



## Effects of various additives on the pyrolysis characteristics of municipal solid waste



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### ABSTRACT

Additives can have a significant impact on the pyrolysis process. The effects of three additives (CaO, MSW char and biomass) on the pyrolysis characteristics of municipal solid waste (MSW) were investigated using a fixed-bed reactor. In addition, the effects of additives and temperature on the MSW pyrolysis product yield, the composition of MSW pyrolysis gases, and the composition of MSW pyrolysis tar were investigated using fixed bed reactor, GC–MS and FTIR, respectively. The results showed that the maximum tar yield of the MSW reached 28.73% at 600 °C and the tar yield decreased with increasing amounts of CaO and MSW. The tar yield began to decrease when the additive amount of CaO was 5% and decreased to 23.05% when the additive amount of MSW char (C) was 30%. Synergistic pyrolysis of the biomass and MSW was observed when the additive amount of the pine increased to 75% (with a tar yield of 37.91%). Regarding gas composition, with increasing additives content, the CO<sub>2</sub> yield decreased, while the CO yield increased. According to the FTIR analysis of the tar, CaO enhanced the condensation of the aromatic rings and converted the aliphatic hydrocarbons, while C reduced the oxygenic groups of the tar. The GC–MS results revealed that the additives decreased the yield of carboxylic acid and ethanol, and increased the ester yield. The additives were also found to have a deoxidation effect that decreased the acid content, potentially improving the quality and stability of the tar.

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### 1. Introduction

The production of municipal solid waste (MSW) in China reached  $1.70 \times 10^8$  tons in 2013, approximately 9% higher than the 2012 level (Zhu et al., 2016). Although MSW is detrimental to humans and the environment, it is also considered a renewable resource because of its easy availability and stable production. Therefore, sustainable disposal of MSW has become essential for the public and environment.

MSW is currently disposed of through landfilling, composting and incinerating. MSW landfilling was once popular, but this method has multiple practical problems, such as contamination of groundwater through leachate production (Fang et al., 2017). MSW composting is an aerobic, microorganism-mediated, solid-state fermentation process by which organic MSW is transformed into more stable products (Oscar et al., 2017). These products can be used as a source of fertilizer for soil improvement, but this approach also suffers from shortcomings, such as a large required

initial investment and long production turnaround times. The thermal treatment of MSW is a promising technology to achieve energy recovery, and this technique includes incineration, pyrolysis and gasification (Cossu, 2011). Pyrolysis, the thermochemical decomposition of organic material in the absence of oxygen in the atmosphere, is the initial stage of incineration and gasification. In an inert atmosphere, MSW produces less NO<sub>x</sub>, SO<sub>2</sub> and dioxin than incineration (Thomas, 2004; Xin et al., 2016), and the volatilization of heavy metals and fly ash is avoided (Wang et al., 2017; Saffarzadeh et al., 2006). Thus, MSW pyrolysis has environmental advantages over conventional MSW disposal.

MSW pyrolysis has been the subject of increasing attention given its flexibility to obtain a combination of solid, liquid and gaseous products (Dina et al., 2017). The solid product of MSW is char, which has a high calorific value and low ash content and can be efficiently combusted with other fuels, such as MSW or coal, in combined heat and power (CHP) plants. Moreover, the dense and porous microstructure of char is associated with high adsorption capacity, making this material suitable for filtration purposes or soil improvement agents (Hu et al., 2017). Liquid and gaseous products of MSW pyrolysis can be further converted into chemicals and fuels.

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Previous MSW pyrolysis studies have focused on reactor development (Williams, 2013), the transformation behavior of pyrolytic pollutants (Yu et al., 2013; Uchimiya et al., 2010), and production characterization under various pyrolysis conditions, such as materials, temperature and heating rate (Honou et al., 2016; Klemetsrud et al., 2016; Lin et al., 2016). Additives, predominantly catalyzers and biomass, can have an important impact on the pyrolysis process and product characteristics. Extensive studies have been conducted to elucidate the effects of additives on coal and biomass pyrolysis (Khan and Seshadri, 1991; Shen et al., 2016; Suelves et al., 2000). CaO is among the most widely used pyrolysis catalysts for its efficient catalytic activity, low cost and abundance. The effect of CaO on pyrolysis or gasification has been addressed in previous studies, but most of these studies were performed in the context of on gasification or pyrolysis of coal and biomass. Khan and Seshadri (1991) found that the addition of CaO accelerates the yield of coal pyrolysis tar and the release of S and O in the tar. CaO can act as a reactant and react with phenolic compounds to form hydrocarbon salts, ultimately leading to a reduction in phenolic components. Chen et al. (2017) investigated the effects of CaO on the product composition of polyethylene, paper pulp and bamboo. The results indicated that the addition of CaO promoted H<sub>2</sub> production but reduced tar yield. Chen et al. (2017) found that upon the addition of CaO, the content of acidic compounds decreased. Under similar conditions, the concentration of evolved H<sub>2</sub> and CH<sub>4</sub> increased, while that of CO<sub>2</sub> decreased. Char as a catalyst to improve the quality of pyrolysis tar and the cracking of tar is attractive because of its alkali and alkaline earth metallic (AAEM) content (Wang et al., 2017). However, most previous studies have focused on the catalytic cracking of coal and biomass pyrolysis products for tar and gas upgrading over char-based catalysts. Wang et al. (2012) found that for pyrolysis with secondary cracking at 600 °C over a char layer of 20% tested coal, the gas yield and light tar content increased, respectively, by 31.2% (vol.) and 25% (mass) relative to the direct pyrolysis of coal at 600 °C. Shen et al. (2016) studied the effects of char on the catalytic cracking of tar from biomass and found that char has a prominently catalytic effect on the conversion of toluene, causing the concentration of CO to increase. Biomass is an important additive in the field of pyrolysis. Research on the co-pyrolysis of MSW and biomass has been of significant interest in the waste-to-energy field, particularly in the case of syngas production from metal catalytic bio-oils and partial oxidation and steam reformation (Zhao et al., 2017a, 2017b).

Although various additives have a variety of effects on the characteristics of coal and biomass pyrolysis products, a systematic investigation on the effects of additives on the pyrolysis characteristics of MSW had not yet been completed. Wood, polyethylene (PE), paper, biomass and other components of MSW have been used separately as MSW to investigate pyrolysis characteristics (Sheth and Babu, 2010; Navarro et al., 2012; Lin et al., 2010). In contrast, in the present study, we investigated the pyrolysis characteristics of MSW as a whole. We also investigated the influence of adding CaO, MSW char (C) and pine on the yield of MSW pyrolysis gas composition. The liquid products of MSW pyrolysis contain significant amounts of water and organic chemicals, such as organic acids and ethanol, which would reduce the fields of possible utilizations (Mante et al., 2012). Previous MSW pyrolysis studies have focused the transform of the pyrolysis liquids into permanent gases such as hydrogen, methane and carbon monoxide (Zhang et al., 2007). The proposed approaches include pyrolysis gas recycling and the catalytic post-treatment of the pyrolysis products (Zhao et al., 2017a, 2017b). The purpose of these methods is to upgrade the pyrolysis products of MSW. However, the purpose of this paper is to investigate the effects of additives on the process of formation of MSW products. So, in this paper, the effects of

additives on the composition and quality of pyrolysis tar from MSW were investigated.

## 2. Materials and methods

### 2.1. Materials

MSW from the Nanyan Waste Transfer Station in Taiyuan, China was collected and labeled in a sealed bag. To reduce the moisture content, MSW was dried on the ground for three days. Inorganic components (e.g., glass, ceramics, metals and dust) were separated by manual selection and screened. Three organic samples were blended extensively to ensure sufficient homogeneity. The content of kitchen waste, plastic, paper, fabric and bamboo in organic MSW was 57.72%, 23.40%, 10.74%, 6.63% and 1.51%, respectively. First, the organic MSW was dried in an electric vacuum drying oven (SLOM, SG-HX250) for 24 h at 105 °C, and then the MSW was crushed to particles smaller than 1 mm using a high-speed crusher and sieved through a 200-mesh standard screen. Pine (P) collected from the China University of Mining & Technology, Beijing was dried, crushed and sieved to obtain particles with an average size of < 0.075 mm. The CaO used in the experiment was of commercial grade (>95%), and its particle size was less than 100 µm. MSW char (C) added to the MSW was produced by heating at 600 °C for 0.5 h. The additives were mechanically mixed with MSW, and the experimental samples (containing CaO, pine or C) were termed MSW + CaO, MSW + P or MSW + C, respectively. The volatile content of the sample is taken as the weight loss at 950 °C (ASTM D3175-89) for 7 min (ASTM, 1997). On each crucible 4–5 g of dried feedstock are spread in thin layers, then the crucibles and samples were placed in a Carbolite AAF1100 furnace and heated to 950 °C and held for 7 min. The average of two samples was taken to further reduce the deviation. The fixed carbon value was obtained by difference (Joseph et al., 2017). Table 1 shows the proximate and ultimate analysis of the samples.

### 2.2. Experimental apparatus and conditions

#### 2.2.1. Fixed-bed reactor

A parallel test was conducted in a fixed-bed reactor (Fig. 1) to investigate the yield of MSW pyrolysis products. The tube reactor was composed of quartz with an inside diameter (ID) of 35 mm and a total height of 700 mm. The length of the furnace was 800 mm, and the maximum temperature was 1150 °C. Nitrogen was flowed into the quartz tube reactor at 20 mL/min for approximately 30 min before pyrolysis to maintain an inert atmosphere. Thirty grams of MSW was spread evenly within the quartz tube reactor, and the N<sub>2</sub> gas flow rate was set to 40 mL/min to purge the volatiles from the reactor. The residence time was 30 min with a heating rate of 20 °C/min, and the pyrolysis temperature was raised from 400 °C to 700 °C in steps of 50 °C. Char from the

**Table 1**  
Proximate and ultimate analysis of samples.

	MSW	MSW char	Pine
(wt.%, daf)			
V	90.39	15.06	85.67
FC	9.61	84.94	14.33
C	47.41	91.93	52.46
H	5.12	1.07	6.42
O	45.72	5.27	39.81
N	1.18	1.34	0.86
S	0.57	0.39	0.45
H/C	1.30	0.14	1.47
O/C	0.71	0.04	0.56

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