INTERFACIAL SURFACE INVESTIGATION OF SUPER-CRITICAL WATER GASIFICATION OF CORN COB

by

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Original scientific paper
DOI: 10.2298/TSCI16S3895J

Super-critical water gasification of biomass is a promising technology for hydrogen production. In order to achieve high hydrogen yield and complete gasification, the operating parameters were investigated and the solid residual was analyzed to study the reaction bottleneck by Fourier transform infrared spectroscopy and scanning electron microscopy. The experimental results showed that most organic functional groups in corn cob were consumed by super-critical water above 500 °C, however, the aromatic substance and cyclic ketone were remained. The K_2CO_3 has the best catalytic effect due to the formation of pore structure in the residual particle surface. The carbon gasification efficiency of 97.97% and the hydrogen yield was 50.28 mol/kg.

Key words: *hydrogen production, corn cob, super-critical water gasification, alkali catalysts, Fourier transform infrared spectroscopy, scanning electron microscopy*

Introduction

With the depletion of the fossil fuel and increasing environmental pollution, more attention has been paid to develop new energy sources, particularly hydrogen. Super-critical water gasification attracts attention because it is a promising hydrogen production from biomass, particularly agriculture wastes [1-3]. Super-critical water provides a homogeneous environment for biomass conversion to omit the inter-phase resistance of heat and mass transfer. The H_2 and CO_2 was achieved after the clean conversion of biomass to a mixture fluid of super-critical water, which has potential of power generation [4-8].

The process of super-critical water is complicated and Fourier transform infrared spectroscopy (FTIR) analyze is an important tool to reveal the reaction products distribution in the process of super-critical water treatment of biomass and its model compound. Qian *et al.* [9] conducted the FTIR and gas chromatography/mass spectrometry (GC/MS) analyze for the woody biomass liquefaction in sub and super-critical water. Williams [10] performed functional group compositional analysis of the oils derived from the gasification of the model biomass compounds and the Cassava biomass waste. Sasaki *et al.* [11] identified the macromolecular structures of the precipitates for the hydrolysis of cellulose in sub- and super-critical water. Fang *et al.* [12] investigated the reaction chemistry and phase behavior of lignin in super-critical water. Zou *et al.* [13] studied bio-oil production from sub- and super-critical water liquefaction of microalgae. The previous achievements provided important information about the reaction

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pathway in the process of super-critical water treatment. However, the parameter mainly covers around the critical point, and the aims of super-critical water treatments are mainly liquefaction.

The non-catalytic gasification of corn cob in super-critical water was investigated and the effects of residence time and temperature were studied with the FTIR to obtain the reaction bottleneck for complete gasification. The KOH, NaOH, K_2CO_3, and Na_2CO_3 were employed as catalyst to obtain the best catalyst taking the reaction solid residual into consideration.

Experimental section

The gasification experiments were conducted in a high-throughput batch reaction systems with six individual channels. Detailed description of the reaction system was published in [14]. Corn cob was collected from the suburban of city of Xi'an, Shaanxi Province. The corn cob was dried and ground until the size of biomass particle was smaller than 180 μm. The ultimate and proximate analysis results are listed as tab. 1. The C, H, S, N, and O present the relative element content by mass in the ultimate analysis for corn cob, respectively. The M, A, V, and FC stand for moisture content, ash content, volatile content and fixed carbon content, respectively. $Q_{\mathrm{b,ad}}$ stands for the bomb calorific value of corn cob as air dried basis. All these reagents were analytical pure. After reaction, the gas produced by the gasification was detected quantitatively and qualitatively by HP7890 gas chromatograph. The residual solid after the reaction was characterized by Bruker Vertex 70 spectrometer made by Germany Bruker and SSX-550 scanning electron microscope (SEM) made by Japanese company SHIMADZU. The FTIR spectra of the samples were obtained by a Bruker Vertex 70 spectrometer.

Table 1. Element and proximate analysis of corn cob

Ultimate analysis (wt.%)					Proximate analysis (wt.%)				$Q_{\mathrm{b,ad}}$ [MJkg^{-1}]
C	H	S	N	O*^{a}	M	A	V	FC	
43.92	6.31	0.47	0.39	4.33	6.29	2.29	79.79	17.92	16.285

*^{a} By difference

Results and discussion

Effect of reaction time

Figure 1 shows the effect of reaction temperature on corn cob gasification in supercritical water. It can be drawn that as the residence time increased, hydrogen fraction, hydrogen yield, and carbon gasification efficiency also increased. However, as the residence time

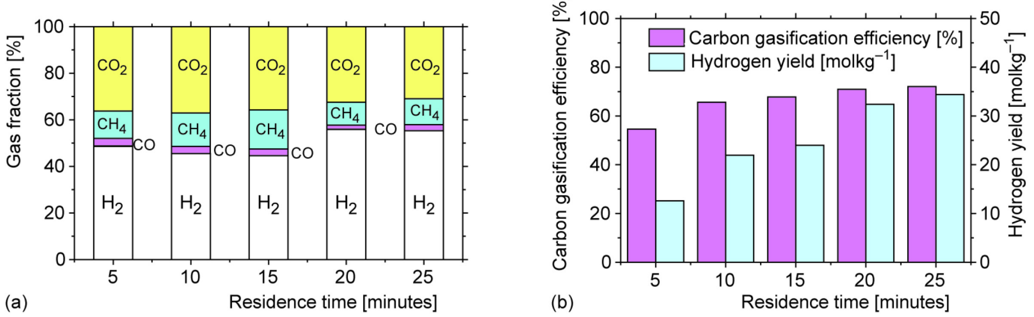

Figure 1. Effect of residence time on corn cob gasification in super-critical water

was more was relatively long, the growth rate was not obvious. It was possible that the gasification in autoclave resulted in the side-reaction, and unwanted produced was generated which was difficult to be gasified again. Therefore, the effect of residence time when the residence time was more than ten minutes was not obvious.

Effect of temperature

The effect of reaction temperature is illustrated in fig 2. It can be seen that reaction temperature played a significant role in corn cob gasification. When the temperature increased from 500 °C to 750 °C, the hydrogen fraction increased more than 60%, and the hydrogen yield increased to 42.14 mol/kg. High temperature increased the free radical reaction pathway to favor gas production reaction.

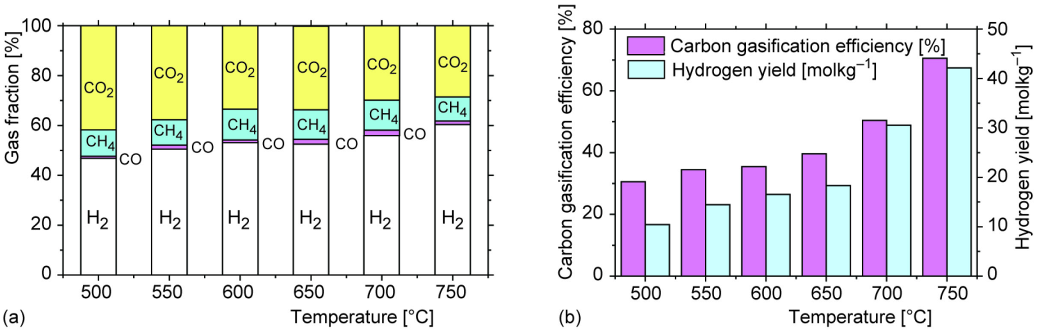

Figure 2. Effect of reaction temperature on corn cob gasification in super-critical water; concentration 10 wt.%, 20 minute; K_2CO_3: corn cob = 1:1, 23~25 MPa

The FTIR spectra of original corn cob (fig. 3) shows that there is a wide range and intensity of peaks in the 3200-3600 cm^{-1} range which was caused by O-H and N-H intensity of vibration, indicating that alcohols, carboxylic acid, amino compound, and amine compound existed. A peak at 2902 cm^{-1} represented the symmetric C-H elastic vibration, which indicated the presence offatty chain. A peak of 1732 cm^{-1} represented the existence of polyxlose. The peak from 1606~1515 proved the protein in corn cob. At a wavelength of 1000 to 1200 cm^{-1}, the peak represented the C-O stretching vibration, indicating that a polysaccharide substance existing in the corn cob, more accurately, which showed the presence of cellulose [15, 16]. The peak between 760 cm^{-1} and 500 cm^{-1} represented the aromatic structure. It can be seen that after super-critical water gasification, most of the peaks disappeared. It was indicated that most of the organic functional groups were consumed during the gasification process. There were two obvious peaks left at 503 cm^{-1} and 617 cm^{-1} and represents cyclic ketone and aromatic compounds.

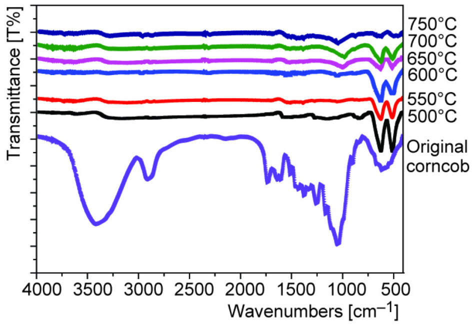

Figure 3. The FTIR characteristics of the original corncob and residual solid in different reaction temperature; concentration 10 wt.%, 650 °C, 23~25 MPa

Effect of different alkali catalysts

The enhancement mechanism of catalyst was investigated as seen in fig 4. It can been seen that as for the hydrogen fraction, K_2CO_3, and Na_2CO_3 did not increase the hydrogen fraction significantly, while KOH and NaOH increased the hydrogen fraction to 62.06% and 65.41%. Because KOH and NaOH absorbed the CO_2 in gas products, and enhance the water gas shift reaction. By the same reason, the hydrogen yield with the catalyst of KOH or NaOH were higher than K_2CO_3 or Na_2CO_3. However, the carbon gasification efficiency of K_2CO_3 or Na_2CO_3 are higher than KOH or NaOH, and reached 70.97%, and 64.18% at 650 °C.

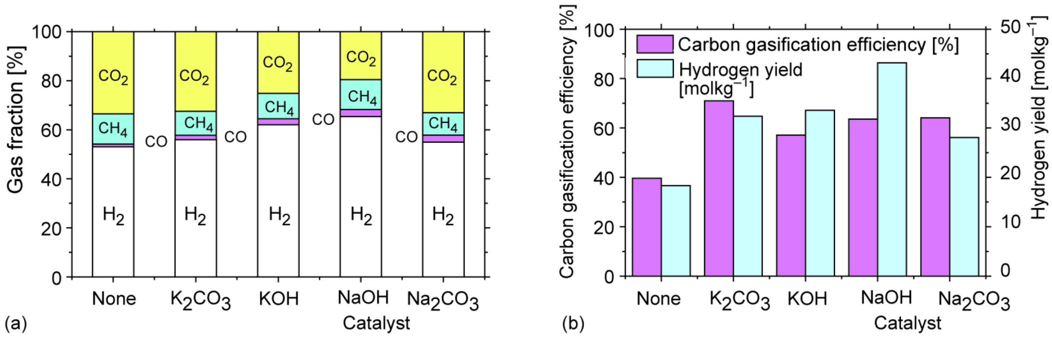

Figure 4. Effect of different catalysts on corn cob gasification in super-critical water; concentration 10 wt.%, 20 min, 650 °C; catalyst corn cob = 1:1, 23~25 MPa

The SEM analyze was seen in fig. 5(a). It can be seen that the original corn cob has typical loosen texture of biomass. In the process of super-critical water gasification, the corn cob particles underwent super-critical water gasification reaction. The coking reaction is a typical unwanted products when the heat and mass transfer was not coupled with chemical re-

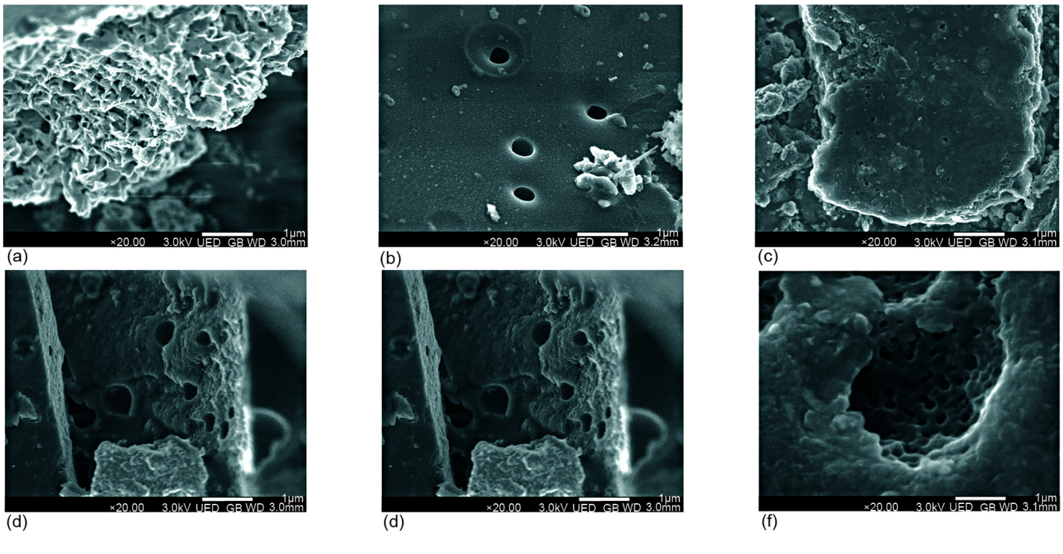

Figure 5. Effect of different catalysts on corn cob gasification in super-critical water; concentration 10 wt.%, 20 min, 650 °C; catalyst corn cob = 1:1, 23~25 MPa; (a) without catalyst, (b) NaOH, (c) KOH, (d) Na_2CO_3, (e) K_2CO_3, (f) K_2CO_3 (×200,000)

actions. The coke is difficult to be gasified again once formed, catalyst may enhance the gasification of the solid residual. It can be seen from figs. 5(b) and 5(c) that with the catalyst of KOH and NaOH, the coke has smooth surface and typical pore structure was formed. It can be observed from figs. 5(d)-(f) that, with the catalyst of K_2CO_3 and Na_2CO_3, the pore structure was more obvious [17, 18].

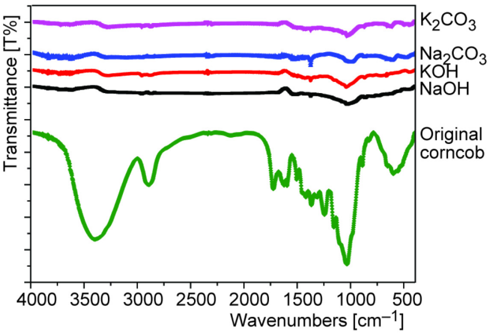

Figure 6. Fourier transformed infrared spectral variation characteristics of the original corn cob and residual solid under different catalysts; concentration 10 wt.%, 650 °C, 23~25 MPa

The effect of different catalyst was investigated as seen in fig. 6. It could be seen that most of the organic functional groups were consumed after catalytic super-critical water gasification. Two peaks were left, and one is within the wavelength of 1000 to 1200 cm^{-1}, which shows the remained polysaccharide substances. The other peak was at approximately 1385 cm^{-1}, represented the existence of carbonate. It can be seen that the carbonate also existed in the reaction catalytic condition of NaOH and KOH, which proved the absorption of CO_2 with NaOH and KOH.

Effect of catalyst loading amount

The effect of catalyst loading was investigated in fig. 7. It is not cost-effective to use excessive amount of catalyst to increase to such a small extent. As the concentration of catalyst decreased from 10% to 5%, the hydrogen yield decreased from 40.65 mol/kg to 35.45 mol/kg. The reducing amplitude is not obvious when the catalyst loading is decreased by 50%. It was believed that super-critical water fluidized bed has potential to gasify coal with small amount of catalyst [5].

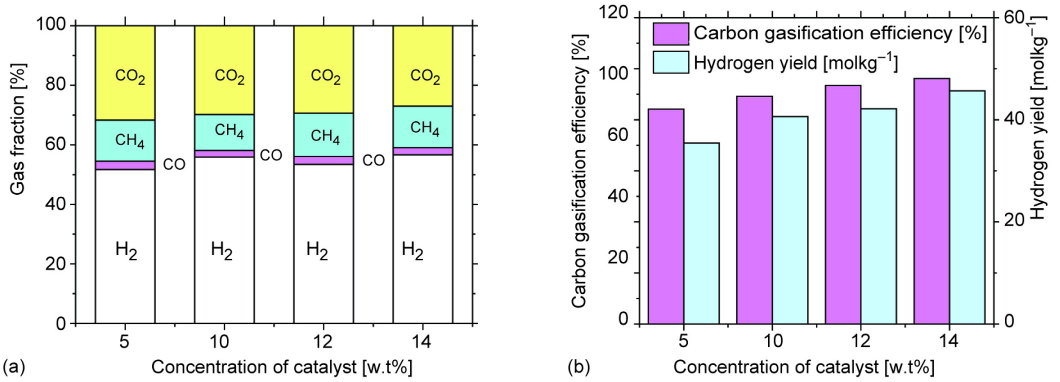

Figure 7. Effect of catalyst loading on corn cob gasification in super-critical water (20 min, 700 °C); concentration 10 wt.%, 700 °C, 20 min, 23~25 MPa

Effect of corn cob concentration

The influence of concentration of corn cob upon the gasification was quite obvious seen in fig. 8. When the concentration of corn cob was 5%, the hydrogen fraction was 58.85, while when the concentration of corn cob was 20 wt.%, the hydrogen fraction was only 31.01%. In autoclave, the heat and mass transfer was not sufficient and high concentration of corn cob resulted in the inhibition of steam reforming reaction and water gas shift reaction, therefore the hydrogen fraction decreased as concentration of corn cob increased. For the same reaction, when the concentration of corn cob decreased from 20 wt.% to 5 wt.%, the carbon gasification efficiency increased from 52.79% to 97.97%.

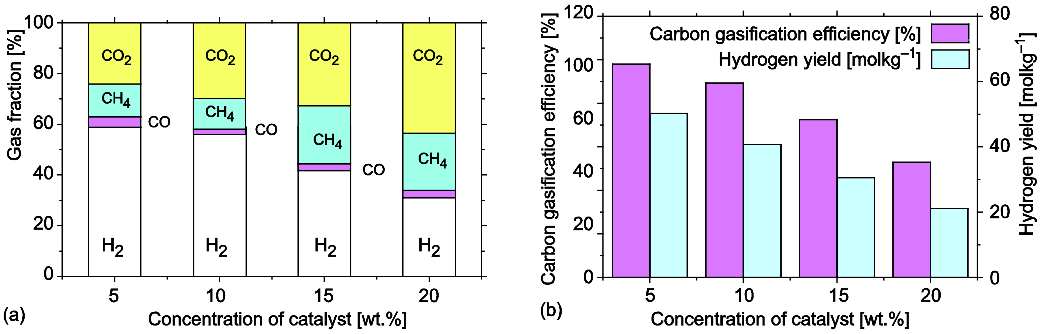

Figure 8. Effect of concentration on corn cob gasification in super-critical water; 700 °C, 20 min, K_2CO_3 corn cob = 1:1, 23~25 MPa

Conclusions

The gasification characteristics of corn cob in super-critical water with an autoclave were obtained in this paper. Main conclusions were drawn:

- The enhancement of reaction temperature and residence time in the gasification results was quite limited. Most organic functional groups were consumed when the reaction temperature was 500 °C. Only aromatic substance and cyclic ketones were remained, and their amount decreased as reaction temperature increased.
- The K_2CO_3 and Na_2CO_3 enhance the formation of pore structure and increased the carbon gasification efficiency. The carbon gasification efficiency of corn cob was 97.97% in super-critical water with K_2CO_3.
- Alkaline catalyst can consumed the organic functional groups. The NaOH and KOH obviously enhanced the hydrogen yield.

Acknowledgment

This work was financially supported by the National Natural Science Foundation of China (Contract No. 51306145 and 51236007) and the National Basic Research Program of China (Contract No. 2012CB215303).

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Paper submitted: January 17, 2016
Paper revised: February 21, 2016
Paper accepted: March 12, 2016