acid and loses sodium hydroxide. To date, no method has been found to fully recover both lignin and sodium hydroxide from black liquor. Therefore, we reported herein our results on the generation of hydrogen, lignin and sodium hydroxide from black liquor using the electrolysis concept.

# 2. Methods and Materials

#### 2.1. Black Liquor

Black liquor with a concentration of 122 g/L of solids and a chemical oxygen demand ( $COD_{Cr}$ ) of 119,198.4 mg/L was obtained from the Guangxi Huajing Co., Ltd. (Nanning, China). The black liquor was generated from gumwood/bamboo by sulfite process containing 18% (wt %) sodium in the dry black liquor solids. By pyrolysis at 700 °C for 5 h, the organic compositions were converted completely, remaining mass of residue accounting for 43.8% of the dry solids. Thereby, the organic components in the dry black liquor are estimated to be 56.2%.

# 2.2. Electrolysis of Black Liquor

The set-up primarily consisted of a cationic electrolytic reactor and a membrane filter, as shown in Figure 1. The cationic electrolytic reactor is the key device in the system [17]; the reactor consisted of a large anode chamber, which is equipped with a cathode plate. A 20 cm<sup>2</sup> cationic exchange membrane (CEM) was used as the separation membrane. The working voltage was 4 V, which produced an average 100 mA of current.





Figure 1. Experimental set-up of the novel black liquor processing system by electrolysis.

The electrolysis reactor is utilized in the chlor-alkali and other industries. In the process of water electrolysis, water (with some added electrolyte) is fed into the reactor, producing hydrogen gas and oxygen gas in the cathode and anode chambers, respectively [18]. In the sodium chloride electrolysis process, saturated salt water is fed into the reactor, generating hydrogen gas and sodium hydroxide in the cathode chamber and chlorine gas in the anode chamber. Here, the electrolysis reactor was utilized to treat black liquor, hydrogen gas, lignin and other organic precipitates were generated in the cathode chamber. A filter was used to remove them from the reactor to maintain the reactor working continually. In addition, the conductivity of diluted black liquor is rather lower; and thereby, it needs greater membrane and plate areas to obtain a suitable production rate.

In comparison with the electrolytic reactor for generating hydrogen fuel from black liquor [19], this black liquor processing system has the following innovations: (1) the space of the electrolytic reactor was separated into a large anode chamber and a cathode plate by a cationic exchange membrane. As a result, besides hydrogen fuel, sodium hydroxide was generated as the main product in the cathode chamber, and the main lignin product was fully precipitated in the anode chamber; (2) the generated hydrogen gas and oxygen gas were generated in the cathode chamber and anode chamber, respectively, and thereby, allowed the generated hydrogen gas be combusted safely; (3) a filter was used to separate the lignin precipitates from the acidified mixture, and thereby, allows the system to work continually.

# 2.3. Description of the Treatment Process

First, 200 mL of black liquor was diluted to 900 mL using the recycled acidic filtrate in beaker 1. Secondly, the diluted solution was fed into the electrolytic reactor 2. In the reactor, NaOH and H<sub>2</sub> were generated in cathode chamber 6; an acidic mixture of different organic acids, lignin and some organic polymers was generated in anode chamber 5. This acidified mixture was filtered by membrane filter 3, yielding wet biomass solids (including lignin and other organic precipitates) and an acidic filtrate. Finally, the acidic filtrate was consequently recycled to dilute new 200 mL black liquor. Operating in 240 h, 1000 mL of black liquor was treated completely, generating as products NaOH, H<sub>2</sub>, and biomass solids and consuming electrical energy. The images of biomass precipitating in the diluted solution were shown in Figure S1 (the Section 1 of the supplementary materials).

## 2.4. Analytical Methods

The sodium hydroxide concentrations were determined via titration with a  $0.1 \text{ M H}_2\text{SO}_4$  solution. The low heat value of the organic polymers was determined using a calorimeter. The mass of the residue solids in the acidified filtrate was tried and weighed.

The mass of hydrogen was determined using an infrared analyzer (Gasboard gas analyzer-3100, Sifang Co., Ltd., Wuhan, China) [3]. First, the hydrogen gas generated in the cathode chamber was collected in a tank under water during electrolysis. The collected gas was diluted to 4 L of total volume with air. Third, the diluted gas was conducted into chamber with dry CaCl<sub>2</sub> powder and cotton to absorb the water in the moisture. And the drying gas was consequently conducted into the infrared analyzer to determine the hydrogen concentration. The volume of hydrogen was determined by multiplying the concentration and the diluted volume, and the mass of hydrogen was determined by multiplying the hydrogen gas volume and its density.

The <sup>1</sup>H-Nuclear Magnetic Resonance (<sup>1</sup>H-NMR) analysis were carried out on an AVANCE III HD 600 MHz instrument (Bruke, Karlsruhe, Germany), using DMSO and TMS as solvent and reference, respectively. A Fourier Transform Infrared Spectrometer (FTIR) instrument (Nicolet IS 50, Thermo Fisher Scientific, Waltham, MA, USA), was used for analysis. Each powdered sample was mixed with KBr, and the mixture was pressured in a mould to get a sample plate. Then the sample plates were analyzed in the range of 4000–300 cm<sup>-1</sup>.

# 3. Results

# 3.1. Identification of Main Products

As presented in Table 1, treatment of 1000 mL (122 g/L of solids) black liquor from the process described above, led to the generation of 52.10 g of dry biomass solids, 30.70 g of sodium hydroxide and 0.82 g hydrogen gas. There were still 33.63 g of residual solids remaining in the acidified filtrate, and there were other amounts of gaseous and volatile compounds released from the system, including  $CO_2$ ,  $O_2$ , methanol, ethanol, formic acid, *etc.* The numbers in Table 1 were obtained by averaging three trials; the recovery ratios of elemental sodium and biomass are 80.4% and 76%, respectively. The detail calculations were shown in the Section 2 of the supplementary materials, and the reaction of gaseous and volatile compounds generated were shown in Section 3 of the supplementary materials.

Masses (g)
30.70
0.82
52.10
33.63

Table 1. Masses of products from 1000 mL black liquor.

#### 3.2. Energy Balance in Treating 1000 mL of Black Liquor

Figure 2 shows the energy conversions involved in treating 1000 mL of black liquor. In this process, the energy inputs were: 345.6 kJ of electrical energy and 1573.8 kJ of heat of the black liquor; while the outputs were: 1239.49 kJ and 117.2 kJ of the heats of biomass solid and hydrogen gas, respectively, and 526.71 kJ of the residual solids. Determined by a calorimeter, a 23.79 kJ/g of the low heat value of biomass solid was obtained and used in the heat calculation. The detail calculations were shown in the Section 4 of the supplementary materials.



Figure 2. Energy balance involved in treating 1000 mL of black liquor.

The electric energy consumption for hydrogen generation under the studied conditions was  $117.07 \text{ kWh/(kg H_2)}$ , which was significantly higher than  $45 \text{ kWh/(kg H_2)}$  in the water electrolysis for hydrogen [20]. The higher electric energy consumption was due to the higher working voltage used to obtain a high production rate in this study. Additionally, the ratio between the heat of the generated biomass and the heat of black liquor was 78.8%.

# 3.3. Investigation of the Composition of the Biomass Solids

#### 3.3.1. Generated Biomass Solids

Tested by ashing and weight, the generated biomass solids contained 0.32% of ash. Figure 3 is the FTIR spectrums of biomass solids, lignin and the precipitates from the acidic filtrate. Shown in Figure 3a is the FTIR spectrums of the generated biomass. Where, the character absorption peaks of lignin at 1512.94 cm<sup>-1</sup> and 1603.14 cm<sup>-1</sup> were presented. Thereby, the generated biomass solids contain lignin can be identified. Besides the character absorption peaks of lignin, there are character absorption peaks at 3396.45 cm<sup>-1</sup>, 2922.22 cm<sup>-1</sup> and 1459.30 cm<sup>-1</sup>, corresponding to the groups of –OH, –CH and –CH<sub>2</sub>, respectively.



**Figure 3.** Fourier Transform Infrared Spectrometer (FTIR) spectrums of biomass solids (**a**); lignin (**b**) and the precipitates from the acidic filtrate (**c**).

Figure 4 shows the <sup>1</sup>H-NMR spectra of biomass solids, lignin and the precipitates from the acidic filtrate. Shown in Figure 4a is the <sup>1</sup>H-NMR spectrum of the generated biomass, where, the characteristic absorption peaks of bamboo lignin at 2.51 ppm, 3.31 ppm and 3.75 ppm are present. Thereby, the presence of lignin in the generated biomass solids contain was confirmed. The absorption peaks at 1.27 ppm were assigned to  $-CH_3$  groups, and the peaks at 2.51 ppm were assigned to  $-CH_2$ . The absorption peaks at 3.31 ppm and 3.83 ppm were assigned to -CH groups on the benzene ring. The absorption peaks at 6.4–7.53 ppm, correspond to the -OH groups.

![](_page_6_Figure_2.jpeg)

**Figure 4.** <sup>1</sup>H-Nuclear Magnetic Resonance (<sup>1</sup>H-NMR) spectra of biomass solids (**a**); lignin (**b**) and the precipitates from the acidic filtrate (**c**).

#### 3.3.2. Precipitated Lignin

Additional experiments were performed to further investigate the mass of lignin containing in the generated biomass solids. 1000 mL of the black liquor was diluted to 2000 mL of solution, which was consequently acidified with 0.1 M sulfuric acid, yielding 39.8 g of lignin and 2000 mL of acidic filtrate. Thereby, the biomass solids generated by electrolysis was regarded as containing 39.8 g of lignin. Besides lignin, there was 12.3 g of other organic precipitates contained in the biomass solids. Shown in Figure 3b is the FTIR spectrum of the lignin precipitated by sulfuric acid. Besides the characteristic absorption peaks of lignin at 1513.66 cm<sup>-1</sup> and 1603.25 cm<sup>-1</sup>, there are characteristic absorption peaks at 3396.35 cm<sup>-1</sup>, 2921.99 cm<sup>-1</sup> and 1459.16 cm<sup>-1</sup>, corresponding to the –OH, –CH and –CH<sub>2</sub> groups, respectively. Shown in Figure 4b is the <sup>1</sup>H-NMR spectrum of the lignin precipitated by sulfuric acid, presenting the absorption peaks of bamboo lignin at 1.25 ppm, 2.51 ppm, and 3.31 and 3.75 ppm. As mentioned ahead, those peaks were assigned to the –CH<sub>3</sub>, –CH<sub>2</sub>, and –CH groups, respectively.

#### 3.3.3. Other Organic Precipitates

Additional experiments were performed to further investigate the generation of the other organic precipitates. After removed lignin by filtration, the remaining 2000 mL of acidic filtrate was fed into the electrolytic reactor and electrolyzed for 96 h. As a result, precipitates were formed, yielding 12.3 g of dry residue solids. Thereby, the generated biomass solids contained 12.3 g of other organic precipitates that can be identified. Shown in Figure 3c is the FTIR spectrum of the organic precipitates generated from the acidic filtrate. There are mainly characteristic peaks at 1512.80 cm<sup>-1</sup> and 1602.75 cm<sup>-1</sup>, corresponding to the small units of lignin, thereby, we conclude that the precipitates generated from the acidic filtrate contain small lignin units. Shown in Figure 4c is the <sup>1</sup>H-NMR spectrum of the organic precipitates generated from the acidic filtrate spentrate from the acidic filtrate spentrate from the acidic filtrate spentrate from the acidic filtrate spentrate. They contained small lignin units, and thereby, its <sup>1</sup>H-NMR contained the characteristic absorption peaks of bamboo lignin at 2.50 ppm, 3.34 ppm. However, the peak at 1.25 ppm assigned to  $-CH_3$  groups was much smaller and the peak at 3.75 was absent, indicating that the structure of the organic precipitates from the acidic filtrate was somewhat different from that of the lignin precipitated by sulfuric acid and the precipitates obtained by electrolysis. The organic proverized and precipitated from the acidified filtrate were shown in the Section 5 of the supplementary materials.

#### 3.4. Investigation of the Working Mechanisms of Black Liquor Electrolysis

As shown in Figure 5, the working mechanisms of black liquor electrolysis are described as follows.

![](_page_7_Figure_8.jpeg)

Anode chamber; 6. Cathode chamber; 7. Anode plate;
Cathode plate; 9. Cationic exchange membrane.

Figure 5. Working mechanisms of black liquor electrolysis.

Black liquor contains sodium lignin and sodium salts of organic acids (NaA), such as sodium form acid and acetate. The sodium lignin dissociates to Na<sup>+</sup> and lignin anion (lignin<sup>-</sup>), and the sodium salts of organic acids dissociate to Na<sup>+</sup> and organic acidic anions (A<sup>-</sup>) in solution. Selective blocking by the cationic exchange membrane prevented the organic acidic ions from penetrating the membrane, while the Na<sup>+</sup> can penetrate the membrane and transfer into the cathode chamber [21]. In the cathode chamber, the dissociated H<sup>+</sup> ions accept electrons and become hydrogen gas when they touched the cathode [22]; and the remaining –OH combines with the incoming Na<sup>+</sup> to form sodium hydroxide. In the anode chamber, the dissociated –OH ions lose electrons and become oxygen gas and water upon contacting with the anode [23]; and the remaining H<sup>+</sup> ions combine with the remain inorganic acidic ions (A<sup>-</sup>) to generate organic acids (HA) [22]. The reactions of sodium hydroxide and lignin generation are expressed as Equations (1)–(8). The generation of organic acid led to the lignin precipitation, which mechanisms are shown as Figure 6.

![](_page_8_Figure_2.jpeg)

Figure 6. Mechanisms of lignin precipitating in the process of black liquor electrolysis.

The following reactions occur in the cathode chamber:

$4H_2O \rightarrow 4H^+ + 4^-OH$	(1) (Water ionization)
$4^-OH-4e^- \rightarrow 2H_2O+O_2 \uparrow$	(2) (Anode reaction)
$NaA \rightarrow Na^+ + A^-$	(3) (Ion-dissociation reaction)
$\mathrm{H^{+}} + \mathrm{A^{-}} \rightarrow \mathrm{HA}$	(4) (Ion-binding reaction)
$HA + Na\text{-lignin} \rightarrow H\text{-lignin} \downarrow + NaA$	(5) (Ion-binding reaction)

The following reactions occur in the cathode chamber:

$$\begin{array}{ll} 4H_2O \rightarrow 4H^+ + 4^-OH & (1) \text{ (Water ionization)} \\ 4H^+ + 4e^- \rightarrow 2H_2 \uparrow & (6) \text{ (Cathode reaction)} \\ 4Na^+ + 4^-OH \rightarrow 4NaOH & (7) \text{ (Ion-binding reaction)} \end{array}$$

The net reaction for the electrolytic reactor is as follows:

Na-lignin + NaA + 
$$4H_2O \rightarrow 2NaOH + H$$
-lignin + HA +  $H_2 \uparrow + O_2 \uparrow$ 

(8)

# 4. Discussion

Treating black liquor by electrolysis consumes rather large amounts of electric energy, and thereby increases the electric energy consumption cost of a pulp mill. However, compared to combustion [6] and gasification [24], treating black liquor via electrolysis has the following advantages: (1) no need to concentrate the thin black liquor, which reduces the enormous amount of energy that is consumed during water evaporation; (2) no lime is consumed in the NaOH regeneration process, thereby, eliminating the energy intensive lime cycle, together with the necessary solid residue disposal system; (3) reduced emissions of  $CO_2$  gas and other poisonous gases [7]; (4) large-scale generation of lignin, which has potential to be converted into bioenergy and bio-materials [13,25,26]; (5) in addition to lignin, other organic components in the solution are recovered via polymerization, thereby reducing the amount of organic pollutants discharged.

Based on the numbers in Figure 2, the electric consumption for treating 1 m<sup>3</sup> of black liquor is 96 kWh that costs about \$9.6 USD. The generated NaOH is about 30.7 kg that is worth about \$10.7 USD. Besides the NaOH, 52.1 kg of biomass solid and 0.82 kg of hydrogen are obtained at the same time; those two products are worth about \$11.2 USD. Therefore, although only 80.4% of NaOH was recovered, treating black liquor by electrolysis might be economically feasible. The detail economic calculations were shown in the Section 6 of the supplementary materials.

The black liquor electrolysis process has lots of potential: (1) the conventional black liquor recovery process in pulp mills discharges large amounts of solid, liquid and gaseous wastes that have a significant environmental impact on the surrounding areas [27], therefore, it is desirable to develop an alternative technology for processing black liquor; (2) the overall energy efficiency of the black liquor electrolysis process is much better than the conventional black liquor process via evaporation, combustion and the lime cycle; (3) treating black liquor by electrolysis generates biomass solids including lignin and other organic precipitates that can be converted to biofuels to substitute fossil fuels to reduce the  $CO_2$  emissions, and thereby benefit the environment [28]; (4) treating black liquor by electrolysis might be fitting to treat the black liquor generated from wheat straw, and the black liquor in a small-scale pulp mill, which get not allow good economic efficiency by installation of general recovery boilers.

## 5. Conclusions

A new black liquor treating system based on the electrolysis concept was studied. The main products were lignin sodium hydroxide, and hydrogen gas. Under the conditions studied, 1000 mL of black liquor (122 g/L solid content) led to the generation of 30.7 g of sodium hydroxide, 52.1 g of biomass solids (containing 39.8 g of lignin and 12.3 g of polymers) and 0.82 g of hydrogen gas, while consuming a total of 345.6 kJ of electrical energy. Therefore, the recovery ratios of elemental sodium and biomass are 80.4% and 76%, respectively. Treating black liquor via electrolysis is an environmentally friendly technology and represents an alternative technology that should be useful in addressing the environmental issues of the future.

Supplementary Materials: The following are available online at www.mdpi.com/1996-1073/9/1/13/s1.

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**Author Contributions:** G.N. involved in the new ideal, spectrum analysis and manuscript preparation. S.W. involved in the device preparation. Z.Z. involved in preparation, determination and analysis of products. All authors reviewed the manuscript.

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![](_page_11_Picture_8.jpeg)

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