



## Hydrogen generation from polyvinyl alcohol-contaminated wastewater by a process of supercritical water gasification

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### Abstract

Gasification of polyvinyl alcohol (PVA)-contaminated wastewater in supercritical water (SCW) was investigated in a continuous flow reactor at 723–873 K, 20–36 MPa and residence time of 20–60 s. The gas and liquid products were analyzed by GC/TCD, and TOC analyzer. The main gas products were H<sub>2</sub>, CH<sub>4</sub>, CO and CO<sub>2</sub>. Pressure change had no significant influence on gasification efficiency. Higher temperature and longer residence time enhanced gasification efficiency, and lower temperature favored the production of H<sub>2</sub>. The effects of KOH catalyst on gas product composition were studied, and gasification efficiency were analyzed. The TOC removal efficiency ( $R_{\text{TOC}}$ ), carbon gasification ratio ( $R_{\text{CG}}$ ) and hydrogen gasification ratio ( $R_{\text{HG}}$ ) were up to 96.00%, 95.92% and 126.40% at 873 K and 60 s, respectively, which suggests PVA can be completely gasified in SCW. The results indicate supercritical water gasification for hydrogen generation is a promising process for the treatment of PVA wastewater.

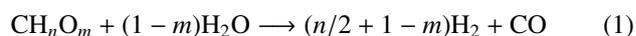
**Key words:** hydrogen generation; supercritical water; gasification; polyvinyl alcohol wastewater

### Introduction

Supercritical water (SCW) is water at a temperature and pressure higher than its critical temperature (647.2 K) and pressure (22.1 MPa). It has characteristics different from either water in normal condition or steam with respect to density, dielectric constant, ion product, viscosity, diffusivity, electric conductance, and solvent ability (Savage, 1999). It is also known that SCW is miscible with most of the organic compounds, and rapidly homogeneous organic chemical reactions are possible in SCW (Siskin and Katritzky, 1991; Poliakoff and King, 2001).

With the rapid development of economy and technology, more and more compounds are produced and emitted into environment as industrial waste. At the same time, the industrialization due to the depletion of fossil fuel and environmental pollution during its combustion, which makes H<sub>2</sub> an attractive alternative energy source (Cortright *et al.*, 2002). Some researchers (Kruse *et al.*, 2005; Calzavara *et al.*, 2005; Matsumura *et al.*, 2005) have suggested that SCW gasification (SCWG) is a promising technology for converting organic compounds to H<sub>2</sub> due to the special characteristics of SCW. In the past few years, H<sub>2</sub> generation from simple molecules like glucose (Yu *et al.*, 1993; Lee *et al.*, 2002; Hao *et al.*, 2003; Sinag *et al.*, 2004) and methanol (Feng *et al.*, 2003; Boukis *et al.*, 2003) or

natural biomass such as lignin (Osada *et al.*, 2004, 2006), cellulose (Minowa and Ogi, 1998; Sasaki *et al.*, 2004), cornstarch (Antal *et al.*, 2000), clover grass (D'Jesus *et al.*, 2005); in SCW has been investigated extensively. The main reactions in the gasification of organic compounds in SCW include steam reforming (Reaction (1)), water-gas shift reaction (Reaction (2)) and methanation reaction (Reactions (3) and (4)) (Boukis *et al.*, 2003; Minowa Inoue, 1999; Tang and Kitagawa, 2005).



Alkali catalyst is one of the effective catalysts for the gasification of organic compounds and can promote the water-gas shift reaction (Reaction (2)) to a greater extent (Elliott *et al.*, 1983, 1986), so the molar fraction of CO can decrease to zero and that H<sub>2</sub> increases significantly. At the same time, gasification efficiency of organic compounds can be enhanced greatly.

Polyvinyl alcohol (PVA, (CH<sub>2</sub>CH(OH))<sub>n</sub>) is widely used in the sizing process of the textile industry and paper coating for its high tensile strength, good flexibility, high thermal and chemical stability, water-solubility and good film-forming capability (He and Gong, 2003). The global production of PVA is about 650000 t/a, and the large amount of discharged PVA from industrial effluents has caused significant environmental pollution (Zhang and

Yu, 2004). The study of PVA wastewater treatment was focused in some oxidation processes (AOP) such as wet air oxidation (WAO), Fenton oxidation and photo-degradation (Won *et al.*, 2001; Giroto *et al.*, 2006). These methods either convert the pollutants to CO<sub>2</sub> and H<sub>2</sub>O directly or function as a pretreatment followed by a biotreatment. Generally, the direct decomposition is very expensive. However, gasification of PVA in SCW apparently has not been reported.

In this study, the possibility of hydrogen energy obtained from wastewater treatment was elucidated, as a model macromolecule polymer organic compound, the characteristics of using SCWG for hydrogen generation from dilute solution of PVA in water were investigated. The relationship of reaction pressure, temperature, residence time, KOH catalyst with the gas molar fraction and gasification efficiency was studied.

## 1 Experimental

### 1.1 Apparatus and reagents

Experiments were performed in a continuous flow reactor. As shown in Fig.1, the apparatus includes feed system, preheater, reactor, condenser, gas-liquid separator and backpressure regulator. The preheater is a stainless steel coil tube (O.D. 8 mm, I.D. 4 mm, length 10 m). The reactor is a stainless steel column (O.D. 80 mm, I.D. 30 mm, length 350 mm) and has a volume capacity of 250 ml. The gas-liquid separator is a stainless steel column with volume capacity of 1 L. The temperature and pressure are controlled by four K-type thermocouples and

a backpressure regulator in this system.

PVA (A.R.) dissolved in de-ionized water was used to simulate PVA-contaminated wastewater. In this study, the PVA concentration was 2 g/L. The homogenous catalysts were prepared by dissolving KOH (A.R.) into de-ionized water.

### 1.2 Chemical analysis

The gas products and total organic carbon (TOC) analysis of liquid effluents were described in the previous literature (Wei *et al.*, 2006).

### 1.3 Terms and definitions

Three parameters, TOC removal efficiency ( $R_{TOC}$ ), carbon gasification ratio ( $R_{CG}$ ) and hydrogen gasification ratio ( $R_{HG}$ ), shall be discussed as the measure of organic compound destruction and gasification efficiency in the SCWG of PVA. The  $R_{TOC}$ ,  $R_{CG}$  and  $R_{HG}$  are defined as Eqs.(1), (2) and (3).

$$R_{TOC} = \frac{M_{TOC_{in}} - M_{TOC_{out}}}{M_{TOC_{in}}} \times 100\% \quad (1)$$

where,  $M_{TOC_{in}}$  is TOC of feed solution,  $M_{TOC_{out}}$  is TOC of outflow.

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

$$R_{HG} = \frac{H_{PG}}{H_{OC}} \times 100\% \quad (3)$$

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

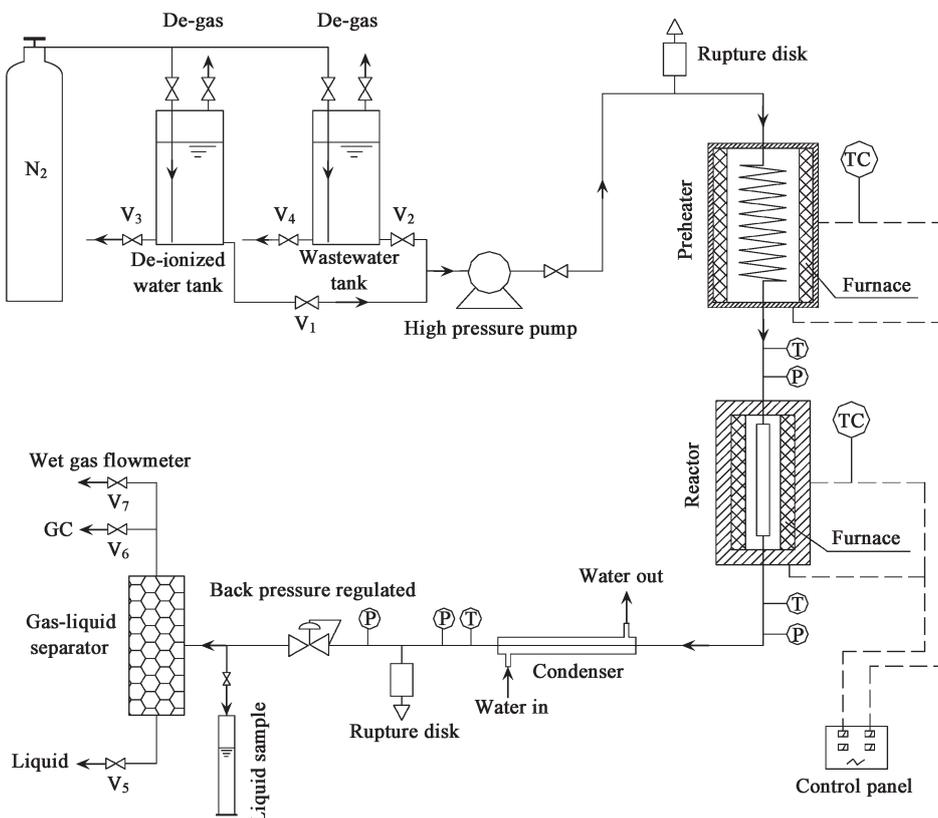


Fig. 1 The sketch of supercritical water gasification equipment.

amount in the gas product;  $H_{PG}$  is the hydrogen amount in organic compounds.

The residence time was calculated according to the flow rate of feed solution and the density of water at reaction conditions as follow:

$$\tau = \frac{V_R \times \rho_w}{F \times \rho_0} \quad (4)$$

where,  $\tau$  is the residence time (s),  $V_R$  is the volume of reactor ( $m^3$ ),  $\rho_w$  is the density of water at reaction condition ( $kg/m^3$ ),  $F$  is the flow rate of feed solution ( $m^3/s$ ),  $\rho_0$  is the density of water at ambient temperature and pressure ( $kg/m^3$ ).

## 2 Results and discussion

### 2.1 Degradation of PVA in SCW

Figure 2 shows the degradation of PVA solution in sub-supercritical water under the conditions of 473–873 K, 25 MPa and residence time of 40 s. The results indicate that PVA decomposition started at 523 K and finished at 623 K, however, there was no TOC removal in this course. This meant the PVA molecules only decomposed to smaller molecules, which could not be further degraded between 523–623 K. However, the  $R_{TOC}$  was 5.89% when the reaction temperature was up to 673 K. Because no gas products was collected until the temperature ramped to 723 K, the increase of  $R_{TOC}$  may be due to the formation of char. The  $R_{TOC}$  reaches 93.03% at 873 K, 40 s, which suggests the PVA is almost decomposed completely to gas at this conditions.

### 2.2 Effect of pressure on PVA gasification

The effect of pressure on PVA gasification was investigated under the conditions of 813 K, 30 s and 20–36 MPa. As shown in Fig.3, the variation of reaction pressure had no significant influence on  $R_{TOC}$ ,  $R_{CG}$  and  $R_{HG}$ , which has been confirmed by some researchers. Lin *et al.* (2002) suggested the hydrogen production was not sensitive to pressure; Boukis *et al.* (2003) confirmed that the pressure variation during 25–45 MPa 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.* (2000)

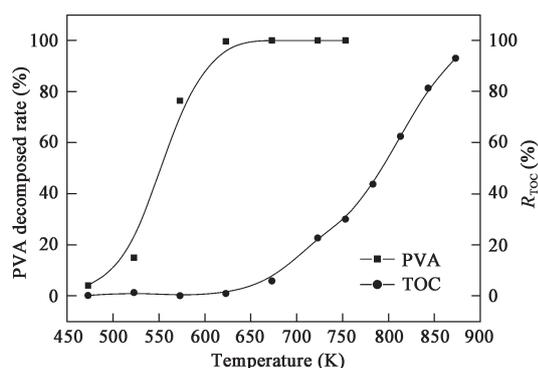


Fig. 2 Effect of temperature on PVA decomposed rate and TOC removal ( $R_{TOC}$ ) at 25 MPa, 473–873 K, and 40 s.

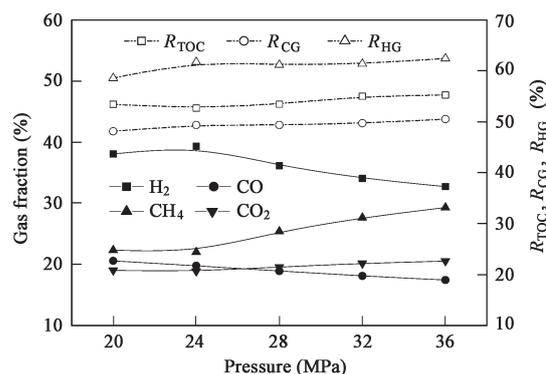


Fig. 3 Effect of reaction pressure on gas fraction,  $R_{TOC}$ ,  $R_{CG}$  and  $R_{HG}$  at 20–36 MPa, 813 K, 30 s.

found that an increase in pressure from 28–34.5 MPa had no significant effect on the gas composition or yields by investigating the gasification of sugarcane bagasse in a cornstarch gel. However, in this study, the  $CH_4$  molar fraction increased from 22.33% to 29.31% and the content of  $H_2$  decreased from 38.07% to 32.72%, and CO decrease from 20.57% to 17.44%. The difference between literature and our study may be because the increase of pressure accelerates the methanation reaction (Reaction (3)), which consumes  $H_2$  and CO and induces the increase of  $CH_4$ . Gradhe and Gupta (2005) also found that the molar fraction of  $H_2$  and CO decreased and the molar fraction of  $CH_4$  increased with pressure in the course of SCW reforming methanol.

### 2.3 Effect of temperature and residence time on PVA gasification

Figure 4 shows the results of gasification in SCW at 723–873 K, 25 MPa and 20–60 s. The gasification of PVA is conducted at an increment of 30 K from 723 to 873 K and 10 s from 20–60 s, respectively. The variation of gas product composition in SCWG of PVA is shown in Fig.4.  $H_2$  molar fraction increased initially and then decreased with the temperature and the peak value was obtained at 843 and 813 K with residence time 20 s and 30 s, respectively, however, the peak value was obtained at 783 K with residence time from 40 to 60 s. It may be concluded that the highest  $H_2$  molar fraction can be obtained at a lower temperature with the increase of residence time. Boukis *et al.* (2003), Minowa and Ogi (1998), and Minowa and Inoue (1999) suggested that the  $CH_4$  was not only produced by the methanation reaction of  $H_2$  and CO (Reaction (3)), but also by  $H_2$  and  $CO_2$  (Reaction (4)) in SCWG of organic compounds, and both the reactions could be accelerated with the increase of temperature and residence time. Thus, the methanation reactions (Reactions (3) and (4)) 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 an equilibrium.

Figure 5 shows the variation of  $R_{TOC}$ ,  $R_{CG}$  and  $R_{HG}$  to reaction temperature and residence time, respectively.

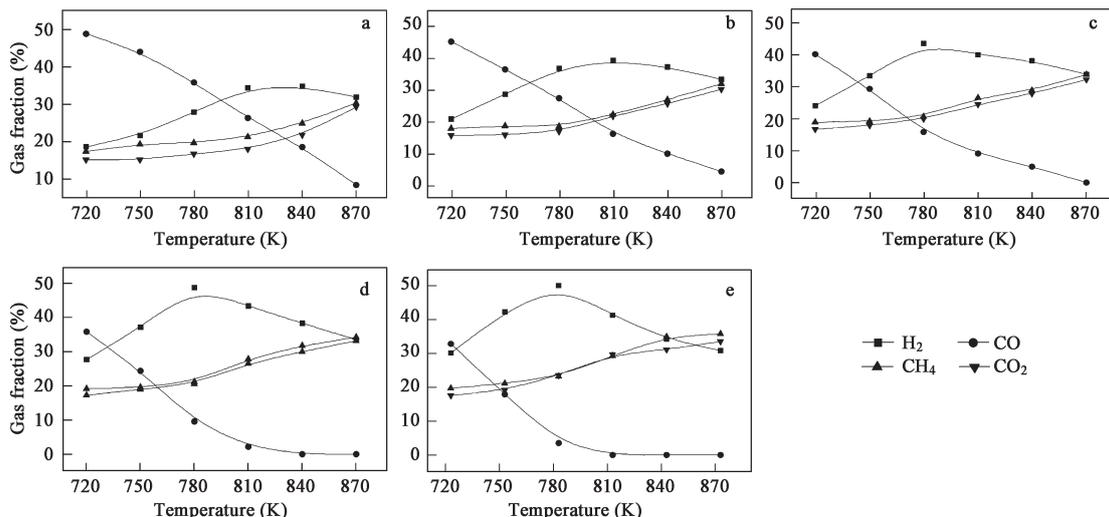


Fig. 4 Effect of temperature on gas fraction at 25 MPa, 723–873 K and 20–60 s. (a), (b), (c), (d) and (e) represent the gas fraction at residence time of 20, 30, 40, 50, 60 s respectively.

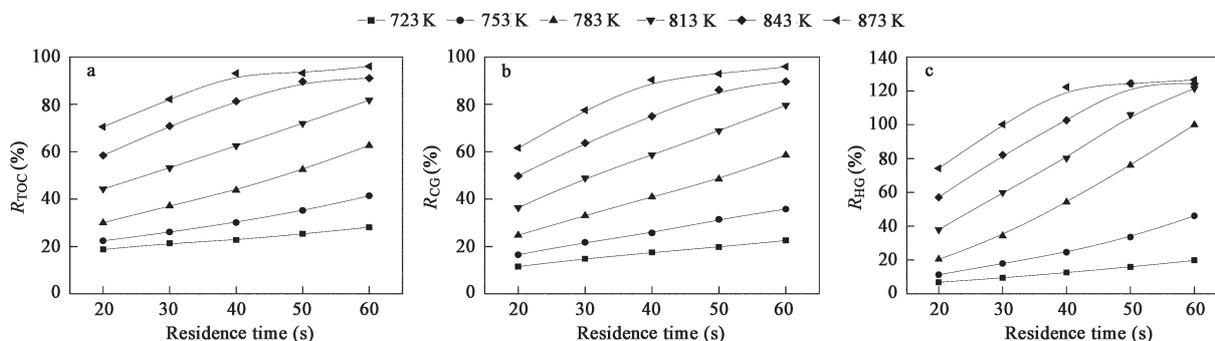


Fig. 5 Effect of residence time on  $R_{TOC}$ ,  $R_{CG}$ ,  $R_{HG}$  at 25 MPa, 723–873 K and 20–60 s. (a), (b) and (c) represent the  $R_{TOC}$ ,  $R_{CG}$  and  $R_{HG}$  respectively.

All the  $R_{TOC}$ ,  $R_{CG}$  and  $R_{HG}$  increase with temperature and residence time.  $R_{TOC}$  and  $R_{CG}$  reach 96.00% and 95.92% at 873 K and 60 s, which suggests the PVA is almost decomposed completely and all of the decomposed organic carbon has been converted to gas.  $R_{HG}$  reaches 126.40% at 873 K and 60 s, which indicates some of  $H_2$  in the product gas comes from water in the SCWG process. Lin *et al.* (2001) and Kruse *et al.* (2003) have confirmed that most of  $H_2$  producing in SCWG of coal and biomass originated from water.

### 2.4 Effect of KOH catalyst on PVA gasification

Figure 6 shows the effects of KOH catalyst concentration on gas molar fraction and gasification efficiency at 813 K, 25 MPa and 40 s. The molar fraction of CO decreased to zero with the concentration of KOH increases from 0–100 mg/L. Kruse *et al.* (2000) reported that CO in gas product dropped from more than 40 vol% to less than 1 vol% when the concentration of KOH increased from 0 to

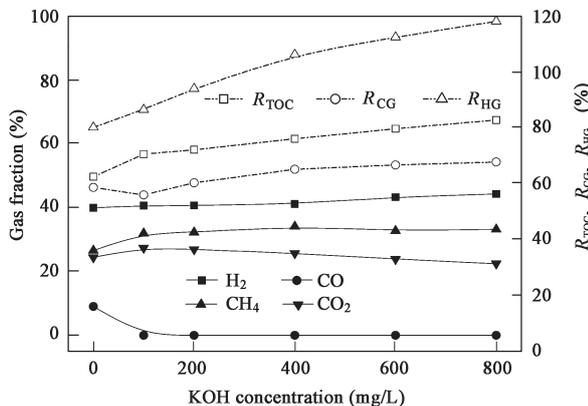


Fig. 6 Effect of KOH concentration on gas fraction,  $R_{TOC}$ ,  $R_{CG}$  and  $R_{HG}$  at 25 MPa, 813 K and 40 s.

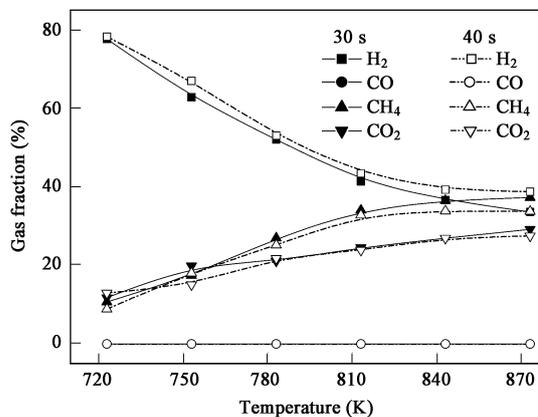


Fig. 7 Gas fraction with 600 mg/L KOH at 25 MPa, 723–873 K, 30 and 40 s, respectively. Both the CO fraction of 30 and 40 s are zero, so the lines of CO fraction at 30 and 40 s are superposed in this figure.

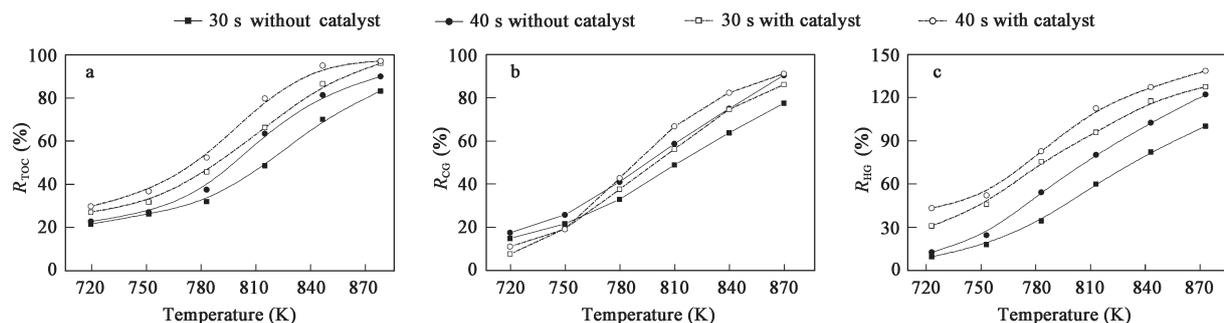


Fig. 8 Comparison of the  $R_{TOC}$ ,  $R_{CG}$  and  $R_{HG}$  with 600 mg/L KOH and without KOH at 25 MPa, 723–873 K, 30 and 40 s, respectively.

5%. D'Jesús *et al.* (2005) also found that the gasification yield rose from 82% to 92% with the concentration of potassium increase from 0 to 0.5% and further increasing in potassium concentration did not improve the gasification yield significantly. In this study,  $CH_4$  fraction increased from 26.57% to 31.9%, however, the fraction of  $H_2$  hardly increased (40.63%–44.31%) when the KOH concentration increased. The reason may be that the methanation reaction is dominative at 813 K for 40 s, so the  $H_2$  from water-gas shift reaction was converted to  $CH_4$  which results in the increase of  $CH_4$  fraction.

Experiments were conducted at KOH concentration of 600 mg/L, temperature of 723–873 K, residence time of 30 and 40 s. As shown in Fig.7, the CO molar fraction decreased to zero. The  $H_2$  content had an abrupt decrease from 77.58% to 33.60%, 78.21% to 38.74% with the temperature increasing from 723 to 873 K at residence time of 30 and 40 s, respectively. The abrupt variation of  $H_2$  molar fraction could be related to the role of the water-gas shift reaction and methanation reaction at different reaction temperature. Taylor *et al.* (2003) considered that the water-gas shift reaction is much slower at lower temperatures. Water-gas shift reaction can be promoted greatly by KOH catalyst but the methanation reaction is not fast at 723 K, which leads to the higher of  $H_2$  content at lower temperature. Methanation reaction is accelerated with the increase of temperature, which decreases the molar fraction of  $H_2$ . So, the molar fraction of  $CH_4$  increased greatly from 10.68% to 37.25% (at 30 s),  $CO_2$  from 11.75% to 29.16% (at 30 s) and  $CH_4$  from 8.88% to 33.75% (at 40 s),  $CO_2$  from 12.91%–27.51% (at 40 s), respectively, with the temperature increasing from 723 to 873 K.

Figure 8 shows the effect of 600 mg/L KOH catalyst on  $R_{TOC}$ ,  $R_{CG}$  and  $R_{HG}$  between 723 and 873 K at 30 and 40 s, respectively. All the  $R_{TOC}$ ,  $R_{CG}$  and  $R_{HG}$  increased with temperature regardless with or without catalyst.  $R_{TOC}$  and  $R_{HG}$  with catalyst were higher than those without catalyst.  $R_{CG}$  with catalyst was lower than that without catalyst at 723–753 K and higher at 783–873 K. Because the gasification efficiency of PVA was lower at 723–753 K, and the carbon in gas was converted to  $KHCO_3$  or  $K_2CO_3$  which remained in liquid as a result of KOH catalysis (Gadhe *et al.*, 2005; Sinag *et al.*, 2004), which makes the decrease of  $R_{CG}$ . The carbon in gas with catalyst was higher than that without catalyst at 783–873 K because both the increases of temperature and KOH catalyst promoted the gasification

efficiency of PVA although a part of carbon in gas was consumed by KOH.

### 3 Conclusions

In this study, hydrogen generation from PVA-contaminated wastewater by SCWG was studied in a continuous flow reactor under the experimental conditions of 20–36 MPa, 723–873 K, residence time of 20–60 s and PVA concentration of 2 g/L. The main gas products were  $H_2$ ,  $CH_4$ , CO and  $CO_2$ . It was demonstrated that  $H_2$  can be obtained by the gasification of PVA wastewater in SCW.

The effects of pressure, reaction temperature, residence time and KOH catalyst on the gas product molar fraction,  $R_{TOC}$ ,  $R_{CG}$  and  $R_{HG}$  were determined. Pressure change has no significant influence on gasification efficiency. Both the higher reaction temperature and longer residence time has a positive influence on gasification efficiency. PVA wastewater can be converted to  $H_2$ , CO,  $CH_4$  and  $CO_2$  completely, the  $R_{TOC}$ ,  $R_{CG}$  and  $R_{HG}$  reach 96.00%, 95.92% and 126.40%, respectively, at 25 MPa, 873 K and 60 s. Lower temperature favors the production of  $H_2$  and the molar fraction of  $H_2$  decreases as a result of the acceleration of methanation reactions with the increase of temperature. Presence of KOH promotes the gasification efficiency and  $H_2$  molar fraction greatly owing to the catalysis of KOH on the water-gas shift reaction. However, the  $H_2$  molar fraction decreases with the increase of temperature due to the acceleration of methanation reactions.

The results indicate supercritical water gasification for hydrogen generation is a promising process for the treatment of PVA wastewater. The reaction kinetics, mechanism and SCWG equipment must be further studied for industrial application.

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