A novel integrated pyrolysis-gasification technology for improving quality of bio-gases from multisource solid wastes

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Abstract. Recovery and utilization of municipal solid waste (MSW) into syngas has already attracted the attention of researchers for years. However, until now the MSW such as sewage sludge and plastics still lack a way of industrial utilization due to the relatively low transformation efficiency or low gas quality. Accordingly, a novel integrated pyrolysis-gasification technology is proposed in this study, in which the volatiles and steam released from the pyrolysis of sewage sludge at 450 °C take part in the gasification of plastic at 600 °C-800 °C, taking advantage of high-water content of sludge to produce high quality bio-gas. At the same time, the synergistic effect between sludge pyrolysis and plastic gasification was explored by product analysis. Compared to pyrolysis or gasification alone, the aromatic degree of the bio-oil obtained by the integrated technology under pyrolysis at 450 °C and gasification at 700 °C weakens. Whereas, the aromatic degree of the bio-oil obtained at 450 °C (pyrolysis) and 800 °C (gasification) deepens, and the yield of C₂H₄ in the bio-gas improves markedly. The higher temperature promotes the decomposition and condensation of macromolecules and also strengthens the influence of volatiles and steam from sludge pyrolysis on the structural fracture of plastics during gasification to some extent. In conclusion, this technology can significantly improve bio-gas yield and quality at high temperature.

1. Introduction
In today’s society with rapid urbanization, sewage sludge production is rising year by year as a result of increasing domestic water consumption. Meanwhile, plastic pollution becomes more and more serious, needing effective treatment urgently. Pyrolysis and gasification, which can dispose and recycle MSW, have been a research hotspot in recent years.

The previous study found that the pyrolysis and gasification within a certain temperature range are conducive to the recycling and utilization of sludge and plastics. Sludge pyrolysis in a low temperature range is beneficial to the reclamation of phosphorus[1] and inhibition of heavy metal release[2, 3], etc. In addition, high yield pyrolysis oil is obtained without wasting a large amount of energy on water evaporation. While, the researches[4, 5] show that water and CO₂ which can be produced by sludge
pyrolysis can also facilitate the cracking of tar. Different gasification reaction paths can be controlled by using different gasification agents such as air, steam and carbon dioxide to obtain different target syngas[6].

Therefore, a novel integrated heat treatment technology was proposed in this study, which combined the pyrolysis and gasification. It uses volatiles obtained from sludge pyrolysis at low temperature as gasification agent, taking part in plastic gasification at high temperature. In order to explore the influence of sludge pyrolysis products on plastic gasification and the synergistic effect, the influence of water on gasification was separated. The experimental material used in this study was air-drying-based sludge. And the effect of gasification temperature on the pyrolysis-gasification experiment was also studied.

2. Materials and methods

2.1. Raw materials

The sewage sludge used in this study was secondary sludge obtained from Tangxunhu (TXH) municipal wastewater plant of Wuhan, China. The sample was dried at 105°C for 48h in the loft drier. Then, it was grinded and sieved to a diameter less than 180μm. Polypropylene (PP) particles were obtained from Sinopharm Chemical Reagent Co.,Ltd. Element H, N and S of the samples were determined by elemental analyzer (EA3000), and element O was calculated by minusing. Proximate analysis was conducted as Proximate Analysis of Coal (GB/T 212--2001).

The ultimate and proximate analysis results are shown in Tab.1. As can be seen, properties of TXH and PP are quite different. TXH has high nitrogen and oxygen content, relatively. The structure of PP, which is almost pure hydrocarbons, is very simple.

| Sample | Proximate analysis | Ultimate analysis |
|--------|--------------------|-------------------|
|        | M  | V  | FC | A  | C  | H  | N  | S  | O  |
| TXH    | 2.20 | 35.96 | 1.49 | 60.35 | 17.74 | 3.21 | 3.00 | 0.39 | 13.11 |
| PP     | 0.06 | 99.83 | 0.04 | 0.07 | 85.51 | 14.40 | 0.06 | 0.01 | 0.02 |

2.2. Experimental procedure

As Fig.1 shows, experimental system consists of nitrogen supply system, pyrolysis-gasification reaction system and products collection system. The pyrolysis-gasification reaction system used a self-designed quartz fixed-bed reactor. The products collection system included bio-oil and bio-gas collection devices. Bio-oil was collected by condensation and organic solvent absorption, and bio-gas was collected in the
gas bag. All experiments were conducted three times to ensure the reliability of the results. Most of the volatiles of sludge released around 450°C[7], while temperature of plastic gasification was around 600-900°C[4, 6]. Therefore, 450°C was chosen as the reaction temperature for sludge pyrolysis while the pyrolysis or gasification of plastic was conducted at 600/700/800°C. Sludge with known loading (2g) was placed in the upper quartz basket, and PP with known loading (2g) in the lower quartz basket. The basket group was put into the upper half of the reactor waiting for the furnace warming up. The furnace began to heat while purging with 200mL/min nitrogen. After the temperature of furnace reached the predetermined temperature, the baskets were quickly dropped off to the heating zone with a heating rate of 10-20°C/s for 30min. The oils of the experiment were condensed in the U-tube and spiral tube using dry ice (about -78°C). Moreover, the oil was completely absorbed by washing bottle for insurance. The oil in the condensing tube was eluted with methanol (Liquid chromatography-mass spectrometer grade, Merck) and dichloromethane (High performance liquid chromatography grade, Fisher Chemical) successively. Bio-oil was defined as the substance dissolved in the solvents but baked at 35°C for 4h without evaporation[7].

In a bit to visually present the difference between coupling experiment of pyrolysis-gasification and simple superposition of sludge pyrolysis and plastic pyrolysis, the concept of theoretical value was introduced, which was weighted averaged by the results of sludge pyrolysis and plastic pyrolysis. Then, the actual value of pyrolysis-gasification was subtracted from the theoretical value, obtaining the difference for analysis.

2.3. Characterization

Analysis of bio-gas obtained from pyrolysis or pyrolysis-gasification experiments was performed by gas chromatograph (TRACE 1300) using TCD module.

The obtained liquid was characterized by gas chromatography-mass spectrometer (Thermo Scientific, Trace 1300 series GC with an ISQ QD MS detector) to get an insight into the molecular composition, which were analyzed with the GC1034C Chemstation and a National Bureau of Standards library (NIST2014) based on retention times and matching mass spectra of standards. The liquid was diluted to 0.5mg/g for optimal analysis and kept at 1±0.1mL conducted by HP-5MS capillary column. The temperature of transfer line was 200°C. The GC oven started at 40°C and was kept for 8min. After that, the heating program was performed at a heating rate of 0.5°C/min reaching 50°C, and it finished until the oven temperature reached 300°C at 5°C/min. The UV spectrum can reflect aromatic degree and aromatics concentration of the liquid sample which are linked to wavenumbers and signal intensity respectively. The liquid samples were diluted to 4ppm[7] and determined by ultraviolet fluorescence spectroscopy (Agilent Cary Eclipse). The scanning rate was 600nm/min, PMT voltage was 900V, and the average time was 0.1s.

3. Results and discussions

3.1. Analysis of product yields in pyrolysis and pyrolysis-gasification

![Fig.2 Product yields of pyrolysis and pyrolysis-gasification](image)
Product yields of pyrolysis and pyrolysis-gasification are shown in Fig.2. The vertical coordinate stands for the temperature of the two heating zones of the reactor. Fig.2(a) shows the product yields of primary pyrolysis at 450°C and secondary pyrolysis at 600/700/800°C of TXH. Fig.2(b) shows the product yields in pyrolysis of PP at different temperatures. It can be seen that as the pyrolysis temperature increases, both bio-oil yield of TXH pyrolysis and PP pyrolysis decreases, and the gas yield increases observably. The results of other studies are similar to those of this study [8, 9]. Fig.2(c) shows the product yields of TXH pyrolysis at 450°C coupled with PP gasification at 600/700/800°C, in which volatiles of TXH pyrolysis are used as gasification agent for PP gasification. It indicates that with gasification temperature increases, bio-oil yield decreases while gas yield increases, which is particularly pronounced at 450°C/800°C. As the temperature increases, the heating rate of samples augments, and the heat transfer rate augments, which leads to part of the bio-oil been more easily decomposed into bio-gas and escape quickly.

Fig.3 The differences between actual and theoretical yields of pyrolysis and pyrolysis-gasification

The results of TXH pyrolysis and PP pyrolysis were averaged as theoretical results of pyrolysis-gasification and compared with the actual results, as shown in Fig.3. It demonstrates that pyrolysis-gasification inhibited the formation of bio-gas by bio-oil at 450°C/700°C to some degree, resulting in more bio-oil and less bio-gas. On the contrast, bio-oil is promoted to bio-gas, resulting in less bio-oil and significantly more bio-gas at 450°C/800°C, which indicating that the pyrolysis-gasification at 450°C/800°C promotes the conversion of bio-oil into bio-gas. The chemical energy barrier of the interaction of sludge pyrolysis coupled with plastic gasification may affect the experimental process.

3.2 Bio-gas distribution of pyrolysis and pyrolysis-gasification

Fig.4 shows the bio-gas distribution of pyrolysis and pyrolysis-gasification. Because of TXH containing high oxygen content, in Fig.4(a), the yields of CO₂ and CO get higher. PP has a simple structure and contains no N or O elements with no solid products. Therefore, in Fig.4(b), the yields of C₂H₆ and CH₄ are relatively large. Both TXH pyrolysis and PP pyrolysis, the bio-gas yields increase with temperature
increased, but the increase rate decreases. The bio-gas distribution of pyrolysis-gasification is dominated by PP pyrolysis because of its large bio-gas yields. In Fig. 4(c), the yields of C2H6 and CH4 swell significantly as gasification temperature get higher. However, the increase rate of C2H6 and CH4 yields ascends with the increase of temperature.

Fig. 5 The differences between actual and theoretical bio-gas yields of pyrolysis and pyrolysis-gasification

The results of TXH pyrolysis and PP pyrolysis were averaged as theoretical results of pyrolysis-gasification, which compares with the actual results, as shown in Fig. 5. All the bio-gas yields of pyrolysis-gasification are less than these of theoretical results at 450°C/700°C. Apart from CO, all bio-gas yields of pyrolysis-gasification are more than these of theoretical results at 450°C/800°C, and C2H6 ascends by 8.6%, which became the main reason for the increasing of bio-gas yields. Namely, pyrolysis-gasification inhibits the formation of bio-gas at 450°C/700°C, and it significantly facilitates the formation of bio-gas at 450°C/800°C, especially C2H6. Pyrolysis-gasification can promote the formation of C2H6 at high temperature. And volatiles like bio-oil, gas and water generated by TXH pyrolysis plus high temperature energy have a certain effect on C-C bond fracture[10]. Large polypropylene molecules split into small hydrocarbons. There are (1)–(4) reaction equations[11] that may occur during the gasification.

\[
C_nH_m + 2nH_2O \rightarrow \left(2n + \frac{m}{2}\right)H_2 + nCO_2 (\Delta H_{298K} > 0) \tag{1}
\]

\[
C_xH_yO_z \rightarrow aCO_2 + bH_2O + cCH_4 + dCO + eH_2 + fC_nH_m - Q_1 \tag{2}
\]

\[
Bio - oil + n_1H_2O \rightarrow n_2CO_2 + n_3H_2 (\Delta H_{298K} > 0) \tag{3}
\]

\[
H_2O + CO \rightarrow H_2 + CO_2 - 41.2MJ/kmol \tag{4}
\]

Small molecules will continue to react with steam (1). The oxygen-containing volatiles of sludge have secondary pyrolysis[10] (2). The bio-oil obtained in gasification will react with steam (3). CO obtained above will react with steam (4). High temperature can promote the forward reaction, which all of these are endothermic reactions, being one of the main reasons for the decrease of CO while the increase of CO2 and H2 at 450°C/800°C.
3.3 Analysis of bio-gas calorific value in pyrolysis and pyrolysis-gasification

Bio-gas calorific value and differences of pyrolysis and pyrolysis-gasification are shown in Fig.6. With temperature increased, the bio-gas calorific value of TXH pyrolysis fluctuates while that of PP pyrolysis decreases. The proportion of C_2H_y with higher calorific value decreases while the proportion of other bio-gas increases, so the bio-gas calorific value declines. The theoretical results were calculated by taking average results of TXH pyrolysis and PP pyrolysis, and compare with the actual results of pyrolysis and pyrolysis-gasification. As the gasification temperature increases, the calorific value difference ascends. C_2H_y proportion of theoretical results gradually decreases, owing to it is more affected by plastic pyrolysis, resulting in a decrease of calorific value. On the other hand, the calorific value of pyrolysis-gasification increases with the gasification temperature increased, and then the difference becomes larger. It means pyrolysis-gasification can improve the bio-gas quality.

3.4 Analysis of bio-oil aromatization in pyrolysis and pyrolysis-gasification

3.4.1 GC-MS analysis

The GC-MS analysis of bio-oil in pyrolysis and pyrolysis-gasification was conducted for the statistics of aromatic degree. The results are shown in Fig.7. From the perspective of temperature, for TXH pyrolysis, when the secondary pyrolysis temperature increases from 600°C to 700°C, the structure of...
aromatics in bio-oil change greatly. Aliphatic hydrocarbons (A-H) disappear, double-ring aromatics (D-R) increase and accounted for more than 50%, and triple-ring (T-R) and quadruple-ring aromatics (Q-R) appear, indicating the aromatic degree deepen. So as for PP pyrolysis, when the temperature increases from 700°C to 800°C, the structure of aromatics in bio-oil also change greatly. However, compared with TXH pyrolysis, PP pyrolysis has lower aromatic degree. The structure of aromatics in bio-oil of pyrolysis-gasification is similar to that of PP pyrolysis, and it changes obviously when the temperature increases from 450°C/700°C to 450°C/800°C.

From the perspective of coupling effect, the aromatic degree of pyrolysis-gasification should be in between TXH pyrolysis and PP pyrolysis. Nevertheless, the results of pyrolysis-gasification are more similar to those of PP pyrolysis experiment at 450°C/600°C and 450°C/700°C, which weakens the high aromatic degree of TXH pyrolysis. The aromatic degree of pyrolysis-gasification doesn’t deepen significantly, suggesting that pyrolysis-gasification inhibits aromatization at 450°C/700°C. At 450°C/800°C, the aromatic degree of pyrolysis-gasification is closer to that of TXH pyrolysis, which weakens the aromatic degree of PP pyrolysis. The bio-oil of pyrolysis-gasification does not contain aliphatic hydrocarbons, and the content of triple-ring and quadruple-ring aromatic slightly increase, suggesting the aromatic degree deepens, partly proving that pyrolysis-gasification promotes aromatization at 450°C/800°C.

Combined with the above, pyrolysis-gasification at 450°C/700°C inhibits the decomposition of bio-oil into gas, and also inhibits polycondensation and cyclization into aromatization, resulting in less bio-gas yield and lower aromatic degree. Moreover, pyrolysis-gasification at 450°C/800°C promotes the thermal decomposition, polycondensation and cyclization of bio-oil, resulting in more bio-gas yield, especially C2Hy, and higher aromatic degree.

3.4.2 UV analysis

![UV analysis](image)

The UV results of the pyrolysis-gasification were converted to 1g feedstock. Fig.8(a) shows the UV curve of TXH pyrolysis, which deviates to the right with the increase of secondary pyrolysis temperature. Namely, aromatic degree becomes higher, but the aromatics content descends. In addition, the curve at 700°C is similar to that at 800°C. The above results are consistent with GC-MS. Fig.8(b) shows the results of PP pyrolysis. As the temperature increases, the curve moves towards right slightly, and the content of aromatics increased observably.

Pyrolysis-gasification results in Fig.8(c) compare with the theoretical results. At 450°C/700°C, there are more double-ring and triple-ring aromatics of pyrolysis-gasification. However, quadruple-ring and above aromatics disappear, while it still exists in theoretical results, which further proves that pyrolysis-gasification could inhibit condensation aromatization at 450°C/700°C. At 450°C/800°C, there are a few none-ring substances and single-ring aromatics of pyrolysis-gasification relatively, while there are more
double-ring, triple-ring, quadruple-ring and above aromatics, which also proves that the pyrolysis-gasification at 450°C/800°C would promote aromatization.

4. Conclusion
A new technology is proposed, which integrates pyrolysis and gasification. Sludge pyrolysis under 450°C can save energy consumption of water evaporation, and get volatiles including bio-oil, steam and bio-gas, which take part in plastic gasification under 600-800°C.

Gasification temperature is an important factor affecting the yield of bio-gas which been produced using integrated pyrolysis-gasification technology. Controlling the temperature can get a higher gas conversion rate and better bio-gas quality. Sludge pyrolysis and plastic gasification at 450°C/800°C maximize bio-gas yield, which C2H6 increases the most and calorific value also ascends.

The aromatic degree of the bio-oil obtained by integrated pyrolysis-gasification at 450°C/700°C becomes lower. On the contrary, the aromatic degree of the bio-oil obtained at 450°C/800°C becomes higher. The higher gasification temperature promotes the decomposition and condensation of macromolecules into aromatic substance and also strengthens the influence of volatiles and steam from sludge pyrolysis on the C-C structure fracture of plastics during gasification to some extent.

References:
[1]. Xiao, K., et al., Investigation on emission control of NOx precursors and phosphorus reclamation during pyrolysis of ferric sludge. Science of The Total Environment, 2019. 670: p. 932-940.
[2]. Han, H., et al., Effects of reaction conditions on the emission behaviors of arsenic, cadmium and lead during sewage sludge pyrolysis. Bioresource Technology, 2017. 236: p. 138-145.
[3]. Han, H., et al., Inhibitory effects of CaO/Fe2O3 on arsenic emission during sewage sludge pyrolysis. Bioresource Technology, 2016. 218: p. 134-139.
[4]. Feng, D., et al., Catalytic mechanism of ion-exchanging alkali and alkaline earth metallic species on biochar reactivity during CO2/H2O gasification. Fuel, 2018. 212: p. 523-532.
[5]. Pinto, F., et al., Effect of gasification agent on co-gasification of rice production wastes mixtures. Fuel, 2016. 180: p. 407-416.
[6]. Lopez, G., et al., Recent advances in the gasification of waste plastics. A critical overview. Renewable and Sustainable Energy Reviews, 2018. 82: p. 576-596.
[7]. Han, H., et al., Evolution of nitrogen/oxygen substituted aromatics from sludge to light and heavy volatiles. Journal of Cleaner Production, 2020. 257: p. 120327.
[8]. Park, H.J., et al., Clean bio-oil production from fast pyrolysis of sewage sludge: Effects of reaction conditions and metal oxide catalysis. Bioresource Technology, 2010. 101(1): p. S83-S85.
[9]. Gautam, N. and A. Chaurasia, Study on kinetics and bio-oil production from rice husk, rice straw, bamboo, sugarcane bagasse and neem bark in a fixed-bed pyrolysis process. Energy, 2020. 190: p. 116434.
[10]. Xiong, Z., et al., Formation of the heavy tar during bio-oil pyrolysis: A study based on Fourier transform ion cyclotron resonance mass spectrometry. Fuel, 2019. 239: p. 108-116.
[11]. Song-lin, X.Z.Z., Research Progress on Biomass Gasification and Catalysts. Biomass Chemical Engineering, 2012. 46(1): p. 39-44.