Supplementary Materials: Generation of Hydrogen, Lignin and Sodium Hydroxide from Pulping Black Liquor by Electrolysis

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1. Biomass Precipitating from Black Liquor

A 200 mL of the black liquor was diluted to 900 mL water solution, and then the diluted solution was fed into the electrolytic reactor. After operated for 48 h, the diluted solution become acidic with pH = 4–5, and lead to biomass precipitating. And thereby, approximately 900 mL of initial acidic filtrate was obtained by filtering. Figure S1 shows the biomass precipitating in the diluted solution by electrolysis.

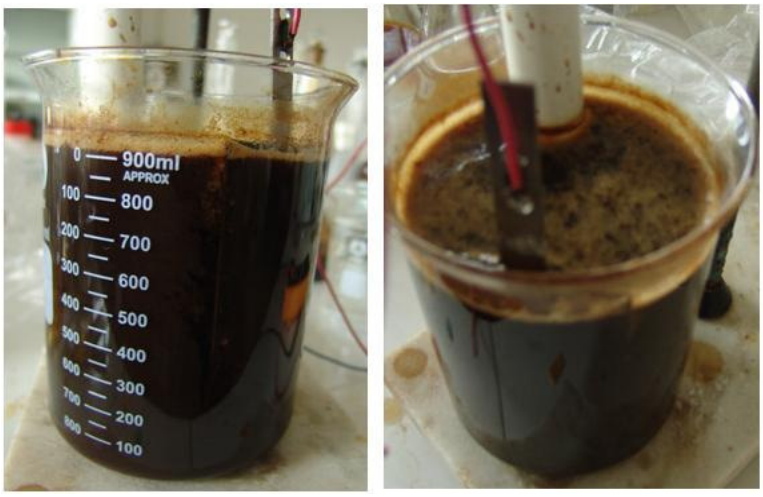

Figure S1. Biomass precipitating in the diluted solution by electrolysis

2. Detail Calculation on the Recovery Ratios of Sodium Element and Biomass

(1) Recovery ratio of sodium element

The recovery ratio of sodium element (r_{Na}) is the mass of sodium element containing in the recovered sodium hydroxide ($M_{Na,\ re}$) divided by the mass of sodium element containing in the original black liquor ($M_{Na,\ BL}$).

$$r_{Na} = M_{Na,\ re}/M_{Na,\ BL}$$
$$= (30.4 \times 23/40)/(122 \times 18\%)$$
$$= 0.804$$
$$= 80.4\%$$

(2) Recovery ratios of biomass

The recovery ratio of biomass (r_{bi}) is the mass of biomass recovered ($M_{bi,\ re}$) divided by the mass of biomass containing in the original black liquor ($M_{bi,\ BL}$).

$$r_{bi} = M_{bi,\ re}/M_{bi,\ BL}$$
$$= 52.1/(122 \times 56.2\%)$$
$$= 0.760$$
$$= 76\%$$

Where, the 56.2% is the ratio of biomass containing black liquor.

3. Consideration of Gaseous and Volatile Compounds Release to the Air

There might be some other masses of gaseous and volatile compounds release to the air, including CO_2, O_2, methanol, ethanol and formic acid, ect. Where, the CO_2 was converted from the reactions of Sodium carbonate acidification and anode oxidation, expressed as Equations (1) and (2). The O_2 was converted from water by anode oxidation, expressed as Equations (3) and (4). And the formic acid was converted from the reactions of Sodium formic acid by acidification, expressed as Equation (5). And the methanol and ethanol might be generated from wood in the time cooking and was contained in the original black liquor.

$$NaCO_3 + 2H^+ \rightarrow 2Na^+ + H_2O + CO_2 \uparrow \quad (1)$$

$$\text{Substrate} - 4e^- \rightarrow aH_2O + bCO_2 \uparrow \quad (2)$$

$$4H_2O \rightarrow 4H^+ + 4^-OH \quad (3)$$

$$4^-OH - 4e^- \rightarrow 2H_2O + O_2 \uparrow \quad (4)$$

$$HCOONa + H^+ \rightarrow Na^+ + HCOOH \quad (5)$$

4. Detail Calculation on Energy Conversions

(1) Electrical energy consumption in treating black liquor

Working in condition of 4 V voltage and average 100 mA for 240 h, the electric energy consumption (E_{ec}) was calculated as following:

$E_{ec} = V \times I \times t$
= 4 V × 0.1 A × 240 × 3600 s
= 345600 J
= 345.6 kJ

(2) Heat of black liquor

H_{BL}= 1000 mL × 1 g/mL × 12.2% × 12.9 kJ/g
= 1573.8 kJ

(3) Heat of biomass solids

H_{bs} = 52.1g × 23.79 kJ/g
= 1239.5 kJ

(4) Heat of hydrogen fuel

H_{H2} = 0.82 g × 142.90 kJ/g
= 117.2 kJ

(5) Residue heat of reactor

$H_{residue,\ reactor} = (H_{BL} + E_{ec}) - (H_{bs} + H_{H2})$
= (1573.8 + 345.6) – (1239.5 + 117.2)
= 526.7 kJ

(6) The energy efficiency of hydrogen generation

$E_{e,\,H2} = E_{ec}/M_{H2}$

$= 345.6\ kJ/0.82\ g$

$= 421.46\ kJ/g$

$= 117.07\ kWh/(kg\ H_2)$

(7) The ratio between the heats of biomass solid and black liquor

$R = H_{BS}/H_{BL}$

$= 1239.49\ kJ/1573.8\ kJ$

$= 78.8\%$

5. Organic Polymerized and Precipitated from the Acidified Filtrate

The 2,000 mL of acidic filtrate (Figure S2a) was fed into the special electrolytic reactor and electrolyzed for 96 h. As a result, the organic components in the acidic filtrate were polymerized and became a mixture including electrolytic precipitates and solution (Figure S2b). Next, that mixture was filtered to obtain 12.3 g of dry residue solids (Figure S2c).

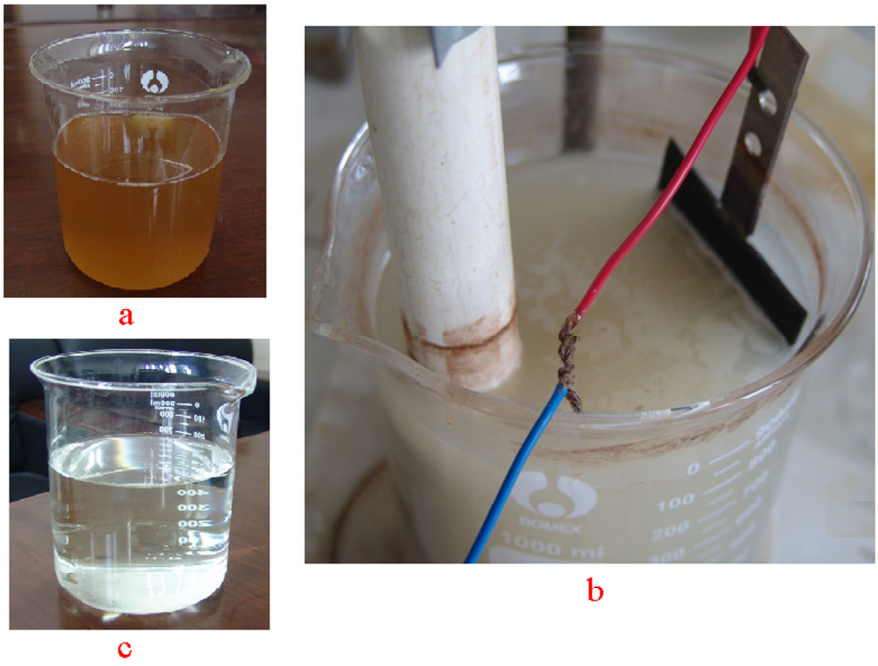

Figure S2. Organic compounds polymerized during electrolysis (**a**: the original acid filtrate; **b**: mixture; **c**: the final acid filtrate separated from the mixture).

6. The Detail Economic Calculation for Treating 1 m³ Black Liquor

Base on the digits in Table 2, the electric consumption for treating 1 m³ of black liquor is 96 kWh, which is worth about 9.6 dollar, provided the cost of electric energy being 0.1 dollar/kWh. The generated NaOH is about 30.7 kg; which is worth about 10.7 dollar, provided the cost of NaOH being 0.35 dollar/kg. The 52.1 kg of biomass solid is worth 10.4 dollar, provided the cost of 0.2 dollar/kg. And 0.82 kg of hydrogen is worth 0.82 dollar, provided cost of 1 dollar/kg.