



# Thermogravimetric and calorimetric characteristics during co-pyrolysis of municipal solid waste components



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## ABSTRACT

The thermogravimetric and calorimetric characteristics during pyrolysis of wood, paper, textile and polyethylene terephthalate (PET) plastic in municipal solid wastes (MSW), and co-pyrolysis of biomass-derived and plastic components with and without torrefaction were investigated. The active pyrolysis of the PET plastic occurred at a much higher temperature range between 360 °C and 480 °C than 220–380 °C for the biomass derived components. The plastic pyrolyzed at a heating rate of 10 °C/min had the highest maximum weight loss rate of 18.5 wt%/min occurred at 420 °C, followed by 10.8 wt%/min at 340 °C for both paper and textile, and 9.9 wt%/min at 360 °C for wood. At the end of the active pyrolysis stage, the final mass of paper, wood, textile and PET was 28.77%, 26.78%, 21.62% and 18.31%, respectively. During pyrolysis of individual MSW components at 500 °C, the wood required the least amount of heat at 665.2 J/g, compared to 2483.2 J/g for textile, 2059.4 J/g for paper and 2256.1 J/g for PET plastic. The PET plastic had much higher activation energy of 181.86 kJ/mol, compared to 41.47 kJ/mol for wood, 50.01 kJ/mol for paper and 36.65 kJ/mol for textile during pyrolysis at a heating rate of 10 °C/min. H<sub>2</sub>O and H<sub>2</sub> peaks were observed on the MS curves for the pyrolysis of three biomass-derived materials but there was no obvious H<sub>2</sub>O and H<sub>2</sub> peaks on the MS curves of PET plastic. There was a significant interaction between biomass and PET plastic during co-pyrolysis if the biomass fraction was dominant. The amount of heat required for the co-pyrolysis of the biomass and plastic mixture increased with the increase of plastic mass fraction in the mixture. Torrefaction at a proper temperature and time could improve the grindability of PET plastic. The increase of torrefaction temperature and time did not affect the temperature where the maximum pyrolytic rates occurred for both biomass and plastic but decreased the maximum pyrolysis rate of biomass and increased the maximum pyrolysis rate of PET plastic. The amount of heat for the pyrolysis of biomass and PET mixture co-torrefied at 280 °C for 30 min was 4365 J/g at 500 °C, compared to 1138 J/g for the pyrolysis of raw 50% wood and 50% PET mixture at the same condition.

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## 1. Introduction

Municipal solid waste (MSW) also known as “trash” or “garbage” is mainly composed of tires, furniture, newspapers, plastics, wood waste, textile residues, glass, grass clippings, food and yard waste (Cheng and Hu, 2010). Industrialization and population growth have caused the significant increase of MSW in the world (Velghe et al., 2011). In the United States, the amount of MSW generated each year has increased by 65% since 1980 to about

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251 million tons per year in 2012 while the amount of MSW generated per capita increased by >20% from 1.7 to 2.0 kg/person/day during the same period (USEPA, 2014). In the United States in 2012, 85 million tons or 34% of the total amount of MSW is recycled and composted while another 29 million tons or 12% of MSW is combusted for energy recovery. The remaining 136 million tons or 54% of MSW is discarded in landfills (USEPA, 2014). The analysis of MSW shows that organic materials are the largest portion of the MSW, which are about 83% of the total waste. Among those organic materials, paper and paperboard contribute to 27.4% of MSW and yard trimmings and food scraps represent 28% of MSW. MSW also has 12.7% of plastics, 8.7% textile, rubber and leather and 6.3% of wood. The inorganic components in MSW include 8.9% metals and 4.6% glass. The remaining 3.4% of

MSW is the miscellaneous such as soil (USEPA, 2014). MSW can be considered as an energy source as it contains a large portion of organic materials (Psomopoulos et al., 2009).

MSW-to-energy technology can be a competitive solution because it can not only produce energy from MSW at low costs but also decrease the volume of MSW disposed in landfill which has associated environmental problems of gas emissions and leachate production (Abu-Qudais and Abu-Qudais, 2000; Baggio et al., 2008; Bellomare and Rokni, 2013). The 1991 national energy strategy in the United States encouraged the conversion of MSW to energy and extensive research has been done on different technologies such as incineration, pyrolysis and gasification for generating energy from MSW (Baggio et al., 2008; Buah et al., 2007). Pyrolysis is a thermochemical process in which biomass is heated to a temperature from 400 °C to 550 °C in the absence of oxygen to produce char (bio-char), non-condensable gases (synthesis gas) and vapors or aerosols (bio-oil). The vapors can be rapidly condensed to form bio-oil, which is a mixture of organic chemicals with water (Agirre et al., 2013; Buah et al., 2007). The yields and properties of bio-oil, bio-char and synthetic gases depend on the operating conditions of a pyrolytic process (Bridgwater, 2012). Pyrolysis is reported to be a promising option for efficient thermal conversion of MSW, besides the conventional incineration method (Velghe et al., 2011). However, it is a complex process to pyrolyze MSW due to a wide variation in the properties of MSW components. The MSW components do not act independently during pyrolysis (Velghe et al., 2011; Zhou et al., 2015a, 2015b). Several studies showed that the interaction among the MSW components with the same origin such as paper and wood was minimal while the interaction between plastics such as polyethylene and biomass was significant during co-pyrolysis of organic MSW components (Sorum et al., 2001; Zheng et al., 2009). There is an increasing interest in co-pyrolysis of biomass and plastic mixtures in recent years. Biomass fractions in MSW can be co-pyrolyzed with plastics such as polyethylene, polypropylene and polystyrene to produce various chemicals and fuels (Oyedun et al., 2014a, 2014b; Xue et al., 2015).

Polyethylene terephthalate (PET) is one of the most abundant plastic wastes in our daily lives. There is no published information on co-pyrolysis of PET plastic and biomass and the effects of torrefaction of a plastic and biomass mixture on the pyrolytic characteristics. A thermogravimetric analyzer (TGA) can be used to study thermal degradation characteristics of materials while a differential scanning calorimeter (DSC) can be used to record heat flow during thermal degradation (Carrier et al., 2011; Sanchez-Silva et al., 2012). The objective of this study was to analyze the thermogravimetric and calorimetric characteristics during pyrolysis of wood, paper, cotton textile and PET plastic in MSW, and co-pyrolysis of a biomass and plastic mixture with and without torrefaction.

## 2. Materials and methods

### 2.1. Materials

MSW samples were collected from a local solid waste transfer station in Greensboro, North Carolina. The residential MSW generated in North Carolina comprises 22% paper, 18% plastics, 6% wood, 37% organics, 4% ferrous metal, 4% glass and 9% other waste including textile and fabric (NCDENR, 2010). In our study, we considered four MSW combustible components of paper, PET plastic, wood and cotton textile. The paper represented a mixture of newspapers, paper towel, cardboard and label papers. The wood was mainly sawdust from the hard wood species. The cotton textile was tattered clothing from households. The PET plastic was mainly

disposable plastic bottles. The sorted samples were dried under the sun. The waste paper, wood and textile after drying were milled separately in a Thomas Wiley Mill with a 1 mm screen (Thomas Scientific, Swedesboro, NJ). As the PET plastic could not be milled in a conventional miller, the PET plastic was cut to small pieces. All samples were stored in transparent plastic containers to be used for the experiments. Table 1 gives the results of proximate and ultimate analyses of the MSW components.

### 2.2. Experimental set up

The pyrolysis of MSW samples was conducted on a TGA-DSC analyzer, which has a maximum heating rate of 100 °C/min to 1000 °C (TA Instrument SDT Q 600). A sample of 10 mg was loaded in an aluminum pan and placed in the TGA-DSC furnace in each experiment. The first set of experiments were conducted to analyze the effect of heating rate on the pyrolytic kinetics of individual MSW components. The experiments were performed from an ambient temperature up to a maximum temperature of 800 °C at a heating rate of 10, 20, 40 and 60 °C/min. The second set of experiments were conducted on co-pyrolysis of a 10 mg mixture of wood and PET plastic at different mass fractions of 30% wood/70% PET, 50% wood/50% PET, and 70% wood/30% PET at a heating rate of 10 °C/min. The third set of experiments were conducted to analyze the effect of torrefaction on the PET grindability, and thermogravimetric and calorimetric characteristics during the pyrolysis of co-torrefied wood and PET mixtures. The torrefied mixture of wood and PET plastic was grinded in a laboratory blender and the grindability was then qualitatively compared to that of raw PET plastic. The product gases were swept by a carrier gas of nitrogen at a flow rate of 60 ml/min. All TGA and DSC results reported in this study were corrected by the baseline obtained from the tests with empty pans.

### 2.3. Kinetics of MSW pyrolysis

The TGA and DTG data were used to determine the kinetic parameters. The temperature dependency of reaction rate constant was represented by the Arrhenius law:

$$k = k_0 \cdot \exp^{-(E/RT)} \quad (1)$$

$k$ ,  $k_0$ ,  $E$ ,  $R$  and  $T$  denote the reaction rate constant, pre-exponential factor, activation energy, gas constant and temperature in Kelvin, respectively.

The conversion rate was written as a function of temperature,  $T$ , and the instantaneous conversion ratio,  $x$ :

$$dx/dt = k_0 \exp^{-(E/RT)} (1 - x)^n \quad (2)$$

where  $n$  is the reaction order.

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

	Paper	Textile (cotton)	Wood	Plastic (PET)
<i>Proximate analysis (% by mass)</i>				
Moisture	5.95	6.85	9.31	Undetectable
Volatile	78.55	82.37	74.96	88.61
Fixed carbon	7.57	10.61	15.49	11.39
Ash	7.93	0.17	0.24	Undetectable
<i>Ultimate analysis (% by mass)</i>				
Carbon	41.43	41.19	45.69	64.22
Hydrogen	6.87	6.97	7.57	4.65
Nitrogen	1.01	0.01	1.89	0.05
Oxygen <sup>a</sup>	49.83	50.99	56.16	30.53
Sulfur	0.86	0.84	1.01	0.55

<sup>a</sup> Calculated from the difference.

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