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Hydrogen Production by Supercritical Water Gasification of Alkaline Black Liquor

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1 Introduction

Black liquor (BL) is a large pollution resource to the environment; it mainly contains alkali wastes, lignin and its derivatives which is hard to degrade. Tomlinson recovery progress is the main method to treat black liquor in the world in nowadays and has 80 years long usage history, but it still has some weaknesses, such as the low efficiency and some safety and environmental problems [1-3]. Supercritical water gasification (SCWG) is an innovative thermo-chemical method for converting biomass and organic wastes into hydrogen-rich gaseous products. SCWG of black liquor has several advantages, for example, compared with other biomass gasification technologies such as air gasification and steam gasification, SCWG can directly deal with the wet biomass without drying. For black liquor always contains above 80 % moisture, SCWG can be much more efficient than other gasification technologies. On the other hand, the alkali salt contained in black liquor is reported to be a kind of effective catalyst for SCWG, which can promote water-gas shift reaction in supercritical water and increase the H₂ content of the gaseous product and decrease the CO content [4-7].

There is no report on SCWG of black liquor in large scale continuous type reactors so far. In present work, we conducted the experiments of black liquor SCWG in a continuous SCWG system developed in State Key laboratory of Multiphase Flow in Power Engineering (SKLMF). The influence of the main operating parameters and the distribution of alkali metal were investigated, a kinetic equation for COD (chemical oxygen demand) removal in SCWG was also achieved in this work.

2 Experimental

The black liquor from wheat straw soda pulping process was achieved from Hanxing paper mill in Shaanxi province of China, and the air-dried basis (a. d.) content of the black liquor is 9.5 %. The results of proximate and ultimate analysis, the heating value and pH value of the black liquor were listed in table 1.

Table 1: The properties of black liquor (a. d.).

Ultimate analysis (% , a. d.)					Proximate analysis (% , a. d.)				LHV (MJ/Kg)	pH
C	H	O	N	S	M	A	V	FC		
33.43	2.77	32.86	0.23	0.13	3.2	27.38	49.32	20.1	11.30	11.3

The experiments were conducted in a continuous SCWG system developed in SKLMF. In this system, quick heating rate of black liquor can be realized by mixing with the preheated

water before the reactor, and thus can advance the SCWG [4, 8]. The temperature was controlled by a PID temperature control system and the temperature deviation was ± 5 °C. The fluid temperature in the reactor was measured by K-type thermocouples as the reaction temperature. The detailed description of this system can be found in our previous paper [9].

The gaseous products were analyzed in Agilent 7890A gas chromatograph with a thermal conductivity detector. The sodium content, COD(chemical oxygen demand) concentration and pH value of the aqueous samples were determined by ICP-AES, spectrophotometer method and glass electrode method respectively.

3 Results and Discussion

3.1 The influence of operating parameter

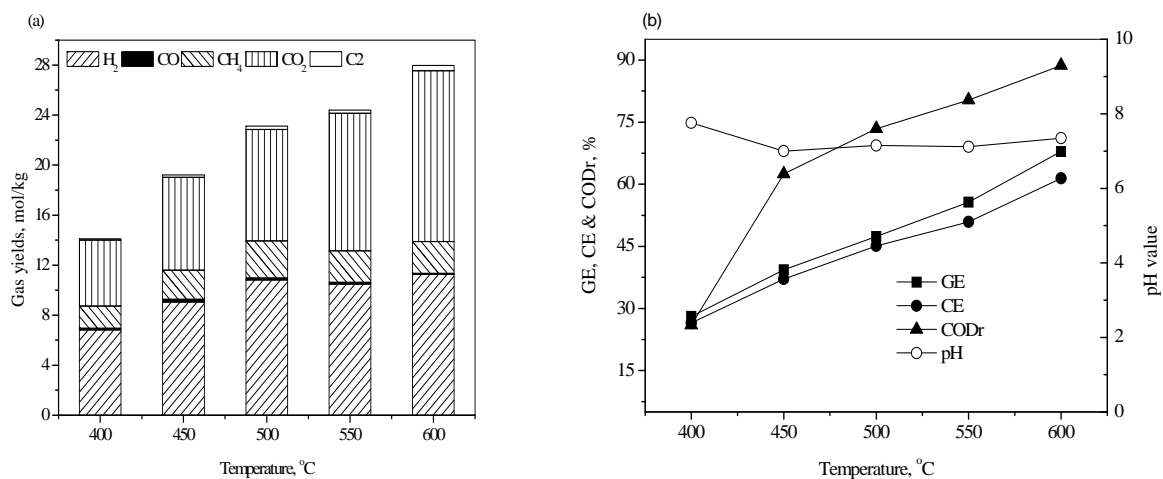


Figure 1: The influence of the temperature on black liquor SCWG (25 MPa, 5 kg/h, 9.5 %BL).

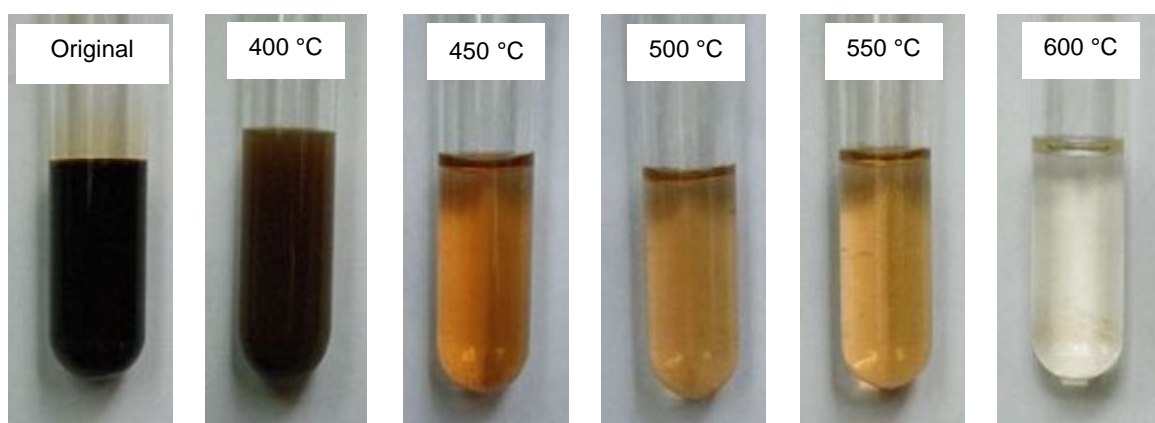


Figure 2: The photos of original BL and liquid residue at different reaction temperatures (25 MPa, 5 kg/h, 9.5 %).

The influence of temperature in the range of 400 °C–600 °C on SCWG of black liquor was investigated in the pressure of 25 MPa, the flow rate of 5 kg/h and the 9.5 % black liquor concentration. It can be seen from fig.1 that with the temperature increasing from 400 °C to 600 °C, the total gas yield, gasification efficiency, carbon gasification efficiency and COD removal efficiency increased from 14.1 mol/kg, 28.05 %, 26.5 %, and 25.97 % to 27.97 mol/kg, 67.89 %, 61.45 % and 88.69 % respectively. These results showed that temperature is a key operating parameter for black liquor SCWG and the increase of temperature can significantly enhance the gasification process.

Fig.2 shows the photos of original black liquor and the liquid residue at different reaction temperatures. It can be seen in fig.2 that the color of liquid residue after SCWG was much lighter than the black liquor. The color became lighter in higher reaction temperature and in 600 °C, the liquid residue became very clear. The pH values of the liquid residue were all decreased and close to neutral which is in the range of 7~7.8, which indicated that SCWG can weaken the alkalinity of black liquor and reduce its environmental contamination.

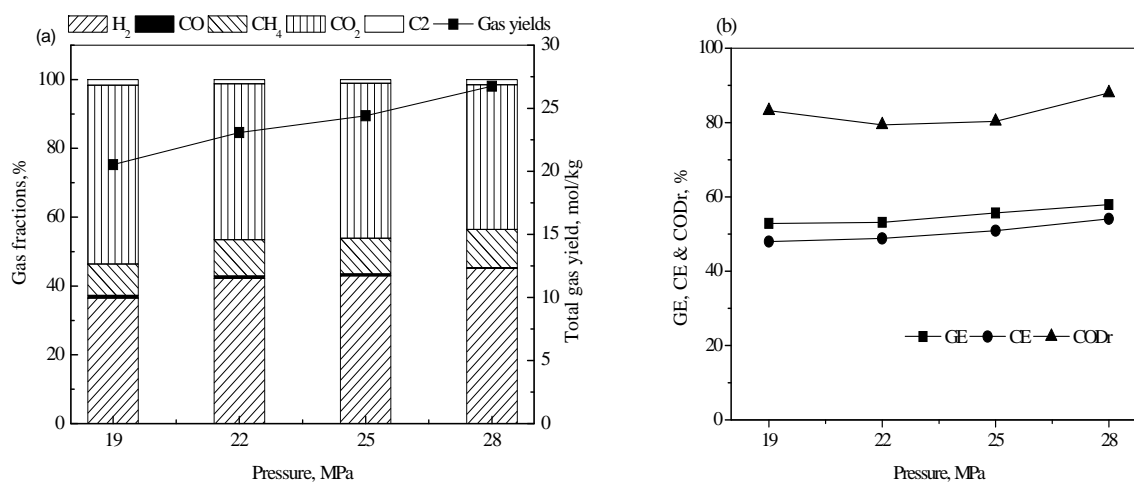


Figure 3: The influence of the pressure on black liquor SCWG (550 °C, 5 kg/h, 9.5 % BL).

The influence of pressure in the range of 19-28 MPa on black liquor SCWG was investigated. The results are shown in fig.3. It can be seen that with the pressure increased from 19 MPa to 28 MPa, the gas fractions of the gaseous products had no significant change. The total gas yield, the gasification efficiency and carbon gasification efficiency only increased slightly. The similar result was reported by Demirbas [10] in SCWG of fruit shell. He suggested that increasing of pressure increased the mass transfer and solvent diffusion rates of water and thus increased the efficiency of the SCWG.

The investigation of the influence of flow rate on supercritical water gasification of black liquor was done in the temperature of 500 °C, the pressure of 25 MPa and the black liquor concentration of 9.5 %. As shown in fig.4, with the flow rate increased from 3 kg/h to 7 kg/h, the total gas yield, the gasification efficiency and the COD removal efficiency decreased from 24.96 mol/kg, 54.05 % and 83.56 % to 20.97 mol/kg, 42.5 % and 70.84 % respectively, while the fractions of the gaseous products had no apparent change with the variation of the flow rate. From the results above, we inferred that SCWG has two steps: (1) the decomposition of

the feedstock and the production of original gases; (2) the reactions between the original gases which can change the composition of the gaseous product. From the above results, we speculated that it need longer residence time to complete step (1), while the reactions in step (2) were so quick that they were not influenced by the change of the residence time. So with longer residence time, which is corresponding to the smaller flow rate, more gases were produced while the composition had no apparent change with the flow rate.

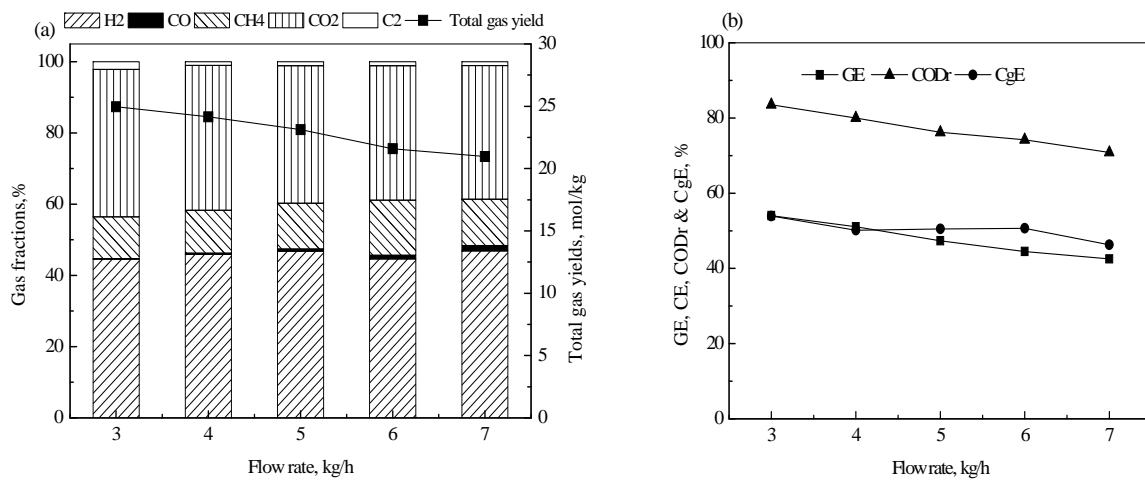


Figure 4: The influence of flow rates on black liquor SCWG (500 °C, 25 MPa, 9.5 % BL).

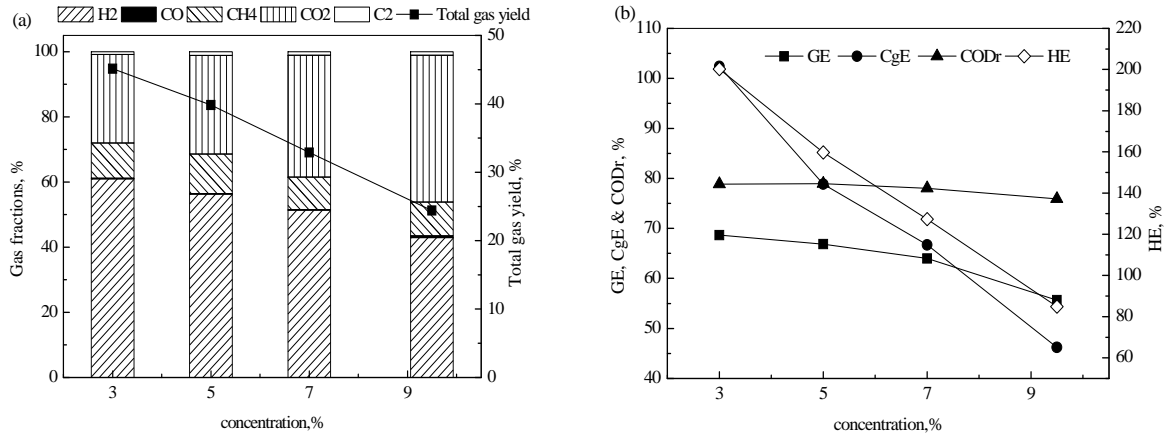


Figure 5: The influence of concentrations on black liquor SCWG (550 °C, 25 MPa, 5 kg/h).

The different concentrations of black liquor were achieved by diluting the primary black liquor with calculated amounts of de-ionized water and gasification at the same experimental condition (550 °C, 25 MPa, 5 kg/h). The results are shown in fig. 5. When the feed concentration decreased from the primary concentration (9.5 %) to 3 %, the fraction of H₂ in the gaseous product increased from 42.95 % to 61.02 %. The total gas yield almost doubled from 24.41 mol/kg to 45.15 mol/kg, the gasification efficiency increased from 55.67 % to 68.66 %, and the hydrogen gasification efficiency increased from 84.9 % to 200.23 %. All these results indicated that the dilution of the black liquor favours SCWG. It is also shown in fig.5 that the hydrogen gasification efficiencies were all above 100 % with the concentration

below 7 %. We attributed these results to the participation of water in the reaction and some of the hydrogen in the gaseous product come from the water.

3.2 The distribution of alkali metal

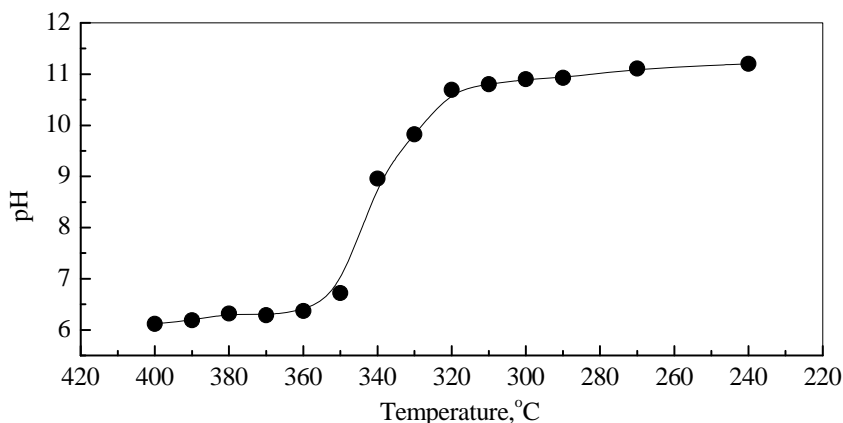


Figure 6: pH values of the effluent in the cooling progress after the complete of experiment.

In the cooling process after the reaction, it was found that as the fluid was cooled to below 360 °C, the pH value of the effluent increased and reached around 11 below 320 °C. The sodium content of the cooling effluent at the temperature of 330 °C examined by ICP-AES is 3165.5 mg/L while that of the liquid residue is 29.4 mg/L in the reaction progress. This result is supposed to be corresponded with the solubility of water around the critical point. As reported by J. W. Tester [11], supercritical water at low density is a poor solvent for ionic species like inorganic salts. We speculated that the sodium salt was condensed in the reactor in reaction process. When the temperature decreased in the cooling process, the sodium salts dissolved in the water and flowed out with the water. So the pH value increased with the decreasing of the temperature.

3.3 Kinetic study of black liquor SCWG

Pseudo first-order reaction was assumed for the COD removal in SCWG and confirmed by the reaction results at the reaction temperatures of 450 °C, 475 °C, 500 °C, 550 °C. The reaction rate constants at different temperatures were obtained by the least squares fitting method and they were in the range of 0.04-0.23 S⁻¹ at the temperatures of 450 °C~550 °C. With the reaction rate constant in different temperature, the activation energy and the pre-exponential factor were calculated and they are 74.38±6.02 kJ/mol and 10^{4.05±0.41}S⁻¹ respectively, so the Arrhenius equation of black liquor SCWG can be described as below:

$$k=10^{4.05\pm 0.41} \exp(74.38\pm 6.02 /RT) (s^{-1}) \tag{1}$$

4 Summary

Black liquor was gasified continuously in supercritical water successfully and the main gaseous products were H₂, CO₂ and CH₄ with little amount of CO, C₂H₄ and C₂H₆. The increase of the temperature and the decrease of the flow rate and black liquor concentration enhanced SCWG of black liquor. The change of the system pressure had limited influence on the gasification effect. The maximal COD removal efficiency of 88.69 % was obtained at the temperature of 600 °C. The pH values of the aqueous residue were all decreased to the range of 6.4~8 while the pH value of cooling effluence below 360 °C increased to about 11 and the sodium content was much higher than that in the aqueous residue. The reaction rate for COD degradation in supercritical water was obtained by assuming pseudo first order reaction. And the activation energy and pre-exponential for COD removal in SCWG were 74.38kJ/mol and $1.11 \times 10^4 \text{ s}^{-1}$ respectively.

Acknowledgements

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Nomenclature

GE: gasification efficiency, the mass of product gas/the mass of BL, %

CE: carbon gasification efficiency, the carbon in product gas/the carbon in BL, %

CODr: COD removal efficiency, 1-COD concentration in liquid residue/COD concentration in BL, %

CgE: cold gas efficiency, LHV of product gas/LHV of BL, %

HE: hydrogen gasification efficiency, the hydrogen in product gas/the carbon in BL, %

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