

## Resource utilization and treatment of landfill leachate using supercritical water gasification

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Received 29 January 2017; Accepted 16 June 2017

### ABSTRACT

Gasification of landfill leachate in supercritical water using batch-type reactor was investigated. The effect of temperature, pressure reaction time, catalyst  $\text{Na}_2\text{CO}_3$  on gas composition, gas yield, TOC and TN removal efficiency were studied. The fixed reaction condition was temperature 380–500°C, pressure 22.5–36.5 MPa, reaction time 5–25 min. The results showed that gaseous products mainly contained  $\text{H}_2$ ,  $\text{CH}_4$ ,  $\text{CO}_2$  and CO. The maximum hydrogen composition was reached to 55.6% at 500°C, 37 MPa and 10 min. And the maximum hydrogen gas yield of 107.15 mol·kg<sup>-1</sup> was achieved under the same condition without addition of catalyst. TOC and TN removal efficiency being 85.56% and 49.88% was obtained at 470°C, 27 MPa. Hydrogen production increased from 43.1% to 57.92% with increase of catalyst  $\text{Na}_2\text{CO}_3$  loading amount from 0 to 10%. Hydrogen composition, gas yield, TOC and TN removal efficiency increased with increase of temperature. GC-MS analysis results indicated gasification liquid phase products of leachate were mainly composed of cyclopentanone, 2-octanone, phenol, p-cresol and nitrogenous compounds. Results from infrared spectrum analysis indicated solid phase products were mainly composed of travertine, ankerite and calcite, and tar and char were not detected in our experiments.

*Keywords:* Landfill leachate; Supercritical water gasification; Hydrogen production; Wastewater treatment

### 1. Introduction

Landfilling, compared to other technologies such as incineration and composting, is a common way to dispose of solid waste. It is reported that about 90% of the municipal solid waste (MSW) is disposed of in landfills in China [1]. Landfill leachate is generated by excess rainwater percolating through the waste layer. Combined physical, chemical and microbial processes in the waste transfer pollutants from the waste material to the percolating water [2]. Landfill leachate contains high concentrations of dissolved organic matter expressed as COD and TOC, inorganic components and heavy metals nitrogen, and need to be treated before discharge. In the past several decades, some conventional landfill leachate treatments have been developed [3–7].

However, due to its complexity, a combination of chemical, physical and biological steps is required to treat leachate for direct discharge into surface water [8]. Research on landfill leachate has been becoming a fascinating area in the field of environmental protection [9].

With the decreasing of fossil fuel, new ways of biomass energy utilization have been studied all over the world in the last decades [10]. Today, hydrogen has become an important kind of raw materials in petrochemical and chemical industry, and there is a growing interesting the use of hydrogen as fuel. Hydrogen is defined as a green attractive energy source and has attracted extensive attention worldwide due to its potential higher energy efficiency and less generation pollutants, which may replace conventional fossil fuels in the future [11–12].

Supercritical water (SCW,  $T > 374.15^\circ\text{C}$ ,  $P > 22.12\text{ MPa}$ ) presents complete miscibility with oxygen and organics, making supercritical water a very suitable medium for the

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biomass pyrolysis, oxidation and reduction of organics [13]. High solubility of the intermediates in the reaction medium significantly inhibits tar and char formation that are one of the main drawbacks of conventional gasification. Supercritical water gasification is an advanced technology which can obtain hydrogen-rich gaseous products from wet biomass without any drying process [14]. Many reports have presented the gasification of waste and biomass to produce hydrogen in the supercritical water condition, with high efficiency of hydrogen production [15–20]. Results in these reports showed that the effect of temperature and residence time on hydrogen yield is positive, but the changes in pressure had no effect on the gas yield.

In recent years, supercritical water gasification of waste and biomass have been widely studied, however, few studies on treatment of landfill leachate in supercritical water are reported. Gasification of landfill leachate in supercritical water can not only treat efficiently the leachate, but also obtain hydrogen.

Gong had reported the treatment of landfill leachate using supercritical water oxidation (SCWO) [21–22]. During SCWO process, organics can be degraded into CO<sub>2</sub> and H<sub>2</sub>O finally in a few minutes or even several seconds via homogeneous oxidation reaction with oxidant in SCW. COD removal efficiency of landfill leachate could reach up to 99.23% at 430°C and 30 MPa. It has been verified by Williams and Onwudili [23] that almost complete oxidation of the organic components of the leachate could be achieved under SCWO. In these reports mentioned above, very high removal efficiency of organic pollutants in leachate was obtained. However, wet biomass in leachate was not utilized effectively to produce clean energy. Therefore, developing a new landfill leachate resource utilization process using supercritical water gasification is attractive.

Gong et al. reported partial oxidation of landfill leachate under supercritical water condition. The results showed that hydrogen gas yield, TOC removal rate and carbon recovery rate of 14.32 mmol·g TOC<sup>-1</sup>, 82.54% and 94.56% was achieved under optimum conditions, respectively [8]. And carbonate and bicarbonate were the most abundant carbonaceous substances in product, whereas CO<sub>2</sub> and H<sub>2</sub> were the most abundant gaseous products. The research indicated that landfill leachate could not only be treated efficiently in supercritical water, but also massive biomass in leachate be gasified to produce hydrogen.

In this study, landfill leachate was treated by supercritical water gasification without oxidant in batch reactor, in order to obtain the hydrogen. We examined the effects of temperature, pressure, reaction time and raw leachate concentration on TOC and TN removal efficiency, gas component, gaseous product yield. The product of leachate gasification was also investigated, which is discussed in detail below.

## 2. Materials and methods

The landfill leachate used in this experiment was collected from municipal solid waste landfill site on Zhengzhou, China. The solid waste deposited in the landfill was domestic garbage such as food waste, paper, plastic and so on. The leachate generated from landfill was collected by pipe

and stored in regulating reservoir. The leachate used in this experiment was collected from reservoir with artificial sampler, which was young with the age of less than 5 years. The characteristics of leachate are shown in Table 1. Nitrogen was used to check the air tightness and eliminate the air in device before experiment, which purity was up to 99%. All the other chemicals used in experiments were purchased with analytical purity. Catalyst Na<sub>2</sub>CO<sub>3</sub> was anhydrous reagents and supplied by the Tianli Chemical Reagent Co., Ltd. the alkaline catalysts Na<sub>2</sub>CO<sub>3</sub> was analytical pure reagents.

In these experiments, temperature, pressure, retention time and catalyst are the independent variables. Each experiment was carried out at desired condition (temperature 380–500°C, pressure 22.5–36.5 MPa, reaction time 5–25 min, catalyst 0–10 wt %). Gas component and gas yield of each gaseous component, TOC/TN removal efficiency are the dependent variables, whose values depends on the value of independent variables.

### 2.1. Apparatus and experimental procedures

The scheme diagram of experimental apparatus is shown in Fig. 1. Supercritical water gasification reactor is produced by Nantong HuaAn supercritical extraction Co. Ltd, which is a batch type with volume of 600 mL. The reactor is made of stainless steel HC276. The highest temperature and pressure for reactor is 650°C and 60 MPa. For the safety, the operation pressure is fixed under 40 MPa. The reactor shell is wrapped in insulation. The inside temperature is regulated and monitored by the temperature control device with ± 1°C precision. The pressure of the reactor is shown in pressure gauge. The cooling coil is fixed in the reactor and to be used for cooling the reactor rapidly with water to ambient temperature at the end of each experiment.

The experimental steps are as follows. Before the experiment, nitrogen is injected into the reactor to avoid the effect of air on the gasification result. According to the temperature and pressure required in the experiment, landfill leachate is charged into the reactor with high pressure metering pump. Then, the reactor is electrical heated with the average heating rate of 3°C/min (In these experiments, the maximum desired temperature is set at 500°C, it will take about 150 min to reach 500°C in reactor). The pressure in reactor increase with rise of temperature, which is determined by the volume of feed solution and temperature. When temperature and pressure reach the set point, this point is recorded as the starting point of the reaction. The setting operation condition was held for 5–25

Table 1  
The characteristics of landfill leachate used in experiments

Parameter	Range
COD, mg·L <sup>-1</sup>	11736–47029
TOC, mg·L <sup>-1</sup>	3207–14810
SS, mg·L <sup>-1</sup>	545–982
NH <sub>3</sub> -N, mg·L <sup>-1</sup>	412–956
TN, mg·L <sup>-1</sup>	449–1326
pH	5–7

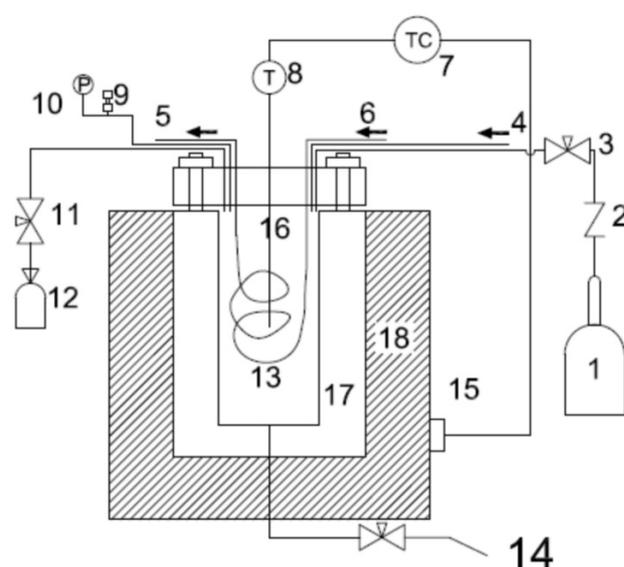


Fig. 1. Scheme diagram of supercritical water gasification system. 1. nitrogen cylinder 2. check valve 3. pressure reducing valve 4. inlet of leachate 5. outlet of cooling water 6. inlet of cooling water 7. temperature control 8. thermocouple 9. safety valve 10. pressure gauge 11. valve 12. gas collecting 13. cooling coil 14. liquid product 15. thermocouple 16. reactor 17. heating coil 18. insulation wall.

min. After the fixed reaction time (5–25 min) is reached, the gasification is suspended, then the cooling water is opened, and reaction temperature, pressure and reaction time are recorded. The effluent is cooled down to room temperature rapidly with cooling water (If the temperature in reactor is 500°C, it will take about 60 min to cool the reactor from 500°C to room temperature). Gaseous products are collected into gasbag for analysis. When the pressure inside reactor decrease to normal level, flushing the reactor using nitrogen, then residual mixtures in reactor are collected into beaker. The mixtures in beaker are separated by filtration. The liquid and solid phase products are analyzed by gas chromatography-mass spectrometry and infrared spectrum, respectively.

In this paper, gasification reaction condition changes as follows: reaction temperature 380–500°C, pressure 22.5–36.5 MPa, reaction time 5–25 min. The experiment is repeated at different conditions. Each experiment was done twice under the same conditions. The results presented in this paper were the average value of two experiments.

## 2.2. Sample analysis

The characteristics of landfill leachate before the supercritical water gasification are specified with the value of COD, SS, TOC and TN. Measurement for the concentration of COD and SS is made using China standard methods (water quality-determination of the chemical oxygen demand-dichromate method (GB11914-89) and water quality-determination of suspended substance-gravimetric method (GB11901-89)). TOC and TN are monitored by N/C 2100 TOC analyzer. The compounds in raw leachate and liquid phase mixtures are analyzed using gas chromatograph and mass spectrum

(GC-MS), Agilent 7890A/5975C. The component of gaseous product generated from gasification is analyzed by DLT-3005P portable infrared gas analyzer. The solid phase residuals are analyzed by infrared spectrum, IR200.

The following TOC/TN removal efficiency, gas component and gaseous product yield equations are utilized to evaluate the gasification characteristics:

## 2.3. TOC/TN removal efficiency

In this paper, the TOC and TN removal efficiency is usually used to indicate the decomposition degree of carbohydrate and nitrogenous compounds in landfill leachate. TOC removal efficiency is calculated using following equation:

$$X_{\text{TOC}} = \left( \frac{\text{TOC}_i - \text{TOC}_e}{\text{TOC}_i} \right) \times 100\% \quad (1)$$

where  $X_{\text{TOC}}$  is TOC removal efficiency (%),  $\text{TOC}_i$  is the TOC concentration in raw landfill leachate ( $\text{mg}\cdot\text{L}^{-1}$ ), and  $\text{TOC}_e$  is TOC concentration of liquid phase effluent ( $\text{mg}\cdot\text{L}^{-1}$ ). TN removal efficiency is calculated using Eq. (1) with TN instead of TOC.

## 2.4. Gas yield

Gaseous products generated from supercritical water gasification are collected and analyzed. The main constituent of gaseous product is hydrogen, methane, carbon dioxide and carbon monoxide. Gas yield of each gaseous component is defined as the molar amount of each produced gas per weight of total organic compounds in landfill leachate added in reactor, which is calculated as following equations.

$$G_{\text{H}_2, \text{CO}_2, \text{CH}_4} = \frac{Y_{\text{H}_2, \text{CO}_2, \text{CH}_4}}{Q \times \text{TOC}_i \times X_{\text{TOC}}} \quad (2)$$

where  $G_{\text{H}_2}$  is the yield of hydrogen ( $\text{mol}\cdot\text{kg}^{-1}$ ),  $Y_{\text{H}_2}$  is the molar amount of hydrogen (mol),  $Q$  is the volume of landfill leachate in reactor (mL),  $\text{TOC}_i$  is the TOC value of initial landfill leachate ( $\text{mg}\cdot\text{L}^{-1}$ ),  $X_{\text{TOC}}$  is the TOC removal efficiency. Similarly,  $G_{\text{CO}_2}$ ,  $G_{\text{CH}_4}$ ,  $G_{\text{CO}}$  is the yield of carbon dioxide methane and carbon monoxide, respectively.

## 3. Results and discussion

Landfill leachate used in these experiments is complicated with large amount of organic compounds. And its gasification in supercritical water is a complex process. Similar to other biomass, landfill leachate gasification gaseous products is mainly composed of hydrogen, methane, carbon dioxide and carbon monoxide [8]. In our experiments, we observed the gas composition included  $\text{H}_2$ ,  $\text{CH}_4$ ,  $\text{CO}_2$  and  $\text{CO}$ .  $\text{H}_2$  and  $\text{CH}_4$  was the main composition. The maximum  $\text{H}_2$  and  $\text{CH}_4$  composition of 57% and 55.1% was observed, and the  $\text{H}_2$  and  $\text{CH}_4$  gas yield was 107.15  $\text{mol}\cdot\text{kg}^{-1}$  and 69.30  $\text{mol}\cdot\text{kg}^{-1}$  at corresponding conditions. The effect of temperature, raw landfill leachate concentration, catalyst and reaction time on gas composition and gas yield would be discussed subsequently.

### 3.1. Effect of temperature on gasification

The effect of reaction temperature on gas composition is shown in Fig. 2. At 30 MPa, 10 min, as the reaction temperature increased from 380°C to 500°C, the fraction of hydrogen increased from 23.4% to 55.2%, while the fraction of methane increased from 12% to 47%, declined to 36%. When pressure increased from 30 MPa to 36 MPa, the fraction of hydrogen increased from 20.7% to 55.6%, and the methane increased from 15% to 55%, then decreased to 38.9% with increase of temperature. We also observed that the fraction of carbon monoxide decreased rapidly with increase of reaction temperature from 380°C to 500°C. The fraction of carbon monoxide declined from 55.48% and 55.4% to 1.9% and 1.1% at 36 MPa, 30 MPa, respectively. Meanwhile, the reduction of carbon dioxide fraction was observed with increase of reaction temperature, which decreased from 7.82% and 8.3% to 2.6% and 2.45% at 36 MPa, 30 MPa, respectively.

The experimental results indicated that the reaction temperature has a positive effect on hydrogen production from landfill leachate gasification in supercritical water. At lower temperature (380°C), the main gas product is carbon monoxide. When the temperature increased from 380°C to 500°C, hydrogen is the main product, which fraction reaches 55.6% and 55.2% at 36 MPa, 30 MPa, respectively. Because of endothermal reaction, the increase of temperature from 380°C to 470°C is beneficial to the water–gas shift reaction [Eq. (3)] and methanation reaction [Eq. (4)], which led to higher fraction of hydrogen and methane, lower carbon monoxide and carbon dioxide fraction. When temperature increased to 500°C, the methanation reaction [Eq. (4)] is inhibited. Hydrogen is the main product. Thus, higher temperature is favor to hydrogen production. The result obtained in our work coincided with the public literature. The aim of this study is to obtain more hydrogen production from landfill leachate. Thus, the optimum temperature for leachate gasification in supercritical water is 500°C.

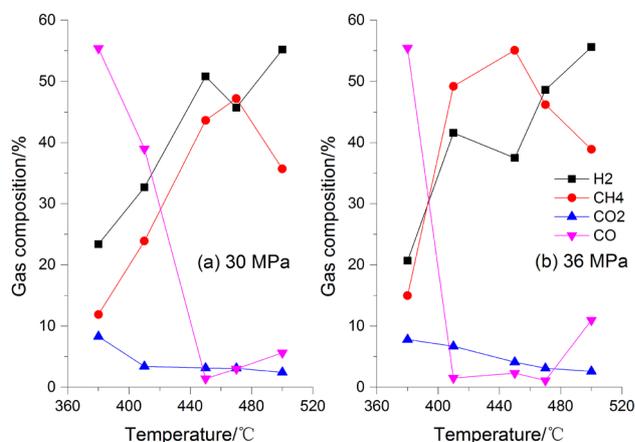
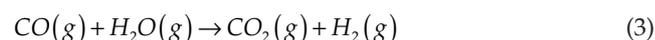


Fig. 2. Effect of temperature on gas composition (pressure 30 MPa, 36 MPa; retention time 10 min).



The same trend of gas yield increasing with reaction temperature is shown in Fig. 3. The hydrogen gas yield also increased from 13.35 mol·kg<sup>-1</sup> and 23.82 mol·kg<sup>-1</sup> to 94.73 mol·kg<sup>-1</sup> and 107.15 mol·kg<sup>-1</sup> at 36 MPa, 30 MPa, respectively. And the methane gas yield also increased from 9.67 mol·kg<sup>-1</sup> to 66.28 mol·kg<sup>-1</sup> at 36 MPa. The same trend was observed at 30 MPa. However, at 36 MPa, the gas yield of carbon monoxide still decreased rapidly from 35.77 mol·kg<sup>-1</sup> to 3.24 mol·kg<sup>-1</sup>. The carbon dioxide gas yield changed from 5.04 mol·kg<sup>-1</sup> to 4.43 mol·kg<sup>-1</sup>. The experimental results suggested that increase of reaction temperature led to increase of hydrogen and methane gas yield, and the higher temperature is favor to hydrogen production.

### 3.2. Effect of pressure on gasification

The effect of pressure on gas composition was obtained at 10 min, 450°C. As shown in Figs. 4 and 5, with an increase of pressure from 22.5 MPa to 36.5 MPa, the molar percentage of hydrogen in gas product decreased straightly from 57% to 37.5%. And the hydrogen yield also decreased from 72.48 mol·kg<sup>-1</sup> to 24.76 mol·kg<sup>-1</sup>.

However, methane gas composition increased from 28.2% to 55.1% with increase of pressure. The methane yield increased slightly from 35.86 mol·kg<sup>-1</sup> to 46.35 mol·kg<sup>-1</sup>, then declined to 36.38 mol·kg<sup>-1</sup>.

The change of carbon dioxide and carbon monoxide fraction and gas yield with increase of pressure was also obtained. Carbon dioxide fraction increased from 2.4% to 4.1% with pressure increased from 22.5 MPa to 36.5 MPa. The gas yield decreased slightly from 3.18 mol·kg<sup>-1</sup> to 2.71 mol·kg<sup>-1</sup>.

In addition, with increase of pressure, the carbon monoxide molar fraction and gas yield declined from 11.30% to 2.30%, 14.37 mol·kg<sup>-1</sup> to 1.52 mol·kg<sup>-1</sup>, respectively.

Generally speaking, pressure had no positive effect upon biomass gasification characteristics in supercritical water [15,16]. The influences of pressure upon the gasification characteristics are complicated. High pressure favors

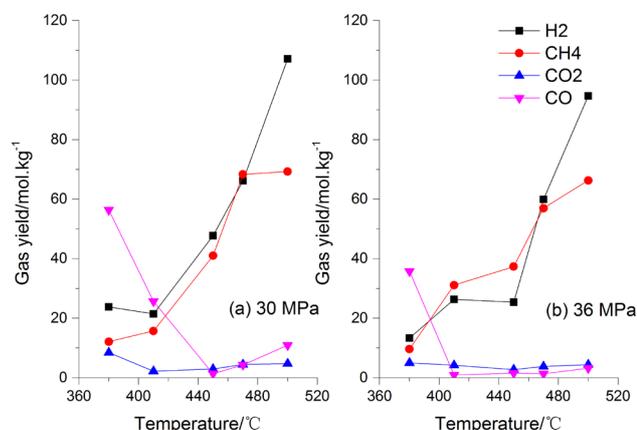


Fig. 3. Effect of temperature on gas yield (pressure 30 MPa, 36 MPa; retention time 10 min).

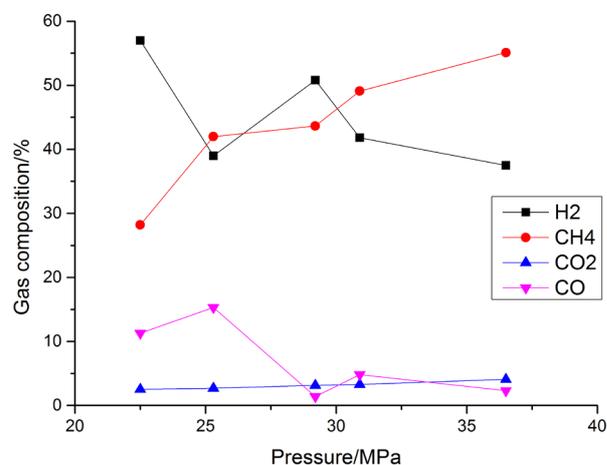


Fig. 4. Effect of pressure on gas composition (temperature 450°C; retention time 10 min).

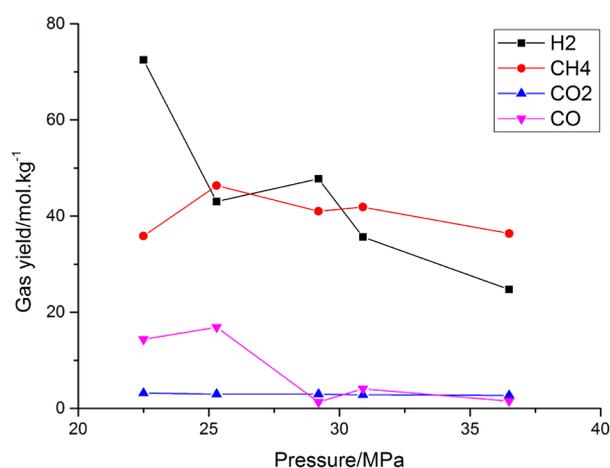


Fig. 5. Effect of pressure on gas yield (temperature 450°C; retention time 10 min).

ionic reaction pathway, which inhibits gas production reactions. In addition, higher pressure leads to higher water density and higher ionic product, so hydrolysis reactions and pyrolysis reactions are promoted. Therefore, higher pressure favors gasification process. In this study, the experimental results suggested that at 450°C, higher pressure is favorable to methanation reaction [Eq. (4)], but adverse to the water–gas shift reaction [Eq. (3)], which lead to higher methane and carbon dioxide production, lower hydrogen and carbon dioxide. In conclusion, the effect of pressure on gas yield indicated that higher pressure is not profitable to hydrogen production. Thus, in order to obtain more hydrogen production, the optimum of pressure for landfill leachate gasification in supercritical water is 22.5 MPa.

### 3.3. Effect of catalyst on gasification

It has been confirmed that the alkali catalysts such as K<sub>2</sub>CO<sub>3</sub>, KOH, Na<sub>2</sub>CO<sub>3</sub>, and NaOH had positive effect on

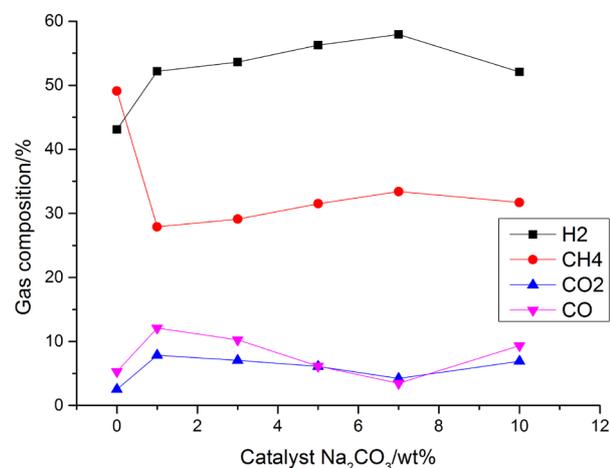


Fig. 6. Effect of catalyst Na<sub>2</sub>CO<sub>3</sub> on gas composition (450°C, 28 MPa, 15 min).

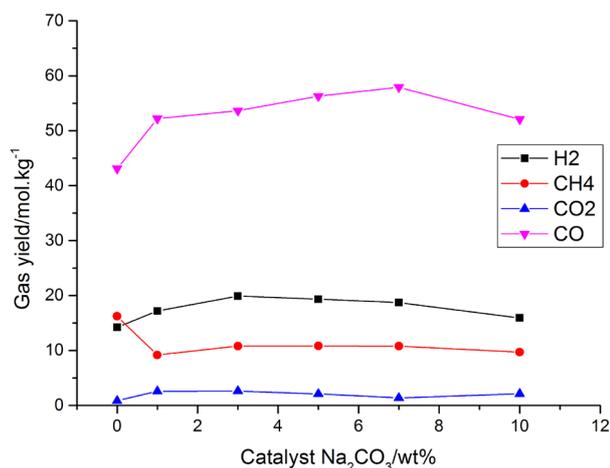


Fig. 7. Effect of catalyst Na<sub>2</sub>CO<sub>3</sub> on gas yield (450°C, 28 MPa, 15 min).

biomass gasification in supercritical water [24–26]. In this experiment, Na<sub>2</sub>CO<sub>3</sub> was added in landfill leachate gasification with different concentration. The effect of Na<sub>2</sub>CO<sub>3</sub> on gasification at 450°C, 28 MPa, 15 min was shown in Figs. 6 and 7.

As shown in Figs. 6 and 7, comparing with 43.1% and 14.2 mol.kg<sup>-1</sup> without catalyst, the hydrogen composition and gas yield increased to 57.92% and 19.90 mol.kg<sup>-1</sup> with catalyst loading amount increasing from 0 to 7 wt%. However, the methane composition and gas yield decreased from 49.1%, 16.23 mol.kg<sup>-1</sup> to 27.9%, 9.18 mol.kg<sup>-1</sup>, respectively. The results indicated adding of Na<sub>2</sub>CO<sub>3</sub> is beneficial to the steam reforming reaction, resulting in increase of hydrogen production. The carbon dioxide and carbon monoxide fraction decreased from 7.83%, 12.11% to 6.9%, 9.33%, respectively. In order to obtain more hydrogen production, the optimum amount of Na<sub>2</sub>CO<sub>3</sub> is 7 wt%, considering with the hydrogen composition and yield in gaseous production.

### 3.4. TOC/TN removal efficiency

Our previous work [22] indicated that up to 99.23% of pollutants in leachate were removed during landfill leachate oxidation in supercritical water at 440°C, 30 MPa. The main purpose of this work was to get hydrogen-rich gas with the decomposition of pollutants in leachate. Thus, TOC, TN removal efficiency of landfill leachate after gasification was also investigated.

As shown in Fig. 8a, at 29 MPa, the TOC, TN removal efficiency increased from 8.36%, 8.33% to 70.53%, 39.71%, respectively, with temperature increase from 380°C to 500°C. The maximum TOC and TN removal efficiency was up to 85.56% and 49.88%, respectively, under corresponding reaction condition. The results indicated temperature had positive effect on TOC and TN removal. Figs. 8b–d suggest that pressure, reaction time and catalyst  $\text{Na}_2\text{CO}_3$  had no obvious effect on TOC and TN removal efficiency. Because of different reaction mechanism between supercritical water gasification and oxidation, hydrocarbons in leachate were converted by several reactions including steam reforming, water-gas shift, methanation, and hydrogenation. The conversion of hydrocarbons in landfill leachate was not completely without oxidant. According to the GC-MS analysis results shown in Fig. 9, partial organic compounds with complex structure were decomposed to low molecular compounds. But, many complicated organics were not decomposed, resulting in relatively low removal efficiency

of pollutants comparison with SCWO. All these experimental results indicated that organics in landfill leachate was not converted completely, which coincided with the relatively lower TOC and TN removal efficiency. Thus, because of existence of many complicated organics in landfill leachate and relatively high concentration of TOC, the effluent could not be discharged to river without treated. According to our previous studies, pollutants in landfill leachate could almost be removed completely in supercritical with addition of oxidants. Thus, it is possible to acquire hydrogen and completely remove pollutants in landfill leachate with addition of oxidant, which would be studied in our next experiments.

### 3.5. Gasification liquid products

The compounds in raw landfill leachate and liquid phase mixtures were analyzed using GC-MS, which were shown Fig. 9. As shown in Fig. 9a, the main compounds in raw landfill leachate were hexanoic acid, pentanoic acid, phenol, p-cresol and other complex carbohydrate with a little amount of nitrogenous compounds. After supercritical water gasification, the liquid products were mainly composed of cyclopentanone, 2-octanone, phenol, p-cresol and nitrogenous compounds. The GC-MS analytic result indicated that low molecular weight carboxylic acid in raw landfill leachate was decomposed, which was not detected

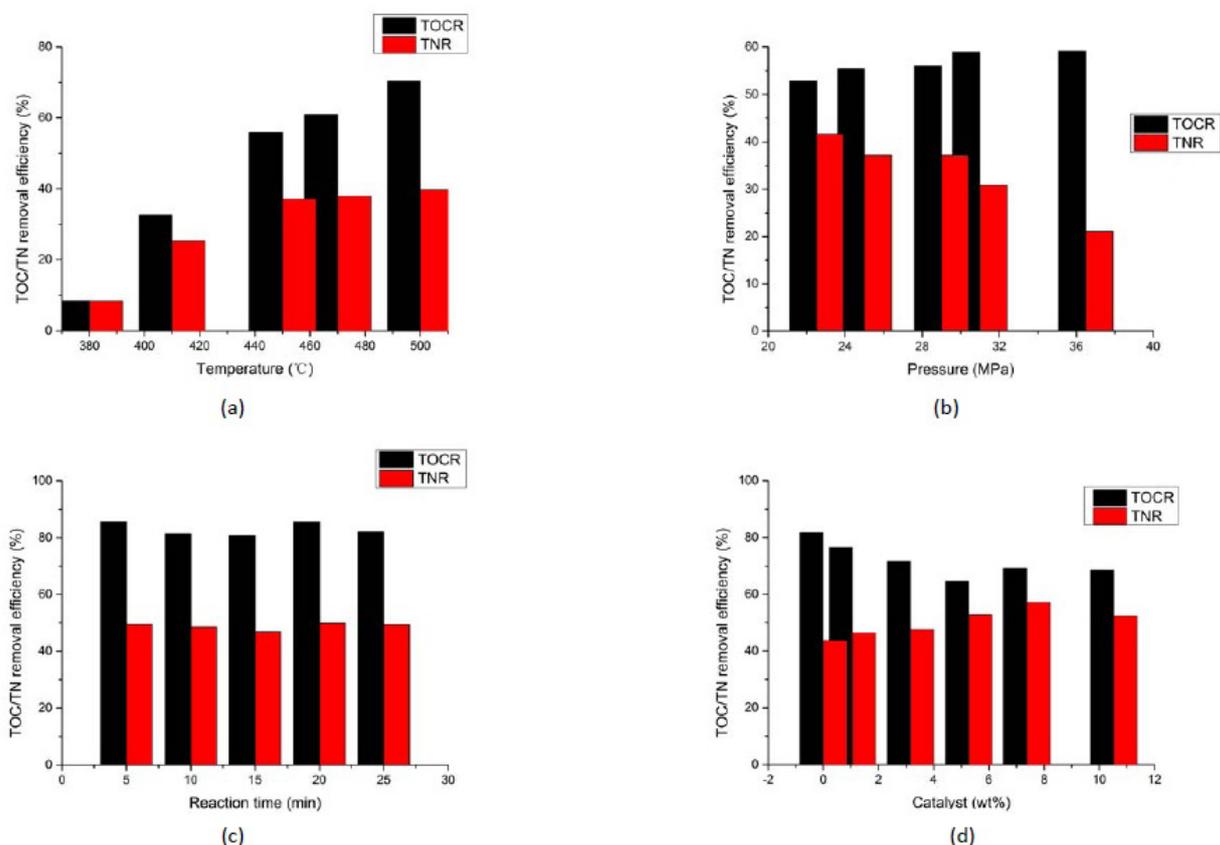
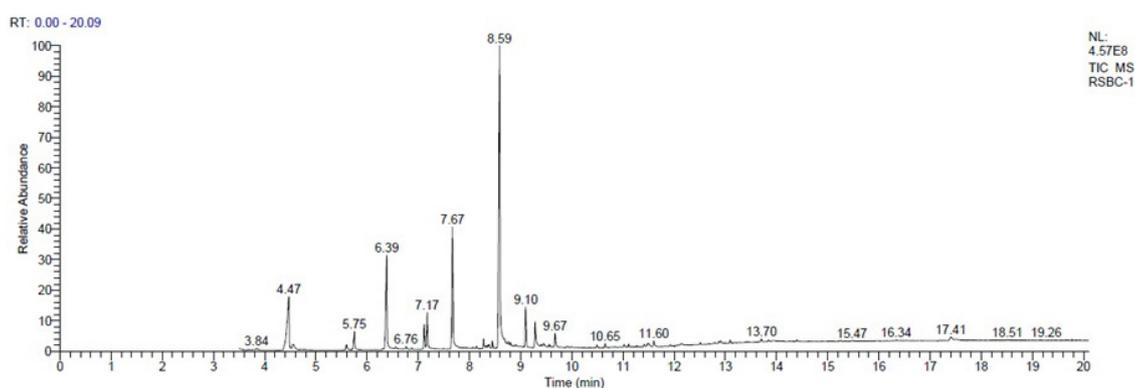
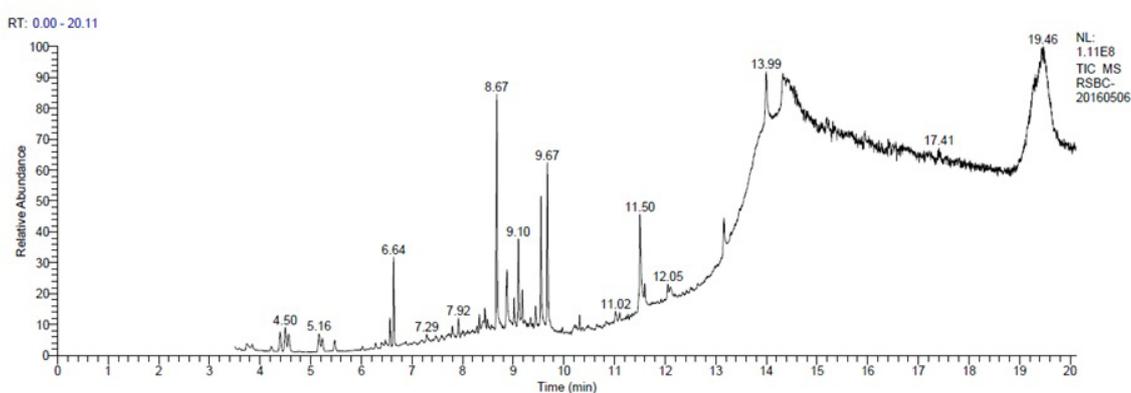


Fig. 8. TOC/TN removal efficiency of landfill leachate gasification in supercritical water (a) effect of temperature; (b) effect of pressure (c) effect of reaction time; (d) effect of catalyst.



(a) raw landfill leachate



(b) liquid product of gasification

Fig. 9. GC-MS analysis result for raw landfill leachate and gasification liquid product (a) raw landfill leachate; (b) liquid product of gasification (450°C, 36.5 MPa, 25 min).

in liquid products. And new type of nitrogenous compounds such as benzenamine and pyridinecarboxaldehyde was observed in liquid products, which indicated decomposition of nitrogenous compounds in raw landfill leachate.

### 3.6. Gasification solid products

It has been reported that tar and char will be generated in the preheating process of SCWO system [27,28]. And the portion of tar and char reaching 57.6% at 500°C and decreased to 24.6% at 650°C in the supercritical water gasification of black liquor was reported [29]. Because of high COD concentration, Gong et al. predicated that tar and char would be generated in the preheater and SCWO system [8]. In our experiments, Infrared spectrum was used to analyze the solid phase product during SCWO gasification. As shown in Fig. 10, the solid products were mainly composed of travertine, ankerite and calcite. These matters generated in landfill leachate gasification were not reported in published studies. Tar and char were not detected in our experiments. Possible reason is that batch gasification reactor was used in our experiments. Landfill leachate was heated at reactor, char and tar generated possibly at preheating process might be converted at reactor.

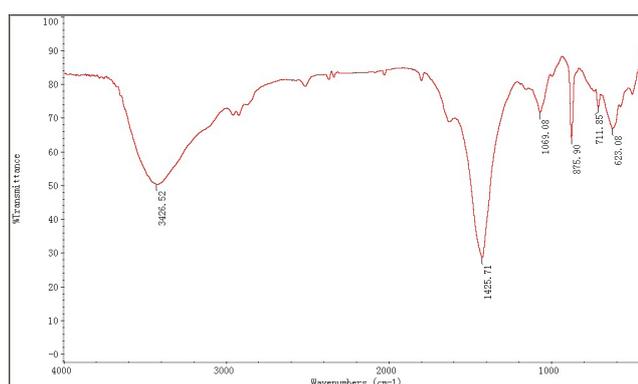


Fig. 10. Infrared spectrum analysis result for landfill leachate gasification solid phase product (450°C, 36.5 MPa, 25 min).

## 4. Conclusions

The experimental results indicated that supercritical water gasification is an effective method to treat landfill leachate with production of hydrogen-rich gas. Hydrogen, methane, carbon dioxide and carbon monoxide were

obtained from landfill leachate gasification. The results showed that hydrogen composition and gas yield increased with increase of temperature, the highest value of 57% and 107.15 mol·kg<sup>-1</sup> was achieved. The TOC and TN removal efficiency also increased with an increase of temperature. The catalyst Na<sub>2</sub>CO<sub>3</sub> loading amount had positive effect on hydrogen production. The effect of pressure on landfill leachate gasification in supercritical water was not obvious.

### Acknowledgement

This work was supported by the National Natural Science Foundation of China (Project No.U1404523, Project No.51308561).

### References

- [1] J.H. Yu, S.Q. Zhou, W.F. Wang, Combined treatment of domestic wastewater with landfill leachate by using A2/O process, *J. Hazard. Mater.*, 178 (2010) 81–88.
- [2] T.H. Christensen, P. Kjeldsen, P.L. Bjerg, D.L. Jensen, J.B. Christensen, A. Baun, H.J. Albrechtsen, G. Heron, Biogeochemistry of landfill leachate plumes, *Appl. Geochem.*, 16 (2001) 659–668.
- [3] B. Zhou, Z.M. Yu, Q.P. Wei, H.Y. Long, Y. Xie, Y.J. Wang, Electrochemical oxidation of biological pretreated and membrane separated landfill leachate concentrates on boron doped diamond anode, *Appl. Surf. Sci.*, 377 (2016) 406–415.
- [4] S. Lee, J. Hur, Heterogeneous adsorption behavior of landfill leachate on granular activated carbon revealed by fluorescence excitation emission matrix (EEM)-parallel factor analysis (PARAFAC), *Chemosphere*, 149(2016) 41–48.
- [5] M. Liu, Y. Peng, T. Liu, H. Xiao, S. Wang, Treatment performance and N<sub>2</sub>O emission in the UASB-A/O shortcut biological nitrogen removal system for landfill leachate at different salinity, *J. Ind. Eng. Chem.*, 32 (2015) 63–71.
- [6] X. Zhao, J.H. Qu, H.J. Liu, C.X. Wang, S.H. Xiao, R.P. Liu, P.J. Liu, H.C. Lan, C.Z. Hu, Photoelectrochemical treatment of landfill leachate in a continuous flow reactor, *Bioresour. Technol.*, 101 (2010) 865–869.
- [7] A.Ž. Gotvajn, J. Zagorc-Končan, M. Cotman, Fenton's oxidative treatment of municipal landfill leachate as an alternative to biological process, *Desalination*, 275 (2011) 269–275.
- [8] Y.M. Gong, S.Z. Wang, H.D. Xu, Y. Guo, X.Y. Tang, Partial oxidation of landfill leachate in supercritical water: Optimization by response surface methodology, *Waste Manag.*, 43 (2015) 343–352.
- [9] S.Z. Wang, Y. Guo, C.M. Chen, J. Zhang, Y. Wang, Supercritical water oxidation of landfill leachate, *Waste Manag.*, 31 (2011) 2027–2035.
- [10] C.H. Wei, C.S. Hu, C.F. Wu, B. Yan, Supercritical gasification for the treatment of o-cresol wastewater, *J. Environ. Sci.*, 18 (2006) 644–649.
- [11] J. Yanik, S. Ebale, A. Kruse, M. Saglam, M. Yuksel, Biomass gasification in supercritical water: part 1 Effect of the nature of biomass, *Fuel*, 86 (2007) 2410–2415.
- [12] Y. Guo, S.Z. Wang, D.H. Xu, Y.M. Gong, H.H. Ma, X.Y. Tang, Review of catalytic supercritical water gasification for hydrogen production from biomass, *Renew. Sust. Energ. Rev.*, 14 (2010) 334–343.
- [13] L.L. Zhang, L. Chen, X.F. Zhao, J.L. Yu, Y.L. Tian, Properties of supercritical water and its application, *Chem. Ind. Eng.*, 20 (2003) 33–38.
- [14] S. Li, Y.J. Lu, L.J. Guo, X.M. Zhang, Hydrogen production by biomass gasification in supercritical water with bimetallic Ni-M/γ-Al<sub>2</sub>O<sub>3</sub> catalysts (M=Cu, Co and Sn), *Int. J. Hydrogen Energ.*, 36 (2011) 14391–14400.
- [15] R. Cherad, J.A. Onwudili, P. Biller, P.T. Williams, A.B. Ross, Hydrogen production from the catalytic supercritical water gasification of process water generated from hydrothermal liquefaction of microalgae, *Fuel*, 166 (2016) 24–28.
- [16] Q.Q. Guan, X.D. Huang, J. Liu, J.J. Gu, R.R. Miao, Q.L. Chen, P. Ning, Supercritical water gasification of phenol using a Ru/CeO<sub>2</sub> catalyst, *Chem. Eng. J.*, 283 (2016) 358–365.
- [17] S. Nanda, J. Isen, A.K. Dalai, J.A. Kozinski, Gasification of fruit wastes and agro-food residues in supercritical water, *Energ. Convers. Manag.*, 110 (2016) 296–306.
- [18] X.H. Su, H. Jin, S.M. Guo, L.J. Guo, Numerical study on biomass model compound gasification in a supercritical water fluidized bed reactor, *Chem. Eng. Sci.*, 134 (2015) 737–745.
- [19] M. Gong, W. Zhu, Z.R. Xu, H.W. Zhang, H.P. Yang, Influence of sludge properties on the direct gasification of dewatered sewage sludge in supercritical water, *Renew. Energ.*, 66 (2014) 605–611.
- [20] M. Gong, S. Nandab, M.J. Romerob, W. Zhua, J.A. Kozinski, Subcritical and supercritical water gasification of humic acid as a model compound of humic substances in sewage sludge, *J. Supercrit. Fluid.*, 119 (2017) 130–138.
- [21] F. Civan, D.H. Özaltun, E. Kipcak, M. Akgün, The treatment of landfill leachate over Ni/Al<sub>2</sub>O<sub>3</sub> by supercritical water oxidation, *J. Supercrit. Fluid.*, 100 (2015) 7–14.
- [22] W.J. Gong, X.J. Duan, Degradation of landfill leachate using transpiring-wall supercritical water oxidation (SCWO) reactor, *Waste Manage.*, 3 (2010) 2103–2107.
- [23] P.T. Williams, J.A. Onwudili, Destruction of environmental organic pollutants by supercritical water oxidation, *Environ. Technol.*, 27 (2006) 823–834.
- [24] S. Nanda, A.K. Dalai, J.A. Kozinski, Supercritical water gasification of timothy grass as an energy crop in the presence of alkali carbonate and hydroxide catalysts, *Biomass Bioenerg.*, 95 (2016) 378–387.
- [25] Z.I. Cheng, H. Jin, S.K. Liu, L.J. Guo, J.L. Xu, D. Su, Hydrogen production by semicoke gasification with a supercritical water fluidized bed reactor, *Int. J. Hydrogen Energ.*, 41 (2016) 16055–16063.
- [26] N. Ding, R. Azargohar, A.K. Dalai, J.A. Kozinski, Catalytic gasification of glucose to H<sub>2</sub> in supercritical water, *Fuel Process Technol.*, 127 (2014) 33–40.
- [27] Y. Guo, S.Z. Wang, C.M. Hu, P.E. Savage, Products, pathways, and kinetics for reactions of indole under supercritical water gasification conditions, *J. Supercrit. Fluid.*, 73 (2013) 161–170.
- [28] M.J. Antal, S.G. Allen, D. Schulman, X.D. Xu, R.J. Divilio, Biomass gasification in supercritical water, *Ind. Eng. Chem. Res.*, 39 (2009) 4040–4053.
- [29] V. Sricharoenchaikul, Assessment of black liquor gasification in supercritical water, *Bioresour. Technol.*, 100 (2009) 638–643.