Effect of Gangue Composite Additives on MSW Pyrolysis

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Abstract. Pyrolysis of MSW (Municipal Solid Waste) with gangue composite additives was conducted in a fixed-bed reactor. The effect of the gangue composite additive on the pyrolysis product yields and the reaction rate of gas production were investigated in this research. The results showed that gangue composite additives have obvious effect on reducing the char yield but increasing the tar yield, except the gangue composite additive activated at 1000°C. The gangue composite additives activated at 500°C, 800°C and 1000°C displayed improvement on the component of H₂, CO and CH₄ yields.

1. Introduction

Each year, large amounts of the municipal solid waste (MSW) discharge throughout the world, in China which was about 200 million tons in 2017. It would lead to environmental problems such as release of acidic substances or heavy metals if MSW is not properly disposed of. On the other hand, MSW is variously composed of food, paper, plastics, glass, textiles, garden waste, etc. In which there is a considerable amount of renewable materials which can be used for energy recovery or production of solid, liquid or gaseous fuels. The current practice of incineration of MSW is regarded as an effective option for energy recovery with public opposition due to undesirable air emission and regulation restriction [¹]. Pyrolysis is an effective process for MSW to decompose to smaller molecules in absence of oxygen at a high temperature, which always produces gas, tar and char [²].

Adding catalysts or additives is a meaningful approach for pyrolysis to improve gas quality, increase energy content and optimize pyrolysis process [³-⁶]. Ni- or Ca- based materials is commonly used in relative researches. Although most expensive catalysts can be recovered, catalyst poisoning by sulfur at high temperature is still not properly settled. Thus, waste treatment with solid waste additives has some advantages over thermal degradation. Some researchers have explored the waste additives but research information and data are limited.

In this study, gangue was used in the catalytic degradation process of MSW for exploring the effects on products. The thermal treatment of catalytic degradation was performed in an oxygen-free fixed-bed reactor with a heating rate of 15 °C/min.

2. Materials and Methods

2.1. MSW and Gangue composite additives
The MSW used in this study was sampled from a typical MSW transfer station located in the southern Beijing. Before the experiments, the samples were dried at 105 °C for 24 h in a recycling ventilation drier, and crushed in a high-speed rotating pulverizer to prepare powder of mean particle size of 1 mm - 2 mm. This is important to avoid the influence of water in biomass on reducing temperature in the reactor. Table 1 shows the main characteristics and component of MSW samples.

| Proximate analysis / %  | Ultimate analysis / % |
|-------------------------|-----------------------|
| Volatiles               | C                     |
| Fixed C                 | H                     |
| Ash                     | N                     |
| Moisture                | S                     |
| LHV / MJ/kg             | O                     |
| 63.75                   | 25.10                 |
| 7.31                    | 2.78                  |
| 25.14                   | 1.89                  |
| 3.80                    | 0.38                  |
| 13.00                   | 44.71                 |

The gangue composite material consists of 92% gangue, 2% Ni(CH₃COO)₂, 2% Mn(CH₃COO)₂, 2% Mg(CH₃COO)₂ and 2% H₂O, which was activated at 0 °C, 500 °C, 800 °C and 1000 °C for 1 h, recorded as A1, A2, A3, and A4, respectively. Test samples were mixed with MSW and gangue composite material (3 wt.%) after pretreatment and kept in desiccators.

2.2. Pyrolysis
The quartz retort in the reactor had a volume of 420 cm³ (3.5cm ID) which was externally heated by an electrical furnace. Temperature was measured by a thermocouple inside the bed. Dosage of samples was 20g for each test. The experiments were carried out to final 900 °C with the rate of 15 °C/min. The vapors together with some char fines residuals then passed through a liquid product collection system consisting of water-ice condenser. Although the ice condenser could maintain the pyrolysis vapors at a very low temperature around 0 °C, there were still some volatiles that could not be condensed and collected in the tar pots, but could be captured in the cotton wool filter instead. After the cotton wool filter, the pyrolysis gases were analyzed off line by gas chromatography for H₂, CO, CH₄ and CO₂. All the yields were calculated and each experiment was performed three times. Reproducibility of the experimental data was calculated within ± 3%.

3. Results and Discussion

3.1. Influences of gangue composite additives on product yields
As shown in Figure 1, the char yields with the 3 wt.% additives were lower than that without additives. This might be caused by the activity of additives, which would effectively help to decompose MSW. The tar yield obtained as 37.5 wt.% without additives and reached to 44.0 wt.%, 43.0 wt.%, 40.0 wt.% and 36.5 wt.% with A1, A2, A3 and A4, respectively. It indicates that the utilization of the non-activated additives is promoting higher tar yield than the activated additives in this experiment. The gas yields were about 15.0 wt.%, 15.5 wt.%, and 18.0 wt.% with the additions of A1, A2 and A3, respectively, lower than that without additives (20.0 wt.%). But it reached about 22.5 wt.% of gas yields with the additions of A4, higher than that without additives.
For the component of product yields, it can be noticed that H$_2$ yields with gangue composite additives were higher than that without additives. H$_2$ yield obtained was 10.21 mL/g with A1, and reached to a higher yield of 11.87 mL/g with A3. This shows that gangue composite additives have obviously effect of increasing the component of H$_2$ yields.

It can be seen that the component of CO yields with activated additives were better than that with non-activated additives. The component of CO yields obtained as 17.57 mL/g, 42.74 mL/g, 28.57 mL/g and 28.11 mL/g with A1, A2, A3 and A4. This shows that gangue activated additives have obviously effect of increasing the component of CO yields.

The component of CH$_4$ yields with activated additives was better than that with non-activated additives. The component of CH$_4$ yields with gangue composite additives obtained as 7.99 mL/g, 15.87 mL/g, 10.58 mL/g and 13.10 mL/g with A1, A2, A3 and A4. This shows that gangue activated additives have obviously effect of increasing the component of CH$_4$ yields at this activation temperature.

The component of CO$_2$ yields with gangue composite additives obtained as 27.15 mL/g without additives. The component of CO$_2$ yields with gangue composite additives obtained as 28.48 mL/g, 48.59 mL/g, 24.53 mL/g and 60.45 mL/g with A1, A2, A3 and A4. This shows that gangue activated additives have a little effect of reducing the CO$_2$ at activation temperature of 800 °C.

It can be seen that the effect of additives activation temperature on gas yields was not the higher activation temperature the better gas yields. To improve the component of H$_2$ and CO yields the catalytic effect with A2 at activation temperature of 500 °C was more apparent. To improve the component of CH$_4$ yields the catalytic effect with A4 at activation temperature of 800 °C are best in this experiment. To reduce the component of CO$_2$ yields the effect with A4 at activation temperature of 800 °C was choice.

### 3.2. Effects of gangue composite additives on the rate of gas production

As is shown in Figure 2, the presence of gangue composite additives in the reactor system resulted in a large increase in the rate of H$_2$ production above 700 °C. All the component of H$_2$ showed a marked increase in the presence of the gangue composite additives at pyrolysis temperature of 800 °C and 900 °C. It is known that H$_2$ is formed at relatively high temperatures by the extensive depolymerisation of the phenyl groups which constitute mostly in biomass lignin or the severe secondary reactions between heavy molecular weight hydrocarbon liquids and light hydrocarbon gases in the evolving volatiles.

As for CO, its production reached to maximum value at 400 °C pyrolysis temperature with additives. Thermal stability of the branched structure of the hemicellulose was poor, easily generated by decomposition of some of the small molecule compounds such as CO$_2$ and CO, etc. or aldehydes at low temperature [7].

As for CH$_4$, the releasing of production can be caused by the cracking of methoxyl–O–CH$_3$[8]. The rate of CH$_4$ production reached to its maximum value at 900 °C pyrolysis temperature with or without

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**Figure 1. Effect of gangue composite additives on product yield.**

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additive. The rate of CH\(_4\) production of pyrolysis temperature 500 °C was 0.27 mL/°C without additive. The rate of CH\(_4\) production of pyrolysis temperature 500 °C was 0.10 mL/°C, 0.07 mL/°C, 0.24 mL/°C and 0.30 mL/°C with A1, A2, A3 and A4. The additive of A4 has certain effect of increasing the rate of CH\(_4\) production in this experiment.

As for CO\(_2\), additives of A1 and A3 performed certain effect on reducing the rate of CO\(_2\) production at 900 °C pyrolysis temperature in this experiment.

![Figure 2](image.png)

Figure 2. Effect of gangue composite additives on the rate of H\(_2\), CO, CH\(_4\) and CO\(_2\) production.

4. Conclusions
In this experiment, the char yields were lower in samples with addition than that without additives. The utilization of the non-activated additives promoted higher tar yield than the activated additives. The gangue composite additives activated at 500 °C, 800 °C and 1000 °C have obviously effect on increasing the component of H\(_2\), CO and CH\(_4\) yields. The influence of gangue composite additives in the rate of H\(_2\) production was above 700 °C.

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