

Supercritical gasification for the treatment of *o*-cresol wastewater

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Abstract: The supercritical water gasification of phenolic wastewater without oxidant was performed to degrade pollutants and produce hydrogen-enriched gases. The simulated *o*-cresol wastewater was gasified at 440–650°C and 27.6 MPa in a continuous Inconel 625 reactor with the residence time of 0.42–1.25 min. The influence of the reaction temperature, residence time, pressure, catalyst, oxidant and the pollutant concentration on the gasification efficiency was investigated. Higher temperature and longer residence time enhanced the *o*-cresol gasification. The TOC removal rate and hydrogen gasification rate were 90.6% and 194.6%, respectively, at the temperature of 650°C and the residence time of 0.83 min. The product gas was mainly composed of H₂, CO₂, CH₄ and CO, among which the total molar percentage of H₂ and CH₄ was higher than 50%. The gasification efficiency decreased with the pollutant concentration increasing. Both the catalyst and oxidant could accelerate the hydrocarbon gasification at a lower reaction temperature, in which the catalyst promoted H₂ production and the oxidant enhanced CO₂ generation. The intermediates of liquid effluents were analyzed and phenol was found to be the main composition. The results indicate that the supercritical gasification is a promising way for the treatment of hazardous organic wastewater.

Keywords: supercritical water; gasification; *o*-cresol; hydrogen-enriched gas; wastewater treatment

Introduction

Phenolic compounds are considered to be hazardous waste. They are water soluble and usually contained in the wastewater of many industries, such as coke ovens, petroleum refineries, petrochemical plants, phenolic resin plants, pharmaceutical plants, and dyeing plants. The concentration of phenolic compounds in the wastewater is too low to be recovered with general process. However, they are high enough to severely cut down the efficiency of the conventional biological technology. Therefore, advanced oxidation technologies prevail in the phenolic wastewater treatment (Santos *et al.*, 2005; Zen *et al.*, 2003).

Supercritical water oxidation (SCWO) is a promising technology in treating the wastewater containing hazardous or refractory organic compounds. Its high efficiency in decomposing the stable organic compound with the aromatic structure has attracted many researchers (Gopalan and Savage, 1994; Martino and Savage, 1997a; Matsumura *et al.*, 2000; Perez *et al.*, 2004). Phenolic compounds are used widely as the model pollutants in their researches. The degradation in the SCWO is quicker and more complete than other advanced oxidation technologies. However, the SCWO process requires higher temperature and pressure (critical point: $T_c=374^\circ\text{C}$, $P_c=22.1\text{ MPa}$) which limits its wide application. A large amount of energy is needed to heat the feed stream to the supercritical temperature. The energy may be compensated by combusting the organic compounds in the wastewater if their concentration is high enough. As a result, more

electricity is required to supply high-pressure air.

With the decreasing of fossil fuels, new ways of biomass energy utilization have been studied all over the world in the last several years. Many researchers have investigated the gasification of biomass to produce hydrogen in the supercritical water condition and a high gasification efficiency is achieved (Antal *et al.*, 2000; Taylor *et al.*, 2003; Yoshida *et al.*, 2004). In the supercritical water gasification, the reaction generally takes place at a temperature over 600°C and a pressure above the critical point of water. When the temperature is higher than 600°C, water becomes a strong oxidant, and its oxygen atoms can be transferred to the carbon atoms of hydrocarbons. As a result, the carbon is oxidized into CO or CO₂. And the hydrogen atoms of the water and the hydrocarbons are released as H₂ and CH₄. During the process, the organic carbons can be oxidized and converted into gas without an oxidant. Since the product gas is hydrogen-enriched, a part of it can be burnt to maintain the high reaction temperature, and the remainder may be served as a fuel used in fuel cells or other facilities (Calzavara *et al.*, 2005). Therefore, developing a wastewater treatment process which is similar with the supercritical gasification of biomass, and can degrade hazardous pollutants completely and produce hydrogen-enriched gases simultaneously, is attractive. It can partially overcome the shortages of the SCWO and improve the application of the supercritical fluid technology in water treatment area.

In this study, *o*-cresol was chosen as the model phenolic compounds to study the gasification of phenolic wastewater in supercritical water. The effect of operation parameters (temperature, time, pressure

and concentration) on the gasification efficiency was investigated. To moderate the reaction conditions and increase the conversion efficiency, a small amount of oxidant and some homogeneous catalysts such as alkali metal salts and transition metal salts were used. The intermediates in the liquid effluents were also analyzed to understand the pathway of *o*-cresol degradation.

1 Materials and methods

1.1 Materials

o-Cresol (99 % purity) was dissolved in distilled water to produce the simulated phenolic wastewater. A 27.5% wt solution of hydrogen peroxide was used as the oxidant, and it was diluted to the desired concentration assuming that one mole of hydrogen peroxide provides half mole of oxygen. The homogenous catalysts were prepared by solving analytical reagents into distilled water.

1.2 Apparatus and procedure

The simulated wastewater was gasified in a continuous plug-flow reactor with the flow rate up to 6 L/h. The following experimental conditions were realizable in this plant. The maximal pressure and temperature were 31.0 MPa (4500 psi) and 650°C, respectively, and the residence time ranged from 0 to 5 min. The centerpiece of the plant was an electrically heated 250 ml reactor made of Inconel 625. The sketch of the plant is shown in Fig.1.

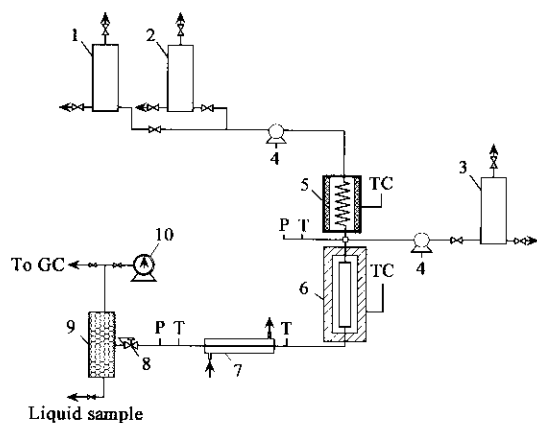


Fig. 1 Sketch of supercritical water gasification equipment

1. distilled water tank; 2. wastewater tank; 3. oxidant or catalysts solution tank; 4. high pressure pump; 5. preheater; 6. gasification reactor; 7. condenser; 8. back pressure regulator; 9. separator; 10. wet gas flowmeter

The procedure of the experiment was as the follows. The *o*-cresol solution was firstly pumped into the pre-heater and heated up to the temperature near the critical point. Then the fluid was mixed with the oxidant or the catalysts (if needed) before going to the reactor. In the reactor, the mixture was rapidly heated up to the desired temperature and the gasification reaction took place. The fluid was then cooled down in a condenser after leaving the reactor. The system

pressure was controlled by a back-pressure regulator which operated from 0 to 34.4 MPa. After the pressure reduced, the two-phase effluent was separated in a gas-liquid separator. The liquid and gas samples were collected and analyzed after at least 60 min till the system was stable.

1.3 Chemical analysis

The total organic carbon (TOC) concentration of the liquid stream was measured with a 1020A TOC analyzer (OI Analytical, USA). The composition of the product gas was analyzed with a 6820 gas chromatography (GC, Agilent Technology, USA.) containing a C-2000 column. The column was equipped with a thermal conductivity detector that was calibrated with calibrating gases. The intermediates of liquid effluents were analyzed with a QP 2010 GC-MS (Shimadzu, Japan) equipped with a HP-5 column (30 m × 0.25 mm × 0.25 μm).

2 Results and discussion

All the experiments were repeated three times. Only four components (H₂, CO₂, CO and CH₄) are considered in the product gases. In this paper, hydrogen gasification rate and TOC removal rate were used to estimate the gasification efficiency. They are calculated according to the following equations:

$$r_{\text{HGR}} = \frac{H_{\text{gas}}}{H_{\text{org}}}$$

where r_{HGR} is the hydrogen gasification rate; H_{gas} is the hydrogen amount in gas product; H_{org} is the hydrogen amount in initial organic material.

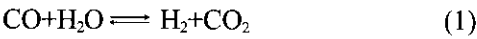
$$r_{\text{TRR}} = \frac{\text{TOC}_0 - \text{TOC}_{\text{eff}}}{\text{TOC}_0}$$

where, r_{TRR} is the TOC removal rate; TOC_0 is the TOC in initial wastewater; TOC_{eff} is the TOC in liquid effluent.

2.1 Influence of operation parameters on gasification efficiency

To investigate the influence of the reaction temperature, the experiments of gasifying 0.02 mol/L *o*-cresol solution were carried out under the conditions: the pressure of 27.6 MPa, the residence time of 0.83 min and the temperatures of 440, 480, 520, 560, 600 and 650°C, respectively. As shown in Fig.2, the r_{HGR} and r_{TRR} increase rapidly with the temperature increasing from 440°C to 650°C. While the r_{HGR} exceeds 100% at the temperatures above 560°C, which indicates that the hydrogen atoms from water are released as H₂ in the product gases. Moreover, the composition of the product gases is different when the reaction temperatures are changed. With the temperature increasing, the contents of H₂, CO₂, and CH₄ increase while that of CO decreases. That is because a water-gas shift reaction happens and

it can be improved at a higher temperature (Sato *et al.*, 2004). The equation of the water-gas shift reaction is shown as follows:



At the temperature of 650℃ , the molar percentage of H₂ and CO₂ is 48.8% and 41.1% , respectively, while that of CO is less than 3%.

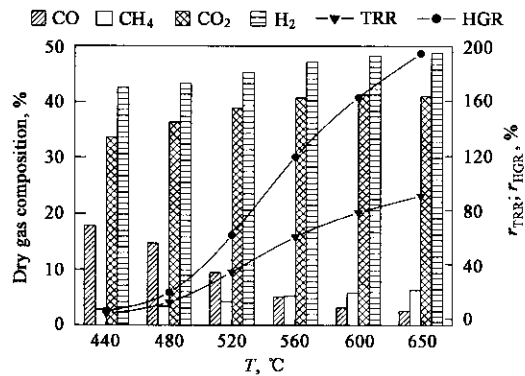
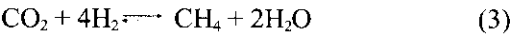
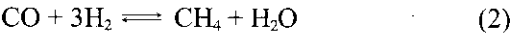


Fig.2 Gasification efficiency at different reaction temperatures
Conditions: 27.6 MPa, 0.83 min and 0.02 mol/L

The influence of residence time on the gasification efficiency is shown in Fig.3. The 0.02 mol/L *o*-cresol solution was gasified at the temperature of 600℃ and the pressure of 27.6 MPa. When the residence time increased from 0.42 min to 1.25 min, the *r*_{HGR} and *r*_{TRR} went up. While the contents of H₂ and CO₂ slightly increased firstly and then decreased. It may be that the reaction of CO converting to H₂ and CO₂ is dominant at a short residence time. While, as the residence time getting longer, the amount of H₂ consumed by the methanation reaction is more than its output and therefore its content decreases. The equation of the methanation reaction is shown as follows:



To investigate the influence of pressure, experiments were carried out at 24.3, 27.6 and 31.0 MPa, respectively. As shown in Table 1, the results

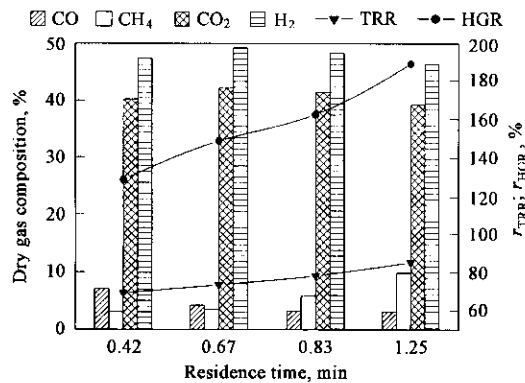


Fig.3 Gasification efficiency at different residence time
Conditions: 600℃, 27.6 MPa and 0.02 mol/L

are not much different. It suggests that the pressure of 24 MPa is enough for supercritical water gasification reaction. However, the influence of higher pressure on the gasification efficiency can not be investigated in the present for the limit of our apparatus.

Table 1 Gasification efficiency at different pressures

Pressure, MPa	Dry gas composition, %				<i>r</i> _{TRR} , %	<i>r</i> _{HGR} , %
	CO	CH ₄	CO ₂	H ₂		
24.3	4.7	4.3	40.3	48.7	76.9	156.4
27.6	3.2	5.8	41.4	48.3	78.2	162.6
31.0	2.6	8.3	40.5	46.9	78.7	170.1

Notes: Conditions: 600℃, 0.83 min and 0.02 mol/L

2.2 Influence of *o*-cresol concentration on gasification efficiency

The pollutant concentration is an important parameter in the wastewater treatment process. To find out the influence of pollutant concentration on the gasification efficiency, experiments were carried out at the *o*-cresol concentration of 0.01, 0.02, 0.04, 0.08, 0.12, and 0.20 mol/L, respectively. As shown in Fig.4, the *r*_{HGR} and *r*_{TRR} decreased with the increasing of the concentration. The reason may be that the wall of Inconel 625 reactor acts as a heterogenous catalyst. Different results were obtained when the supercritical gasification reaction was carried out in the reactors made of different materials (Yu *et al.*, 1993). In our previous work, more CH₄ was produced and its molar percentage was more than 20% when *o*-cresol was gasified in a 316 SS reactor. When *o*-cresol concentration was high, the wall of the reactor was entirely occupied by the adsorbed *o*-cresol molecules which prevent other molecules from reaching the surface. Thus the degradation rate slowed down. Basing on the analysis above, we can reach the conclusion that increasing the residence time can improve the gasification; the experimental results also prove the conclusion (Fig.3). Besides, the catalysts may increase the *r*_{TRR} and *r*_{HGR} at a high organic concentration. Because the catalyst can supply more active centers which can accelerate the degradation rate of organic compounds. The efficacy of the catalyst will be further discussed in Section 2.4. On the other hand, the gasification efficiency reduction at a higher concentration arises from the decreasing of water and carbon ratio. The equilibrium of the water-gas shift reaction is affected by the content of water (Rice *et al.*, 1998). In Reaction (1), decreasing the amount of water may shift the equilibrium to the left and decrease the outputs of H₂ and CO₂. It is seen in Fig.4 that the contents of H₂ and CO₂ decrease while those of CH₄ and CO increase with the *o*-cresol concentration growing.

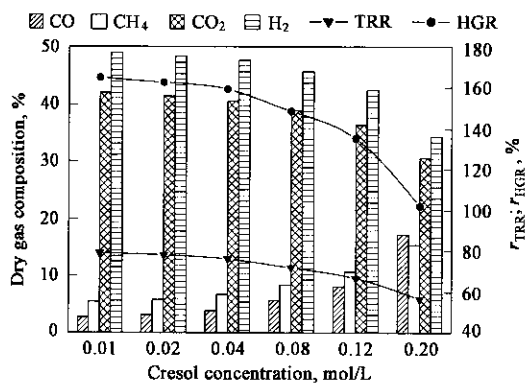


Fig.4 Gasification efficiency at different *o*-cresol concentrations
Conditions: 600°C, 27.6 MPa and 0.83 min

2.3 Influence of oxidant on gasification efficiency

In the SCWO process, the organic compound can be completely converted to CO₂ and H₂O at 400—500°C within one minute with excessive oxidant (Perez *et al.*, 2004). Therefore, the oxidant can greatly increase the conversion rate of the organic carbon at a lower temperature. Experiments were carried out to gasify 0.02 mol/L *o*-cresol solution with the oxidant at different oxygen equivalent ratio (0, 0.15, 0.36 and 0.54) at 520°C (Fig.5). With the oxygen equivalent ratio increasing, the r_{TRR} increased, while the r_{HGR} did not go up and a decrease happened when the oxygen equivalent rate was 0.54. The main composition of the dry product gas is CO₂ when the oxidant is added. That is because when the oxidant concentration is lower, the organic carbon is preferentially oxidized into CO. However, it is easier for the organic carbon to be oxidized into CO₂ when the oxidant concentration is higher. Therefore, the content of CO slightly goes up firstly and then decreases with the oxygen equivalent ratio increasing. Since the concentration of CO₂ increases while that of CO decreases, the equilibrium of the water-gas reaction shifts to the left and the content of H₂ drops rapidly. It can be concluded that oxidant may raise the r_{TRR} , but not the r_{HGR} .

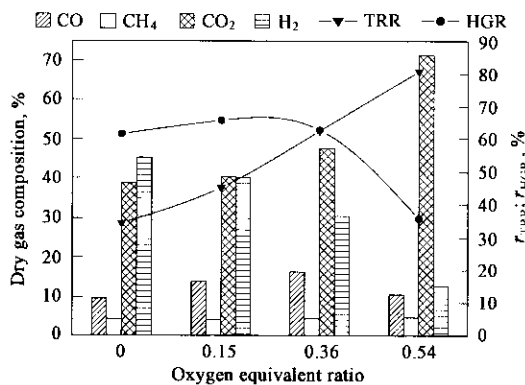


Fig.5 Gasification efficiency at different oxygen equivalent ratios
Conditions: 520°C, 27.6 MPa, 0.83 min, and 0.02 mol/L

2.4 Influence of catalysts on gasification efficiency

Compared with the supercritical water oxidation process, the supercritical gasification reaction needs a higher temperature that makes it less practicable. Many works show that some catalysts can improve the water-gas shift reaction and accelerate the gasification rate (Eillott and Sealock, 1983; Xu *et al.*, 1996; Minowa *et al.*, 1998; Watanabe *et al.*, 2002). Thus, proper catalysts may reduce the gasification temperature. In this work, some transition mental nitrates and alkali salts were chosen as the homogenous catalysts to study their effect on the gasification efficiency at a lower temperature. The concentration of the *o*-cresol solution was 0.02 mol/L and the reaction temperature was 520°C. It is shown in Table 2 that Na₂CO₃ and KOH lead to a drop of CO content in the gas phase and correspondingly an increase of H₂ and CO₂ content. The reason is that the water-gas shift reaction is improved in these cases. When the concentration of KOH is up to 10 mmol/L, the product gas contains 54.3% (molar) H₂ and a trace of CO. And the r_{TRR} and r_{HGR} is 70.7% and 175.8%, respectively. The results are similar with those obtained in the gasification reaction at 600°C without a catalyst. It indicates that higher gasification efficiency is attainable in a more moderate condition with effective catalysts. For the transition metal salts, Mn(NO₃)₂ and Co(NO₃)₂ can improve the TOC removal but do not affect the composition of the product gases. The behavior of Ni(NO₃)₂ is similar to KOH, but its effect is weaker. Usually, it is regarded that nickel can catalyse the formation of CH₄ in a hydrogenation process (Gadhe and Gupta, 2005). But the experimental results show that CH₄ content does not increase while H₂ and CO₂ content go up when Ni(NO₃)₂ is added. Therefore, the increase of the gasification efficiency is via the improvement of water-gas shift reaction with Ni(NO₃)₂ catalysis.

Table 2 Experimental results with different catalysts							
Catalysts	Me ⁺ , mmol/L	Dry gas composition, %				r_{TRR} , %	r_{HGR} , %
		CO	CH ₄	CO ₂	H ₂		
No catalyst	-	9.5	4.3	38.9	45.3	34.4	61.6
Fe(NO ₃) ₃	0.4	8.3	4.6	39.9	46.2	37.6	69.0
Cu(NO ₃) ₂	0.4	5.6	3.8	41.1	48.4	38.2	74.1
Mn(NO ₃) ₂	0.4	8.4	3.9	40.3	46.2	41.7	74.9
Co(NO ₃) ₂	0.4	10.2	5.5	37.8	45.2	43.4	79.8
Ni(NO ₃) ₂	0.4	2.8	5.1	41	49.7	49.5	106.1
Na ₂ CO ₃	0.5	1.9	4.7	41.9	50.3	51.4	110.7
KOH	0.5	1.7	3.7	42.1	51.1	52.3	112.7
KOH	2.0	0.6	4.3	41.8	52	57.2	129.9
KOH	10.0	0	4.6	40.1	54.3	70.7	175.8

Notes: Conditions. 520°C, 27.6 MPa, 0.83 min and 0.02 mol/L

2.5 Potential conversion pathway discussion

The intermediates of the liquid effluents were analyzed with GC-MS to deduce the potential conversion pathway. The experiments were carried out at the temperatures of 440°C, 520°C and 600°C, respectively, and the residence time was 0.42 min.

As shown in Table 3, when the reaction temperature is 440°C, the main composition of the liquid effluent is *o*-hydroxybenzaldehyde, phenol and undegraded *o*-cresol. At 520°C, the intermediate is mainly composed of phenol and several dimmers, such as dibenzofuran, biophenols and naphthols. When the temperature is up to 600°C, the dimmers are decomposed and single-ring aromatics are dominant. Phenol is the major composition of all the liquid products. Basing on the analysis above and other reports (Gopalan and Savage, 1994; Martino and Savage, 1997a, 1997b; Matsumura *et al.*, 2000; Sinag *et al.*, 2003), a potential pathway of the *o*-cresol gasification is given in Fig.6. At first, *o*-cresol is degraded in two parallel paths. Its methyl is oxidized into *o*-hydroxybenzaldehyde or demethylated into phenol. Since hydroxybenzaldehyde is unstable in the supercritical water, it is converted to phenol or the ring-opening product rapidly. And then the phenol is

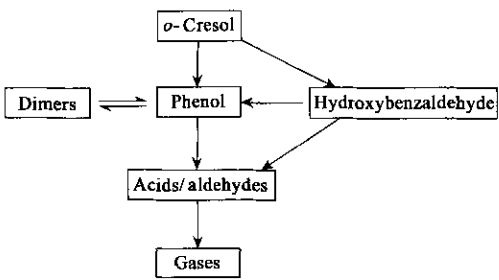


Fig.6 Simplified conversion pathways of *o*-cresol gasification

degraded into the ring-opening product at higher temperature.

3 Conclusions

In this study, the supercritical gasification of the wastewater containing *o*-cresol was investigated. The experimental results show that phenolic compounds in wastewater can be degraded rapidly and almost completely in the supercritical gasification process. Meanwhile, a hydrogen-enriched gas is produced and its main composition is H₂, CO₂, CO and CH₄. The total molar percentage of H₂ and CH₄ is higher than 50%. Increasing the reaction temperature and residence time can increase the gasification efficiency. While, the gasification efficiency is reduced when the pollutant concentration increases. It is proved that oxidant may increase the r_{TRR} , but decrease the r_{HGR} . The r_{TRR} and r_{HGR} increase at a lower temperature if the alkali salts catalysts such as Na₂CO₃ and KOH are used. Meanwhile, the content of H₂ also goes up. The increase of the gasification efficiency is via the improvement of water-gas shift reaction with catalysts.

Compared with the SCWO process, the supercritical gasification process does not need an oxidant, but its reaction temperature is slightly higher. In our work, it is found that some catalysts can reduce the reaction temperature to a certain extent. Therefore, more attention should be paid on developing better catalysts, which can greatly increase the gasification efficiency at lower temperatures and higher hydrocarbon concentrations.

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Table 3 Main organic compounds in the liquid effluent of *o*-cresol supercritical gasification

Compound	Structure	Peak area ratio, %		
		440°C	520°C	600°C
Phenol		13.72	39.85	44.26
<i>o</i> -Hydroxybenzaldehyde		17.65	0.39	-
<i>o</i> -Cresol		42.50	6.87	-
Indanone		-	1.43	3.51
1,1'-Biophenol		2.69	5.94	-
3,3'-Biophenol		1.83	3.63	-
1,2-Dihydroxynaphthalene		-	3.02	0.68
2-Naphthol		-	2.16	0.55
Dibenzofuran		-	3.92	0.40

Notes: Conditions. 27.6 MPa, 0.42 min and 0.02 mol/L

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