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Hydrogen Production from Landfill Leachate using Supercritical Water Gasification

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Landfill leachate generated during the landfill process of municipal solid waste contains high concentration of pollutants and has adverse effects on the environment. Leachate is very difficult to be treated to meet the strict quality standards for direct discharge into surface water. Supercritical water gasification might provide an effective conversion method for leachate to hydrogen energy. Gasification of landfill leachate in supercritical water using batch-type reactor was investigated. The effect of temperature, pressure and retention time on gas component and COD, TOC removal efficiency was researched. Experiments were conducted under conditions of 380 – 500 °C, 22.5 – 37.5 MPa, 5 – 25 min. The experimental results showed that gaseous products mainly contain H_2, CH_4, CO_2 and CO. The volume percentage of H_2 reaching up to 55.2 % was obtained at 500 °C, 30 MPa and 10 min. Moreover, COD, TOC removal efficiency being 91.96 %, 84.81 % was obtained at 470 °C, 27 MPa, 25 min. Hydrogen component and COD, TOC removal efficiency increased with the increase of temperature. The suitable retention time is 25 min for leachate gasification in supercritical water. The main liquid intermediate organic products are caproic acid, propionic acid, valeric acid, butyric acid, carbolic acid and p-cresol etc.

1. Introduction

Landfill leachate is commonly generated during the landfill process of municipal solid waste, which contains high concentration of pollutants and has adverse effects on the environment (Gong and Duan, 2010). The composition of leachate is complicated, especially its high concentrations of COD (Chemical Oxygen Demand, COD (30,000 – 60,000 mg/L), NH_3-N (500 – 2,000 mg/L), carbon, nitrogen, and phosphorous out of proportion, and so on (Li et al., 2010). Many researches on landfill leachate treatment have been developed, such as electrochemical oxidation (Zhou et al., 2016), adsorption (Lee and Hur, 2016) and biological treatment (Liu et al., 2015). However, due to its complexity, landfill leachate is difficult to be treated by conventional methods. Research on landfill leachate has been becoming a fascinating area in the field of environmental protection (Wang et al., 2011).

With the decreasing of fossil fuel availability, new ways of biomass energy utilization have been studied all over the world in the last decades (Wei et al., 2006). Supercritical water ($T > 374.15$ °C, $P > 22.12$ MPa) presents complete miscibility with oxygen and organics, making supercritical water a very suitable medium for the biomass pyrolysis, oxidation and reduction of organics (Zhang et al, 2003). Supercritical water gasification is an advanced technology which can obtain hydrogen- rich gaseous products from wet biomass without any drying process (Li et al., 2011). Many reports have presented the gasification of biomass to produce hydrogen in the supercritical water condition with high efficiency of hydrogen production, involving in microalgae (Cherad et al., 2016), glucose (Molino et al., 2016), fruit waste (Nanda et al., 2016) and so on. In the supercritical water gasification, the main products are hydrogen, carbon dioxide, carbon monoxide, methane and ethylene. Hydrogen and methane could be used as clean energy.

In recent years, researches on oxidation (Civan et al., 2015) and partial oxidation (Gong et al., 2015) of landfill leachate in supercritical water were reported. In our previous work (Gong and Duan, 2010), supercritical water oxidation of landfill leachate with hydrogen peroxide as oxidant was carried out without catalysts. It was shown that 99.23 % of COD removal efficiency and 98.06 % of BOD (Biological Oxygen Demand, BOD) removal

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efficiency in landfill leachate was achieved at 430 °C, 30 MPa. These previous works indicate that landfill leachate could be treated efficiently in supercritical water, but massive biomass in leachate was not used as resource. Therefore, developing a new landfill leachate treatment process using supercritical water gasification is attractive. In this study, landfill leachate was treated by supercritical water gasification, in order to obtain the hydrogen from leachate. The effect of operation parameters, such as temperature (380 – 500 °C), pressure (22.5 – 37.5 MPa) and retention time (5 – 25 min) on gas component and COD, TOC (Total Organic Carbon, TOC) removal efficiency was investigated.

2. Materials and methods

2.1 Materials

The landfill leachate used in this experiment was collected from municipal solid waste landfill site in Henan, China. The solid waste deposited in the landfill is 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 is young with the age of less than 5 y. The characteristics of leachate are as follows: COD 2,782 – 47,029 mg/L, TOC 673 – 14,810 mg/L, SS (Suspended Solid, SS) 245 – 982 mg/L, NH_3-N 412 – 956 mg/L, TN (Total Nitrogen, TN) 530 – 1,326 mg/L, pH 5 – 7. Nitrogen was used to check the air tightness and eliminate the air in device before experiment, which purity is up to 99 %. All the other chemicals used in experiments were purchased with analytical purity.

2.2 Supercritical water gasification system

A diagram of the experimental apparatus is shown in Figure1 (where 1: nitrogen cylinder, 2: check valve, 3: pressure reducing valve, 4: inlet of landfill leachate, 5: inlet of cooling water, 6: outlet 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). Supercritical water gasification reactor is produced by Jiangsu Gaoke 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 the reactor are 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.

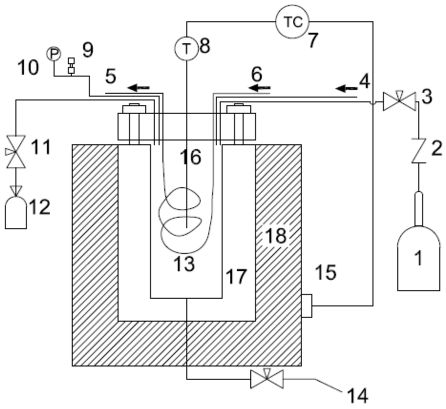


Figure 1: Scheme diagram of supercritical water gasification system

2.3 Analytical methods

The characteristics of landfill leachate are specified with the value of COD and TOC, which indicated the removal of organic pollutants. Measurement for the concentration of COD is made using China standard methods. TOC is monitored by N/C 2100 TOC analyser. The compounds in leachate are analysed using gas chromatograph and mass spectrum (GC-MS), Agilent 7890A/5975C.

In this paper, the COD and TOC removal efficiency is usually used to indicate the decomposition degree of pollutants in leachate. The main constituent of gas product is hydrogen, methane, carbon dioxide and carbon monoxide. Gas component of each gaseous product is defined as the volume of each produced gas per total volume of gas product.

3. Results and discussion

3.1 Effect of reaction temperature on gasification

The effect of reaction temperature on gas component is shown in Figure 2. At 30 MPa, 10 min, as the reaction temperature increased from 380 to 500 °C, the volume percentage of hydrogen increased from 23.4 % to 55.2 %, while the fraction of methane increased from 12 % to 47 % (at 450 °C), then reduced to 35.7 %. When pressure increased from 30 to 35 MPa, the fraction of hydrogen increased from 20.7 % to 55.6 %, and the methane increased from 15 % to 55 % (at 470 °C), then decreased to 38.9 %. We also observed that the fraction of carbon monoxide declined from 55.48 % and 55.4 % to 1.9 % and 5.65 % at 35 MPa, 30MPa, 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 35 MPa, 30 MPa, respectively.

The experimental results indicated that the reaction temperature has a significant effect on landfill leachate gasification in supercritical water. At lower temperature (380 °C), the main gas product is carbon monoxide. When the temperature increased from 380 to 500 °C, hydrogen is the main product. Because of endothermal reaction, the increase of temperature is beneficial to the water–gas shift reaction - Eq(1) - and methanation reaction - Eq(2). When temperature increased to 500 °C, the methanation reaction - Eq(2) is inhibited. Thus, higher temperature is favour to hydrogen production. The results obtained in our work coincided with the public literatures.

$$CO(g)+H_2O(g)\rightarrow CO_2(g)+H_2(g) \tag{1}$$

$$CO(g)+3H_2(g)\rightarrow CH_4(g)+H_2O(g) \tag{2}$$

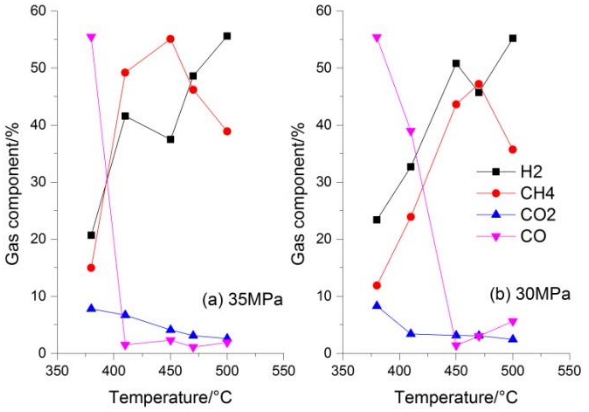


Figure 2: Effect of temperature on gas component

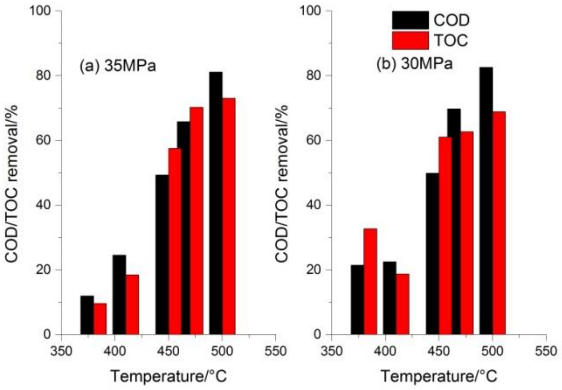


Figure 3: Effect of temperature on COD/TOC removal

In these experiments, we also observed the decrease of COD, TOC in landfill leachate during gasification in supercritical water. The COD, TOC removal efficiency is shown in Figure 3. At 30 MPa, 380 °C, COD and TOC removal efficiency is only 21.42 % and 32.71 %, which indicated very low conversion of pollutants in landfill leachate. But, temperature increased to 500 °C, COD and TOC removal efficiency increased to 82.6 % and 68.87 %. When, the pressure increased from 30 to 35 MPa, the same trend was observed. COD and TOC removal efficiency increased from 11.95 % and 9.6 % to 81.16 % and 73.03 % with an increase of temperature from 380 to 500 °C. The decrease of COD, TOC in leachate indicated that partly hydrogen obtained from gasification may come from decompose of pollutants.

GC-MS analysis result of leachate gasification liquid product is shown Table 1. After 10 min gasification, the main organic compounds in effluent are caproic acid, propionic acid, valeric acid, butyric acid, carbolic acid and p-cresol etc. Partial organic compounds with complex structure were decomposed to low molecular compounds. However, because of existence of complicated organic in leachate and relatively high concentration of COD, the effluent could not be discharged to river without treated. According to our previous studies, pollutants in leachate could almost be removed completed in supercritical with addition of oxidants. Thus, it is possible to acquire hydrogen and complete remove pollutants in leachate with addition of oxidant, which would be studied in our next experiments.

Table 1: The main intermediate organic products in liquid effluent (450 °C, 36.5 MPa, 10 min)

Peak area ratio/ %	Compound	Molecular Formula
26.42	caproic acid	$C_6H_{12}O_2$
9.34	propionic acid	$C_3H_6O_2$
8.72	valeric acid	$C_5H_{10}O_2$
8.49	butyric acid	$C_4H_8O_2$
5.76	carbolic acid	C_6H_6O
3.54	p-cresol	C_7H_8O
2.06	isovaleric acid	$C_5H_{10}O_2$
1.58	enanthic acid	$C_7H_{14}O_2$

3.2 Effect of reaction temperature on gasification

The effect of reaction pressure on gas component was obtained at 10 min, 380 and 450 °C. As shown in Figure 4, with increase of pressure from 22.8 to 24.6 MPa, the percentage of hydrogen in gas product increased straightly from 4.9 % to 24.97 %. Beyond the point of 24.6 MPa, hydrogen fraction reduced from 24.97 % to 20.7 % with pressure increased from 24.6 to 37.5 MPa. However, a reverse trend of hydrogen volume percentage was observed at 450 °C, which decreased from 57 % to 37.5 %. The result indicated that the effect of pressure on hydrogen production is not as positive as temperature. A comparison of the hydrogen volume at 380 °C, 450 °C indicated that higher temperature lead to higher hydrogen production under at same pressure condition.

We also observed that the volume percentage of methane changed with pressure, which increased from 4 % to 15 % and from 28.2 % to 55.1 % with increase of pressure at 380 °C, 450 °Cy. The result indicated that the effect of pressure on methane production is not clear at lower temperature. But under higher temperature condition, the pressure is beneficial to methane production. CO_2 fraction increased from 3 % to 9.48 %, then declined from 9.48 % to 7.82 % with increase of pressure at 380 °C, which increased from 2.5 % to 4.1 % at 450 °C. In addition, at different temperature, the CO fraction declined with increase of pressure.

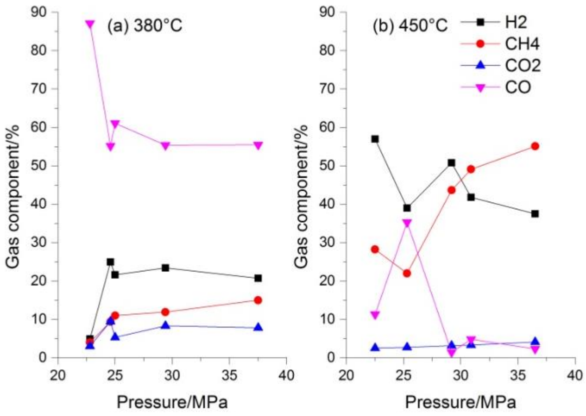


Figure 4: Effect of pressure on gas component

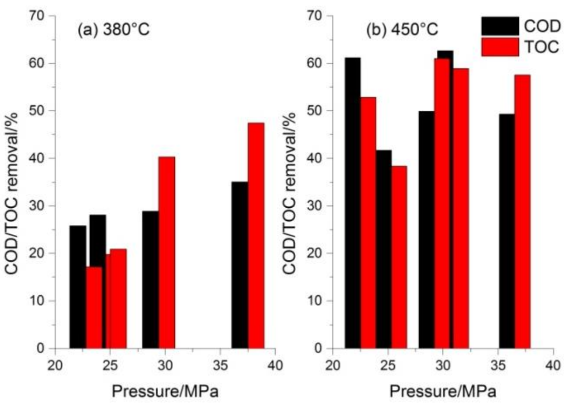


Figure 5: Effect of pressure on COD/TOC removal

As shown in Figure 5, at 380 °C, TOC removal efficiency increased from 17.18 % to 47.47 %with increase of pressure, while COD removal efficiency reduced from 25.82 % to 10.77 %, then increased to 35.05 %. At 450 °C, the removal efficiency of COD, TOC changed from 62.66 %, 61.02 % to 49.32 %, 57.66 % with increase of pressure, the trend is random. But, the lowest COD, TOC removal efficiency value of 41.73 %, 38.37 % is obtained at lower pressure, and the highest value of 62.66 %, 61.02 % is obtained at higher pressure. The experimental results indicated that the effect of pressure on COD, TOC removal efficiency is not obvious, even random.

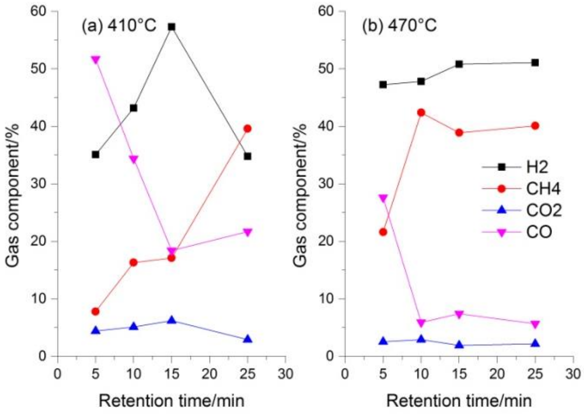
Generally speaking, the influences of pressure upon the gasification characteristics are complicated (Guan et al., 2016). High pressure favors ionic reaction pathway, which inhibits gas production reactions. In addition, higher pressure leads to higher water density and higher ionic product, so hydrolysis reactions and pyrolysis reactions are promoted. In this study, the experimental results suggested that at lower temperature, higher pressure is favor to the water–gas shift reaction. However, at higher temperature, higher pressure favors the methanation reaction, and the effect of pressure on hydrogen production is not clear.

3.3 Effect of retention time on gasification

As shown in Figure 6, hydrogen volume percentage increased from 35.1 % to 57.3 %, then declined from 57.3 % to 34.8 % with retention time extension from 5 to 25 min at 410 °C. The peak point of 57.3 % was observed when retention time was fixed at 15 min. At 470 °C, hydrogen volume percentage did not change obviously with extension of retention time, which increased from 47.25 % (at 5 min) to 51.08 % (at 25 min). Methane volume percentage improved from 7.8 % to 39.6 % (at 25 min). At higher temperature 470 °C, methane volume percentage increased from 21.6 % to 42.4 %, then reduced to 40.1 %.

Moreover, at 410 °C, the highest of carbon dioxide volume percentage was obtained at 15 min, which is 6.2 %. Meanwhile, carbon monoxide component declined from 51.7 %, 27.61 % to 21.7 %, 5.61 %, with extension of retention time at 410 °C, 450 °C.

As shown in Figure 7, COD, TOC removal efficiency increased from 31.94 %, 12.16 % to 47.68 %, 25.04 % with increase of retention time from 5 to 25 min, at 410 °C. At 470 °C, the same trend was observed, the highest COD, TOC removal efficiency of 91.96 %, 84.81 % was observed with retention time fixed at 25 min. In conclusion, the effect of retention time on gas composition and COD removal, TOC removal is different. Extension of reaction time is favor to gasification of landfill leachate in supercritical water. In order to obtain more hydrogen, methane, COD removal, TOC removal, appropriate retention time is suggested to be 25 min.



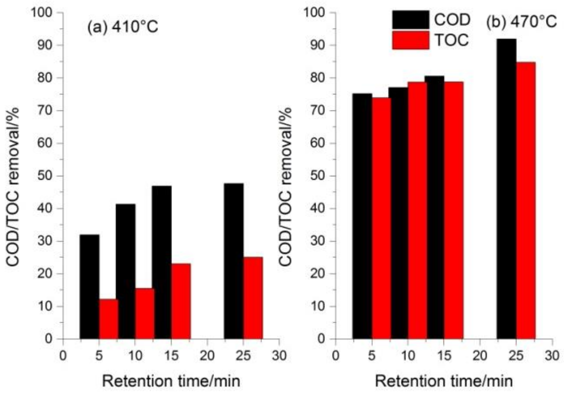


Figure 6: Effect of retention time on gas component *Figure 7: Effect of retention time on COD/TOC removal*

4. Conclusions

In this study, treatment of landfill leachate using supercritical water gasification was investigated. The 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 leachate after gasification. The results showed that hydrogen volume percentage increased with an increase of temperature. The COD, TOC removal efficiency also increased with an increase of temperature. The main organic compounds in effluent are caproic acid, propionic acid, valeric acid, butyric acid, carbolic acid and p-cresol etc. Partial organic compounds with complex structure were decomposed to low molecular compounds. The pressure and retention time also had effect on hydrogen production and COD, TOC removal, but the trend was not similar with temperature. The suitable retention time of 25 min was achieved for leachate gasification in supercritical water.

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