Asian Journal of Chemistry; Vol. 26, No. 23 (2014), 8115-8117

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2014.17585

Treatment Process for Phenolic Wastewater

WEIPING LI[1,*], PEIJIANG HAN[1], YIRAN SHI[1], FANG HE[2], HAOJIE DUAN[1] and PEIFENG YANG[1]

[1]School of Energy and Environment, Inner Mongolia University of Science and Technology, Baotou, P.R China
[2]Research and Development Center of Herb's Resources Corp., Chongqing 401346, P. R. China

*Corresponding author: Tel/Fax: +86 472 5951569; E-mail: zhaotiantao2015@163.com

Received: 11 March 2014; *Accepted*: 26 May 2014; *Published online*: 15 November 2014; AJC-16307

Hydrogen production from waste using supercritical water gasification (SCWG) is a promising approach towards cleaner fuel production and a solution for hard to treat wastes. In this paper, the catalytic gasification of phenolic wastewater was investigated in a batch reactor at 26-34 MPa, 510-550 °C, residence time of 2-5 min. The results showed that the main gas products were H_2, CO, CO_2 and CH_4. When residence time was 5 min, temperature is 550 °C, hydrogen gasification ratio reached up to 135 %. Supercritical water gasification was proved to be an efficient technology for phenolic wastewater treatment.

Keywords: Treatment, Phenolic wastewater, Supercritical water gasification.

INTRODUCTION

Phenol and phenolic compounds are of widespread use in many industries, such as polymeric resin production and oil refining. As a result, these compounds are commonly encountered in industrial effluents and surface water[1]. Because of their toxicity to human and marine life, increasingly stringent restrictions have been imposed on the concentrations of these compounds in the wastewater for safe discharge. In Taiwan, for instance, the phenol concentration in the industrial wastewater for safe discharge has been reduced from 2 to 1 mg/L due to health consideration. Hence, treatment of industrial wastewater containing phenolic compounds is a necessity[2].

Supercritical water gasification (SCWG) is a novel biomass conversion technology and can convert biomass into hydrogen-rich gas. For the unique properties of water above its critical point (22.1 MPa, 374.2 °C), SCWG has many advantages *e.g.*, (1) the homogeneous reaction environment can be formed in SCWG because most organics and gases can be dissolved in supercritical water. This can reduce the mass transfer resistance and improve the reaction rate. (2) Supercritical water gasification is more suitable for the treatment of high-moisture biomass or organic waste because no drying process is needed in this technology. (3) No hazardous emission, such as NOx, SO_2 and fine particles is formed from the gasification, even when the feedstock contains nitrogen and sulfur elements[3,4]. As a result, SCWG attracted much attention around the world. Considerable development and progress have been made in the last decades, which can be referred in some recent researches[5-15].

In this study, SCWG was applied to treat phenolic wastewater in a 0.6 L batch autoclave under the experimental conditions of 24-36 MPa, 510-550 °C and residence time of 2 to 5 min. The present study reports on the operational features of SCWG for carbon gasification ratio (R_{CG}), hydrogen gasification ratio (R_{HG}).

EXPERIMENTAL

All the experiments were performed in a batch reactor. As shown in Fig. 1, the apparatus includes feed system, preheater, reactor, condenser, gas-liquid separator and backpressure regulator. Supercritical water gasification of phenolic wastewater was carried out in a 0.6 L batch autoclave. Firstly, water and phenolic wastewater (concentration was 2500 mg/L) was put into the reactor and then the system was flowed by nitrogen to remove the air within the system; the valves around the reactor were closed when the air was removed entirely. Liquid samples (about 20 mL) were periodically withdrawn from the reactor and analyzed.

Chemical analysis: The gas samples were analyzed according to ASTM D1946-2011, ASTM D2597-2010 and DIN 51872-4-1990 methods, through a Perkinelmer Clarus 680 model GC coupled with two TCD and one FID detectors.

Two parameters, carbon gasification ratio (R_{CG}), hydrogen gasification ratio (R_{HG}) will be discussed as the measure of organic compound destruction and gasification efficiency in the SCWG of phenolic wastewater. The R_{CG} and R_{HG} are defined as eqn. 1 and 2.

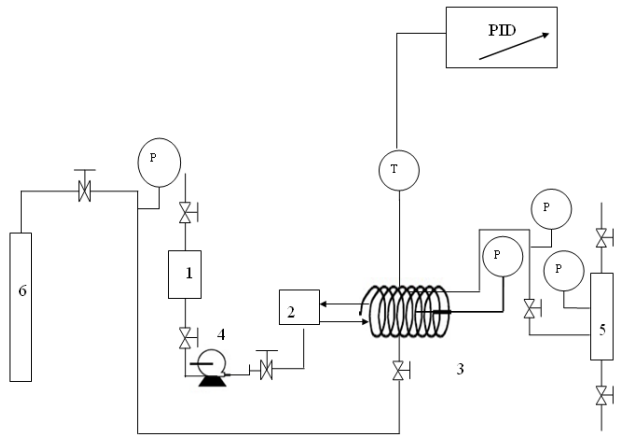

Fig. 1. Schematic diagram of the experimental setup. 1. Oxidant container 2. Heater 3. High-pressure autoclave 4. High pressure pump 5. Gas-liquid separator 6. Nitrogen cylinder

$$R_{CG} = \frac{C_{PG}}{C_{OC}} \times 100\ \% \quad (1)$$

$$R_{HG} = \frac{H_{PG}}{H_{OC}} \times 100\ \% \quad (2)$$

where, C_{PG} is the carbon amount in the gas product; C_{OC} is carbon amount in organic compounds, H_{PG} is the hydrogen amount in the gas product; H_{OC} is the hydrogen amount in organic compounds.

RESULTS AND DISCUSSION

Effect of pressure on phenolic wastewater gasification: The effect of pressure on phenolic wastewater gasification was investigated under the conditions of 520 °C, 3 min and 26 MPa. As it is shown in Fig. 2, changing the reaction pressure had no significant influence on R_{CG} and R_{HG} and this has been proved by many researchers. Boukis *et al.*[16] confirmed that the pressure variation during 25-45MPa had no evident effect on the gas composition and conversion at 873 K and 15 s in the course of SCW reforming methanol. Antal *et al.*[17] found that an increase in pressure from 28-34.5MPa had no significant effect on the gas composition or yields by investigating the gasifi-cation of sugarcane bagasse in a cornstarch gel. However, in this study, the CH_4 molar fraction increased from 23.14 to 29.25 % and the content of H_2 decreased from 37.34 to 31.45 % and CO decrease from 21.62 to 16.38 %.

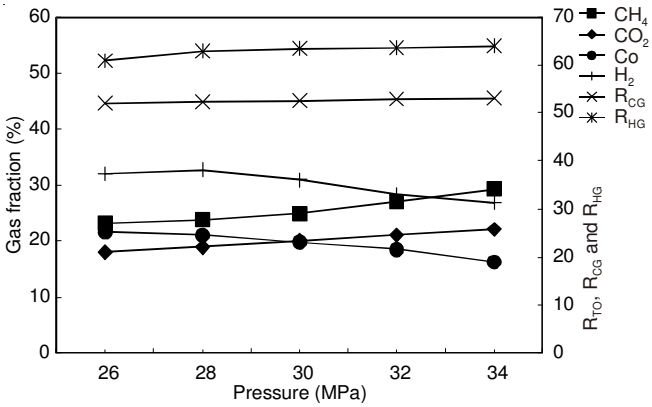

Fig. 2

Effect of temperature and residence time on phenolic

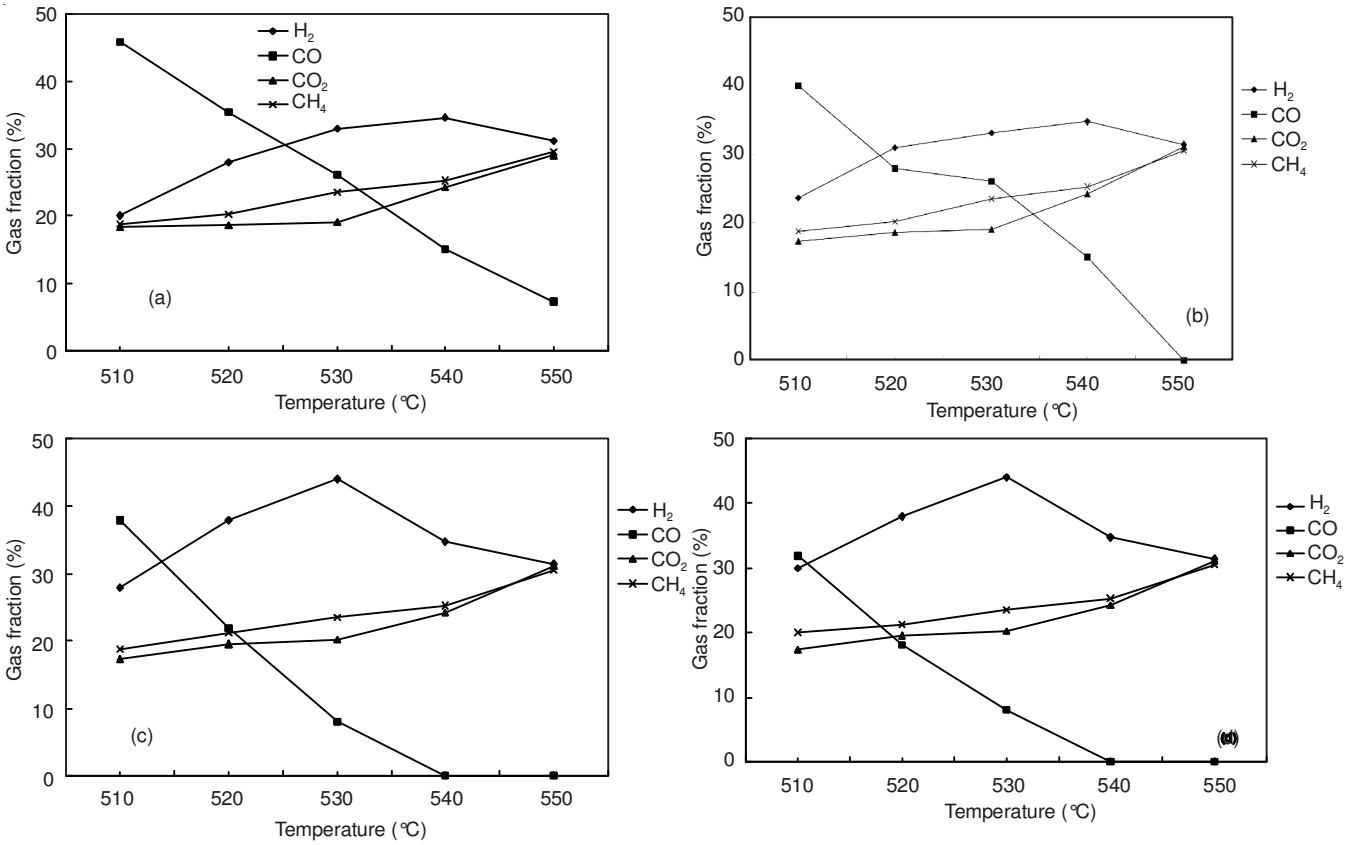

Fig. 3. Effect of temperature on gas fraction at 30 MPa, 510-550 °C, 2-5 min. (a), (b), (c), (d) represent the gas fraction at residence time of 2, 3, 4, 5 min respectively

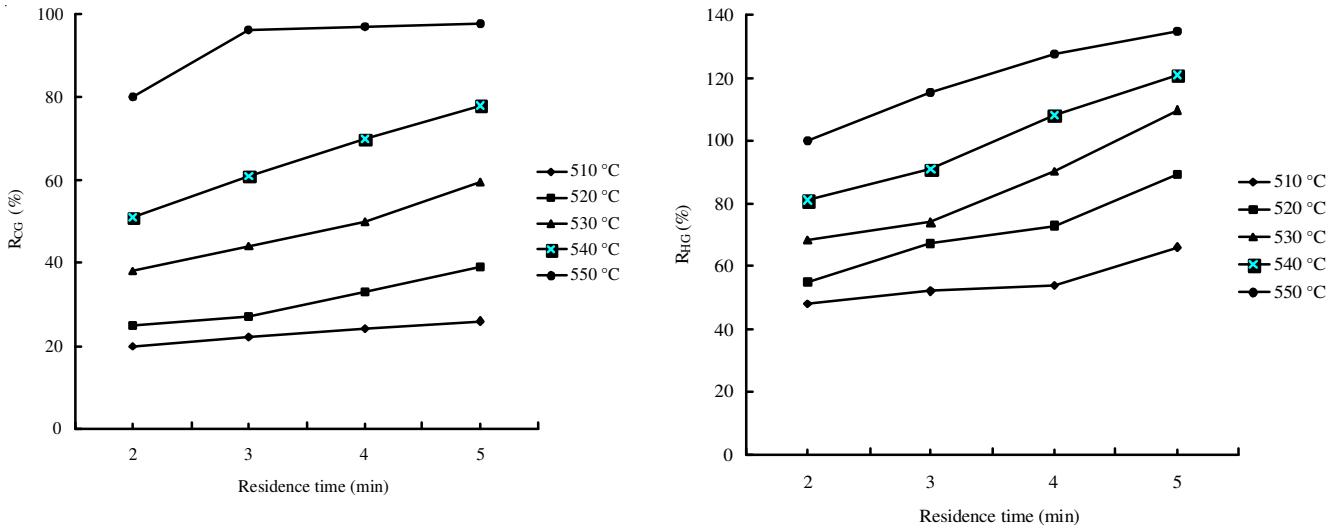

Fig. 4. Effect of residence time on R_{CG}, R_{HG} at 30 MPa, 510-550 °C, 2-5 min. (a), (b) represent the R_{CG} and R_{HG}, respectively

wastewater gasification: Fig. 3a, 3b, 3c and 3d showed the results of phenolic wastewater gasification in SCW at 30MPa, 510-550 °C, 2-5 min. At first H_2 molar fraction increased and the peak value was obtained at 550 and 530 °C with residence time 2 and 3 min, respectively. However, the peak value was obtained at 540 °C with residence time from 4 to 5 min. It may be concluded that the highest H_2 molar fraction can be obtained at a lower temperature with residence time increasing.

Minowa *et. al.*[18,19] suggested that the CH_4 was not only produced by the methanation reaction of H_2 and CO, but also by H_2 and CO_2 in SCWG of organic compounds and both the reactions could be accelerated with the increase of temperature and residence time. Thus, the methanation reactions become dominant in the SCWG system with the increase of temperature and residence time and then, the H_2, CO and CO_2 are consumed. So the molar fraction of H_2 was reduced and the content of carbon dioxide did not increase significantly. Finally, the H_2, CO, CH_4 and CO_2 come to equilibrium.

Fig. 4 showed the variation of R_{CG} and R_{HG} to reaction temperature and residence time, respectively. All the R_{CG} and R_{HG} increased with temperature and residence time increasing. R_{CG} reached 97.96 % at 550 °C and 5 min and it is suggested the phenolic wastewater is almost decomposed completely and all of the decomposed organic carbon has been already converted to gas. R_{HG} reached 135 % at 550 °C and 5 min, which indicated some of H_2 in the product gas comes from water in the SCWG process.

Conclusion

In this study, SCWG was applied to treat phenolic wastewater in a 0.6L batch autoclave under the experimental conditions of 26-34 MPa, 510-550 °C, residence time of 2-5 min. The main gas products were H_2, CH_4, CO and CO_2. The results showed that H_2 can be obtained by the gasification of phenolic wastewater in SCW. Phenolic wastewater can be converted to H_2, CO, CH_4 and CO_2 completely; R_{CG} and R_{HG} reached 97.96 and 135 %, respectively, at 30 MPa, 550 °C and 5 min.

REFERENCES

1. S.J. Wang and K.C. Loh, *Enzyme Microb. Technol*., **25**, 177 (1999).
2. S.H. Lin and C.S. Wang, *J. Hazard. Mater*., **B90**, 205 (2002).
3. B. Veriansyah, J. Kim, J.D. Kim and Y.W. Lee, *Int. J. Green Energy*, **5**, 322 (2008).
4. Y. Matsumura, T. Minowa, B. Potic, S.R.A. Kersten, W. Prins, W.P.M. van Swaaij, B. van de Beld, D.C. Elliott, G.G. Neuenschwander, A. Kruse and M.J. Antal Jr., *Biomass Bioenergy*, **29**, 269 (2005).
5. A. Kruse, *Biofuel Bioproducts Biorefining*, **2**, 415 (2008).
6. C.Q. Cao, L.J. Guo, H. Jin, S.M. Guo, Y.J. Lu and X.M. Zhang, *Int. J. Hydrogen Energy*, **38**, 13293 (2013).
7. A.A. Peterson, F. Vogel, R.P. Lachance, M. Froling, J.M.J. Antal and J.W. Tester, *Environ. Sci*., **1**, 32 (2008).
8. S.M. Guo, L.J. Guo, J.R. Yin and H. Jin, *J. Supercrit. Fluids*, **78**, 95 (2013).
9. Q.Q. Guan, C.H. Wei, P. Ning, S.L. Tian and J.J. Gu, *Environ. Sci*., **18**, 844 (2013).
10. N. Ding, R. Azargohar, A.K. Dalai and J.A. Kozinski, *Fuel*, **118**, 416 (2014).
11. O. Sawai, T. Nunoura and K. Yamamoto, *J. Supercrit. Fluids*, **79**, 274 (2013).
12. L.Y. Peng, M.D. Bao, Q.F. Wang, F.C. Wang and H.J. Su, *Bioresour. Technol*., **151**, 236 (2014).
13. R. Muangrat, J.A. Onwudili and P.T. Williams, *Appl. Catal. B*, **100**, 440 (2010).
14. J.B. Gadhe and R.B. Gupta, *Ind. Eng. Chem. Res*., **44**, 4577 (2005).
15. A. Kruse, D. Meier, P. Rimbrecht and M. Schacht, *Ind. Eng. Chem. Res*., **39**, 4842 (2000).
16. N. Boukis, V. Diem, W. Habicht and E. Dinjus, *Ind. Eng. Chem. Res*., **42**, 728 (2003).
17. M.J. Antal Jr., S.G. Allen, D. Schulman and X. Xu, *Ind. Eng. Chem. Res*., **39**, 4040 (2000).
18. T. Minowa and T. Ogi, *Catal. Today*, **45**, 411 (1998).
19. T. Minowa and S. Inoue, *Renew. Energy*, **16**, 1114 (1999).