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Effects of additives on the co-pyrolysis of municipal solid waste and paper sludge by using thermogravimetric analysis

Shiwen Fang, Zhaosheng Yu *, Yan Lin, Yousheng Lin, Yunlong Fan, Yanfen Liao, Xiaoqian Ma

School of Electric Power, South China University of Technology, 510640 Guangzhou, China
Guangdong Province Key Laboratory of Efficient and Clean Energy Utilization, 510640 Guangzhou, China

HIGHLIGHTS

- The co-pyrolysis of biomass with additives (MgO, Al_2O_3 and ZnO) was researched.
- Municipal solid waste, paper sludge and their blends were used as the biomass.
- The initial temperature, residue mass, index *D* and activation energy were studied.
- Various additives had different effects on different proportions of MSW and PS.

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ABSTRACT

By using thermogravimetric analysis (TGA), the effects of different additives (MgO, Al_2O_3 and ZnO) on the pyrolysis characteristics and activation energy of municipal solid waste (MSW), paper sludge (PS) and their blends in N_2 atmosphere had been investigated in this study. The experiments resulted that these additives were effective in reducing the initial temperature and activation energy. However, not all the additives were beneficial to reduce the residue mass and enhance the index *D*. For the different ratios of MSW and PS, the same additive even had the different influences. The catalytic effects of additives were not obvious and the pyrolysis became difficult with the increase of the proportion of PS. Based on all the contrast of the pyrolysis characteristics, MgO was the best additive and 70M30P was the best ratio, respectively.

1. Introduction

With the parallel rise in population and living standards in China, the generation of municipal solid waste (MSW) is also increasing rapidly, at an annual rate of 8–10% (Liu et al., 2014a). By 2012, the national amount of MSW clean-up reached 1.71 Gt/a and dry PS production was 0.26 Gt/a (Fang et al., 2015). Moreover, over 200 million tons of MSW had been produced based on a predicted value by 2015 (Cheng and Hu, 2010). A large proportion composition of MSW derives from biomass, which is food waste, fruit waste, paper, textiles, cotton, leather, wood, trees and branches. Slag, ceramics and plastics are also been contained (Hu et al., 2015; Liu et al., 2014a). Furthermore, MSW is regarded as a kind of renewable energy. 90% of paper mill wastewater's solid and semisolid waste becomes sludge after treated by physico-chemical and biochemical methods (Jiang and Ma, 2011). The main component of paper sludge (PS) is lower organic matter, such as amino acid, humic acid, polycyclic aromatic hydrocarbon, heterocyclic compounds and organofluorine compounds, etc. (Xie and Ma, 2013). Therefore, handing of this great amount of PS has become an urgent environmental issue. Today, the main methods of disposing the MSW and PS are landfill, incineration, composting and ocean dumping which will soon be prohibited (Werther and Ogada, 1999). So it is badly in need to find some new methods to deal with the disposal problem.

Pyrolysis is defined as the thermal destruction of organic materials in the absence of oxygen and it is the basis of almost all available thermochemical processes (Zheng et al., 2009). Biomass produced a hydrocarbon rich gas mixture, an oil-like liquid and a carbon rich solid residue, when it was heated in the absence of oxygen (Demirbas, 2004). Recently, a number of scholars have studied the co-pyrolysis characteristics which were influenced by heating rate, terminated temperature and so on. Zhou et al. (2015a) studied the interactions of three MSW (orange peel, tissue

* Corresponding author at: School of Electric Power, South China University of Technology, 510640 Guangzhou, China. Tel.: +86 20 87110232; fax: +86 20 87110613.
E-mail address: zsyu@scut.edu.cn (Z. Yu).

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paper and PVC) components during pyrolysis. The interaction of orange peel and tissue paper was slight. The interaction of tissue paper and PVC was significant. The interaction of orange peel and PVC inhibited the production of alkyls and alkenes, and weakened the peaks of HCl and C_6H_6. Lu et al. (2013) studied the thermogravimetric analysis and kinetics of co-pyrolysis of raw wood and coal blends. The synergistic effect of co-pyrolysis between these two materials was slight. The co-pyrolysis kinetics of the fuel blends was also analyzed. However, the work on co-pyrolysis behavior between MSW and PS was less been found.

In order to improve the efficiency of pyrolysis or ameliorate the effect of pyrolysis, catalytic pyrolysis comes into being. A number of studies have reported the effect of self-made catalyst and some scholars have studied the metal oxides in microwave pyrolysis. The main focus of analysis is on the effects of gas, liquid products and energy consumption. Liu et al. (2014b) attempted to obtain value-added products through catalytic pyrolysis of distillers dried grain with soluble by nickel-based. The catalysts were characterized with NH_3–TPD, XPS, H_2–TPR. GC/MS analysis indicated that the bio-oil contained some value-added compounds such as 2-furaldehyde, 2-furanmethanol, 3-pyridinol, dodecane, etc. Li et al. (2013) researched the influence of microwave power, metal oxides and metal salts on the pyrolysis of algae. The effect of three metal oxides could be arrayed as MgO > CaO > CuO. The effect of microwave absorption was $ZnCl_2 > NaH_2PO_3 > MgCl_2$. However, the influences of metal oxides on pyrolysis through thermogravimetric (TG) and the analysis of kinetics are almost none.

So far the co-pyrolysis technology is still in development. The applications of metal oxides in the catalytic gasification, combustion and microwave pyrolysis have been extensively studied. It is interesting to study the pyrolysis with the additives of metal oxides. The ash content of PS accounts for about 60% not easy to be used. However, it is urgent to deal with it. In the case of a small reduction of the effectiveness of the use of MSW, PS was added to MSW to deal with together. The co-pyrolysis behaviors and kinetic behaviors between MSW, PS and their blends with metal oxides through TGA were studied in this paper. Owing to the characteristics of colorless, tasteless, high melting point and difficult to dissolve in water, MgO, Al_2O_3 and ZnO were chosen as the additives and they had the catalytic actions. Thermogravimetric date (TG) and differential thermogravimetry (DTG) profiles, co-pyrolysis characteristics, kinetics analysis and the comparison of additives and mixing ratios were analyzed to determine the optimal conditions for this waste treatment process.

2. Methods

2.1. Materials

In this study, the paper sludge (PS) investigated was collected from a paper mill in Guangdong Province in China. The municipal solid waste (MSW) was a complicated mixture of components. According to the literature wrote by Zhou et al. (2014), the contents of food and fruit waste were 46.4%, wood was 4.7%, paper was 18.2% and polyvinyl chloride (PVC) was 30.7%, respectively. The components of MSW were listed in Fig. 1. Food and fruit waste, wood and paper were collected from a resident area of South China University of Technology; PVC was acquired from the waste classification; metal oxides were bought from a regent shop. The ultimate analysis and proximate analysis were tested according to GB/T212-2008, GB211-84 and ASTM D5373-08, respectively. The Vario EL cube elemental analyzer was used for the ultimate analysis. Then, the ultimate analysis and the proximate analysis of MSW and PS were listed in Table 1. Before the experiments started, pretreatments of MSW and PS were carried out. The samples of MSW and PS were air-dried at 105 °C for 24 h, and then crushed, ground and sieved into the desired particle size (<178 μm). The PS solid wastes content of the blend ratios were set by mass as 0%, 30%, 50%, 70%, and 100%, which were named as 100MSW, 70M30P, 50M50P, 30M70P, and 100PS, respectively. The samples were mixed in a micro rotary mixer for 2 h then air-dried at 105 °C for 24 h. Afterwards, fully mixed 5% additives with the mixture through adequately vibration to ensure the total mass was 5 ± 0.1 g. Finally, 5 ± 0.1 mg mixed samples were performed for TGA experiments. The final samples were stored in desiccators.

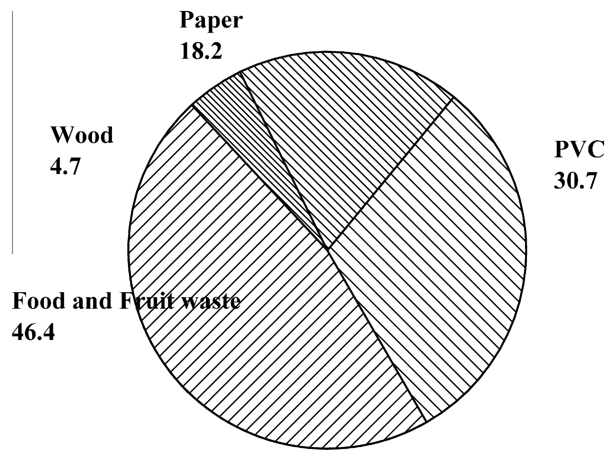

Fig.1 The composition of MSW on as received basis (wt.%).

Fig. 1. The composition of MSW on as received basis (wt.%).

Table 1
The ultimate analyses and proximate analyses of MSW and PS on dry basis.

Samples	Ultimate analyses (wt.%)					Proximate analyses (wt.%)		
	C	H	O	N	S	Volatile	Fixed carbon	Ash
PS	16.46	1.63	20.22	0.7	1.42	39.16	1.27	59.57
MSW	45.28	6.14	39.47	1.28	0.23	77.52	14.88	7.60

2.2. Experimental facility and method

The METTLER TOLEDO TGA/DSC1 thermogravimetric simultaneous thermal analyzer was examined experimentally for the co-pyrolysis experiments. The microbalance of this instrument is very sensitive (<0.1 μg) and its temperature precision is ±0.5 °C. The samples for non-isothermal co-pyrolysis experiment were heated from 100 to 900 °C in N_2 atmosphere with a flow rate of 80 ml/min, at heating rates of 10, 20 and 30 °C/min. All the initial quality of the samples were 5 ± 0.1 mg to make sure that the heat transfer limitations can be ignored and minimize the probability of error. Before the experiment started, several blank experiments (without samples) were carried out to gain the baselines which were used as corrections. To ensure the accuracy of the experimental results, all the experiments were conducted twice and the reproducibility was satisfied.

2.3. Kinetics model

The kinetic equation of common type can be generally described as Eq. (1) (Jiang et al., 2012; Mishra and Bhaskar, 2014):

$$d\alpha/dt = k(T)f(\alpha) \tag{1}$$