Thermogravimetric and Calorimetric Characteristics during Co-Pyrolysis of Municipal Solid Waste Components

Emmanuel Ansah^a, Lijun Wang^{b,c,*}, Abolghasem Shahbazi^{bc}

^a Department of Energy and Environmental Systems

^b Department of Natural Resources and Environmental Design

^c Department of Chemical, Biological and Bioengineering

North Carolina Agricultural and Technical State University, 1601 E Market Street

Greensboro, NC 27411, U.S.A.

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°C to 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

* Corresponding author, Tel: +1 336 285-3833, Fax: +1 336 334-7270, Email: lwang@ncat.edu

(L.J. Wang)

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. H₂O and H₂ peaks were observed on the MS curves for the pyrolysis of three biomass-derived materials but there was no obvious H₂O and H₂ 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.

Keywords: Pyrolysis; torrefaction; municipal solid waste; waste to energy; biomass; plastics

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 251 million tons per year in 2012 while the amount of MSW generated per capita increased by more than 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 (Sørum 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; Oyedun et al., 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:

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

k , k_o , E , R and T denotes 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 :

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

where n is the reaction order.

The instantaneous conversion ratio was calculated by

$$x = (w_o - w)/(w_o - w_f) \quad (3)$$

136 where w_o is the initial mass of the sample, w is the residual mass at any given time, and w_f is
 137 the final mass at the end of the pyrolysis.

138 With the definition of the heating rate as $\beta = dT/dt$, Equation (2) can be re-written as:

$$139 \quad dx/dT = k_o/\beta \cdot \exp(-E/RT) \cdot (1-x)^n \quad (4)$$

140 Re-arranging and integrating Equation (4), the following expression can be obtained:

$$141 \quad (1-x)^{1-n}/1-n = k_o/\beta \int_0^T \exp(-E/RT) dT \quad n \neq 1 \quad (5a)$$

$$142 \quad -\ln(1-x) = k_o/\beta \int_0^T \exp(-E/RT) dT \quad n = 1 \quad (5b)$$

143 Since $\int e^{-E/RT} dT$ in Equation (5) has no exact integral, $e^{-E/RT} dT$ can be expressed as an
 144 asymptotic series and integrated with the higher order terms ignored, which gives Equation (5)
 145 as:

$$146 \quad (1-x)^{1-n}/1-n = k_o RT^2/\beta E [1 - (2RT/E)] \exp(-E/RT) \quad n \neq 1 \quad (6a)$$

$$147 \quad -\ln(1-x) = k_o RT^2/\beta E [1 - (2RT/E)] \exp(-E/RT) \quad n = 1 \quad (6b)$$

148 Equation (6) can be expressed in logarithmic form as:

$$149 \quad \ln[(1-x)^{1-n}/T^2(1-n)] = \ln[k_o R/\beta E [1 - 2RT/E]] - E/RT \quad n \neq 1 \quad (7a)$$

$$150 \quad \ln[-\ln(1-x)/T^2] = \ln[k_o R/\beta E [1 - 2RT/E]] - E/RT \quad n = 1 \quad (7b)$$

151 If $2RT/E \ll 1$ is assumed, Equation (7) becomes:

$$152 \quad \ln[(1-x)^{1-n}/T^2(1-n)] = \ln[k_o R/\beta E] - E/RT \quad n \neq 1 \quad (8a)$$

$$153 \quad \ln[-\ln(1-x)/T^2] = \ln[k_o R/\beta E] - E/RT \quad n = 1 \quad (8b)$$

154 The pyrolytic reaction is assumed to follow the first order reaction kinetics with $n = 1$, which
 155 gives:

$$156 \quad \ln[-1/T^2 \ln(1-x)] = \ln[k_o R/\beta E] - E/RT \quad (9)$$

157 According to Equation (9), the plot of $\ln[-1/T^2 \ln(1-x)]$ as a function of $1/T$ gives a straight
 158 line and the slope of the line is E/R and the intercept of the line is $\ln((k_o/\beta) \cdot (R/E))$ as

shown in Figure 4. The value of the pre-exponential factor k_o was calculated by substituting the β , R , and E . These parameters were obtained for heating rates of 10°C/min, 20°C/min, 40°C/min and 60°C/min. The activation energy, E , and pre-exponential factor, k_o for the pyrolysis of MSW components at different heating rates are given in Table 2.

2.3 Mass spectrometry of evolved gases

The evolved gases from the pyrolysis of each MSW component under nitrogen were transferred to a mass spectrometer (MS) with an electron ionization voltage of 70 eV and mass spectra up to 150 a.m.u. The temperature of the sample transferring line was maintained at 300°C to prevent the condensation of exhausting gas. The MS was operated in a peak jump mode by scanning and identifying ions of mass to charge ratios (m/z) in the range 0-150 a.m.u. The signals were identified at the mass spectra of 2, 16, 18 and 44 a.m.u which corresponded to hydrogen gas (H_2), methane (CH_4), water (H_2O) and carbon dioxide (CO_2), respectively.

2.4 Co-torrefaction of biomass and plastic mixture

Co-torrefaction of different MSW components was used to enhance the grindability of plastics and the interaction between biomass and plastics during co-pyrolysis. Wood was used as a representative biomass-derived component in MSW. A mixture of wood and PET plastic at a mass ratio of 1:1 (consisting of 5 g wood and 5 g of PET plastic) was torrefied at 230°C, 250°C or 280°C for 30 min or 60 min in temperature controlled electric furnace (Thermo Fischer Scientific) connected to a nitrogen purge gas. The torrefied mixture was grinded in the laboratory blender and samples were further pyrolyzed in the TGA-DSC unit.

2.5 Heat flow and caloric requirement during MSW pyrolysis

The DSC analysis provides quantitative and qualitative information about physical and chemical changes that involve endothermic and exothermic reactions (Shadangi and Mohanty, 2014). The heat flow during endothermic and exothermic reactions is characterized by the positive or negative peaks of a DSC profile. The total caloric requirement during pyrolysis includes the heat required to dry, heat and degrade biomass, and aggregate the char generated. The caloric requirement during the pyrolysis of the MSW components was calculated by integrating the DSC curves using Simpson's one-third integral method in Microsoft Excel (He et al., 2006):

$$Q/W_o = \int_0^t ((W C_p dT/dt + WH)/W_o) dt \quad (10)$$

where W_o initial mass of sample (g), W instantaneous mass of sample during pyrolysis (g), C_p specific heat capacity of sample (J/g K), and H heat flow (J/g s).

3. Results and discussion

3.1 Pyrolysis of individual MSW organic components

3.1.1 Thermogravimetric and calorimetric characteristics

Fig. 1 shows the TGA and DTG profiles during the pyrolysis of individual MSW components of wood, paper, textile and PET. The samples were initially equilibrated at 110°C to remove their moisture. The PET plastic did not show any weight loss at the dehydration stage (<110°C) while wood had the highest moisture content at 9.4%. There was no significant weight loss for all dried MSW components until the active pyrolysis stage occurred. The active pyrolysis stage occurred from 220°C to 380°C for paper, wood and textile, which had the same origin of biomass. The active pyrolysis of the PET plastic occurred at a much higher temperature range between 360°C and 480°C. As shown in Fig. 1(B), only one peak was observed at the active pyrolysis of paper

and textile as the dominant component of paper and textile is cellulose and their hemicellulose content is negligible. However, the wood showed a preceding shoulder peak at the temperature between 280°C and 320°C due to the overlap between the pyrolysis of hemicellulose and cellulose. As seen in Fig. 1(B), the plastic 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 weight of paper, wood, textile and PET were 28.77%, 26.78%, 21.62% and 18.31%, respectively. The final stage of weight loss is the char formation and aggregation where the weight decreased at a very low rate to the end of the pyrolysis at 800°C.

As seen in Fig 2, there was an endothermic peak at 300°C on the paper DSC curve, at 310°C for textile and at 360°C for wood, which was attributed to the endothermic reaction for the pyrolysis of cellulose as reported in the literature (Yang et al., 2007). The PET plastic showed different calorimetric characteristics from those biomass derived materials. The DSC curve of the PET showed a slight endothermic peak at 240°C, which was attributed to the phase transition of the plastic. As there was another endothermic peak at 412°C on the PET DSC curve, the active pyrolysis of the plastic absorbed heat. The final stage was the heating and aggregation of the residual char which started at 380°C for paper, wood and textile and 450°C for PET plastic.

The heat requirement of the pyrolysis process was the sum of the heat for the increase of the sample temperature and the heat of reactions. As seen from Fig. 2 and Table 2, the textile required the highest amount of heat at 2483.2 J/g during its pyrolysis at a temperature up to 500°C while the wood required the least amount of heat at 665.2 J/g during the pyrolysis at the

same condition. The paper and PET required 2059.4 J/g and 2256.1 J/g to be pyrolyzed at the same condition, respectively.

3.1.2 Kinetic parameters for the pyrolysis of individual MSW components

Fig. 3 shows the effect of the heating rate on the pyrolysis rate for individual MSW components. It can be seen from Fig. 3 that the increase of heating rate increased the maximum pyrolysis rates, the temperature for the maximum pyrolysis rates, and the temperatures at the end of the active pyrolysis stage while there was no significant change in the starting temperature of the active pyrolysis stage.

Table 3 gives the activation energy and pre-exponential factor that were calculated for the DTG data of individual MSW components shown in Fig.4. The activation energy (E) increased from 41.47 to 52.61 kJ/mol for wood, from 50.01 to 72.29 kJ/mol for paper and from 36.65 to 56.41 kJ/mol for textile when the heating rate was increased from 10 to 60°C/min. Among these three biomass-derived MSW components, the wood generally had the lowest activation energy while the paper had the highest activation energy as heating rate increases. The PET plastic had much higher activation energy than the biomass-derived components, which increased from 181.86 kJ/mol to 223.92 kJ/mol when the heating rate increased from 10 to 60°C/min. The increase in the activation energy with heating rate might be caused by the heat transfer limitation which required longer time for the purge gas to come into equilibrium with the actual sample temperature. The delayed decomposition as a result of increased activation energy might be attributed to the limitation of heat transfer due to shorter residence time of the sample at a certain temperature range of active pyrolysis if the heating rate was higher (Mehrabian et al., 2012).

3.1.3 Evolved gas profile of individual MSW components pyrolysis

Figures 5 shows the mass spectrometric (MS) profiles of the gases generated from the pyrolysis of MSW components of wood, textile, paper and PET plastic. It can be seen that the amounts of evolved gases as indicated by the peaks of MS profiles were consistent with the weight changes as indicated by the DTG profiles shown in Fig. 1. The initial peak on the H₂O MS curves at a temperature below 200°C corresponded to the removal of unbounded or absorbed moisture from the samples. Wood showed a pronounced H₂O peak at the temperature below 200°C as it had high moisture content. The second peak on the H₂O MS curves for three biomass derived samples was the water generated by reactions at the active pyrolysis stage (Singh et al., 2012). However, there were no obvious peaks on the H₂O MS curves for PET plastic. Therefore, the bio-oil generated during the pyrolysis of PET plastic had a negligible amount of H₂O and thus was highly viscous as reported in the literature (Dimitrov et al., 2013; Miskolczi and Nagy, 2012).

It can be seen from Fig.5 that both CO₂ and CH₄ were generated during the pyrolysis of the three biomass-derived MSW components and PET plastic at the active pyrolysis stage. However, the pyrolysis of paper showed a second peak at 670°C on both CO₂ and CH₄ MS curves which might be attributed to the decomposition of calcium carbonate used as a filler in the paper.

At the active pyrolysis, there was no obvious peak on the H₂ curve for the PET plastic but there were H₂ peaks for the three biomass derived samples. The H₂ production from the biomass-derived samples at the temperature of active pyrolysis might be attributed to the secondary

reaction such as steam reforming of CH₄ and bio-oil (Sanchez-Silva et al., 2012). However, as the active pyrolysis of PET plastic did not produce H₂O as shown in Fig. 5(A), the active pyrolysis of PET plastic did not produce H₂ via the further steam reforming reactions. It can be seen that the H₂ MS signal increased at the char formation and aggregation stage, which might be caused by the thermal cracking of bio-oil at a high temperature.

The active pyrolysis of wood is characterized by the shoulder peaks on the CO₂, CH₄ and H₂O MS curves, which were caused by the overlap of the decomposition of hemicellulose, cellulose and lignin in the wood at different temperatures.

3.2 Co-pyrolysis of the biomass and plastic in MSW at different mass fractions

The pyrolytic characteristics of MSW depends on its composition as the individual MSW components showed different pyrolytic characteristics as discussed in Section 3.1. Fig. 6 shows the TGA and DSC curves during co-pyrolysis of mixtures of wood (representing biomass-derived components in MSW) and PET plastic (representing plastic components in MSW) at different mass fractions. For comparison, both the TGA and DSC curves were also calculated by a weighted sum method, in which the total instantaneous mass (mass at any time, t) and heat flow of the mixture at a given temperature was determined by summing the instantaneous mass (mass at any time, t) and heat flow of an individual component at the same temperature given in Fig. 1 and Fig. 2, respectively, multiplied with the mass fraction of the individual component in the mixture using the following equation:

$$Y_{msw} = \sum_{i=1}^2 c_i w_i \quad (11)$$

where Y_{msw} is the estimated or predicted mass or heat flow of the MSW mixture at a given temperature, w_i are the instantaneous mass or heat flow of the individual MSW components (1: wood, 2: PET plastic) obtained at the same temperature, and c_i is mass fractions of two MSW components in the mixture.

It can be seen from Fig. 6 that the active pyrolysis sections of the TGA curves obtained by experiments well agreed with those ones determined by the weighted sum method when the mixture had less wood than PET plastic (30% wood / 70% PET). However, if the sample had more wood than PET plastic (70% wood / 30% PET), there was a slight disagreement between experimental and estimated values using the weighted sum method. The heat flow curves followed the similar pattern. Therefore, there was a significant interaction between wood and PET plastic if the wood fraction was dominant. Similar results were reported in the literature (Sørum et al., 2001; Zheng et al., 2009; Zhou et al., 2015a). The higher measured pyrolytic rate than the predicted value for the active pyrolysis of the mixture with more wood might be attributed by the significant amount of water generated during the pyrolysis of biomass, which could enhance the pyrolysis of PET plastic in the mixture. There was a small difference at the stage of char formation and aggregation between the measured and estimated TGA curves. The amount of char formed from the co-pyrolysis of the mixtures were slightly lower than the estimated values by the weighted sum method.

During co-pyrolysis of the mixture of wood and PET plastic, there were two obvious active pyrolysis stages for wood and PET plastic. The overlap of these two active pyrolysis stages occurred at the temperature from 360°C to 400°C. The mass of the residue at the starting

temperature of the overlap increased with the increase of the plastic content in the mixture as the active pyrolysis of plastics occurred at much higher temperature than that of wood. Similar results about the effect of plastics content in MSW on its pyrolytic characteristics were reported in the literature (Cozzani et al., 1995; Zhou et al., 2015a, 2015b).

Fig.7 shows the total heat requirement during co-pyrolysis of wood and PET plastic mixture at different mass fractions. The amount of heat required for the co-pyrolysis of the mixture increased with the increase of plastic mass fraction in the mixture as the pyrolysis of PET plastic required more heat than that of wood (as seen in Fig. 2). The total amount of heat required for the co-pyrolysis of a mixture with 70% wood and 30% PET at 500°C was 455 J/g, compared to 1671 J/g for the co-pyrolysis of a mixture with 30% wood and 70% PET plastic at the same temperature.

3.3 Pyrolysis of the co-torrefied wood and plastic in MSW

The mixture of wood and plastic was torrefied to enhance the grindability and interaction during pyrolysis. It can be seen in Fig. 8 that the particle size of the biomass-plastic mixture generated by grinding at the same condition decreased with increasing torrefaction temperature and time. Torrefaction can weaken the tight structure of the biomass as its constituent components of cellulose, hemicelluloses and lignin have different degrees of decomposition during torrefaction. The PET plastic component undergoes glass transition phase during torrefaction if the temperature is higher than 240°C (as seen in Fig. 2). The mixture of wood and PET plastic became more brittle and fragile during torrefaction at proper temperature and time, which could

improve the grindability of the co-torrefied wood-plastic mixture and decrease the energy consumption of grinding.

Table 4 gives the yields and fixed carbon content of the mixture of wood and PET plastic at the mass ratio of 1:1 torrefied at different temperatures and times. The yield decreased and the fixed carbon increased with the increase in torrefaction temperature and time. The yield was 77.7% when the mixture was torrefied at 280°C for 30 min. At 280°C, there was no decrease in the yield when the torrefaction time was further increased from 30 min to 60 min. The temperature at 280°C might be the maximum temperatures at which a large fraction of cellulose become thermally stable (Joshi et al.). The fixed carbon of the torrefied mixture increased significantly, compared to that of the mixture prior to the torrefaction. The fixed carbon contents of the mixture torrefied at 280°C for 30 min and 60 min were 17.1% and 20.8%, compared to 7.4% for the raw mixture.

Fig. 9 shows the TGA and DTG curves during the pyrolysis of the co-torrefied mixture of wood and PET plastic. As seen from the TGA curves in Fig. 9, there was an overlap of two active pyrolysis stages of wood and plastic, which started at 380°C. The torrefaction decreased the mass of the residue at the starting temperature and temperature range of the overlap, and increased the biochar mass. The temperature range for the overlap of two active pyrolysis stages of wood and plastic decreased with the increased torrefaction temperature.

As seen from the DTG curves in Fig. 9, there were two major peaks during the pyrolysis of co-torrefied mixture of wood and PET plastic: the first peak at the temperature from 200°C to 380°C

for the decomposition of wood and the second peak at the temperature from 380°C to 480°C for the decomposition of PET plastic. The maximum pyrolysis rate of wood that occurred at 350°C decreased with the increase of the torrefaction temperature and time. The maximum pyrolysis rates of the wood in the mixture torrefied at 280°C for 30 min and 60 min were 5.40%/min and 3.66%/min, respectively, compared to 6.60% for the wood in the mixture without torrefaction. However, the maximum pyrolysis rate of the PET plastic that occurred at 430°C increased significantly with the torrefaction temperature and time. The maximum pyrolysis rates of the PET plastic component in the mixture torrefied at 280°C for 30 min and 60 min were 10.69%/min and 14.23%/min, respectively, compared to 8.31% for the PET plastic component in the mixture without torrefaction. It can also be seen from Fig. 9 that the torrefaction did not affect the temperature where the maximum pyrolytic rates were achieved for both wood and PET plastic. It can be seen from the DTG curves in Fig. 9 that a small shoulder peak occurred around 300°C on the raw mixture. However, this peak was diminished for the torrefied mixture. This could be attributed to the decomposition of thermally unstable extractives and hemicelluloses in the wood during torrefaction. The decomposition of thermally unstable extractives and hemicelluloses in the wood during torrefaction increased the lignin content in the torrefied samples, which was main contributor of fixed carbon.

Fig. 10 gives the heat flow and heat requirement for the pyrolysis of wood and PET plastic mixtures co-torrefied at different temperatures and times. The torrefaction significantly increased the amount of heat required during pyrolysis. The amounts of heat for the pyrolysis of the wood and PET plastic mixture co-torrefied at 280°C for 30 min and 60 min were 4365 J/g and 4505 J/g at the temperature of 500°C (as seen in Fig. 10), respectively, compared to 1138 J/g for the

pyrolysis of the 50% wood and 50% PET plastic mixture without torrefaction (as seen in Fig. 7). The heat requirement for pyrolyzing the co-torrefied wood and PET plastic decreased with the decrease of torrefaction temperature and time. The amounts of heat required to pyrolyze the wood and PET plastic mixture co-torrefied at 230°C for 30 and 60 min were 3396 J/g and 4124 J/g, respectively.

4. Conclusions

The pyrolysis of PET plastic occurred at 360 to 480°C, which was much higher than 220 to 380°C for the biomass derived components of wood, paper and textile. The increase of heating rate increased the maximum pyrolysis rates, the temperature for the maximum pyrolysis rates, and the temperatures at the end of the active pyrolysis stage while there was no significant change in the starting temperature of the active pyrolysis stage. The amount of heat required for wood pyrolysis at 500°C was 665 J/g, which was much lower than 2256 J/g for PET plastic and 2059 J/g for paper. There was significant interaction occurred during co-pyrolysis of wood and PET mixture if the wood was dominant in the mixture. The amount of heat required for the co-pyrolysis of the mixture increased with the increase of plastic mass fraction in the mixture as the pyrolysis of PET plastic required more heat than that of wood. Torrefaction at a proper temperature (>250°C) and time (>30 min) increased the PET grindability, enhanced the mixing and interaction between wood and PET plastic, and the amount of heat required during co-pyrolysis. The increase of the torrefaction temperature and time decreased the maximum pyrolysis rate for wood but increased for PET plastic. Torrefaction significantly increased the amount of heat required during pyrolysis. During the pyrolysis at a temperature up to 500°C, the amount of heat for the wood and PET plastic mixture co-torrefied at 280°C for 30 min were 4365

J/g, compared to 1138 J/g for the pyrolysis of the raw 50% wood and 50% PET plastic mixture without torrefaction.

Acknowledgements

A contribution of North Carolina Agricultural and Technical State University, supported by funds provided by U.S Department of Agriculture (USDA NIFA awards: NC.X-294-5-15-130-1 and 2013-38821-21141) and U.S National Scientific Foundation (Grant #: HRD-1242152).

Mention of a trade name, proprietary products, or company name is for presentation clarity and does not imply endorsement by the authors or the university.

References

- Abu-Qudais, M.D., Abu-Qdais, H.A., 2000. Energy content of municipal solid waste in Jordan and its potential utilization. *Energ. Convers. Manage.* 41, 983-991.
- Agirre, I., Griessacher, T., Rösler, G., Antrekowitsch, J., 2013. Production of charcoal as an alternative reducing agent from agricultural residues using a semi-continuous semi-pilot scale pyrolysis screw reactor. *Fuel Process. Technol.* 106, 114-121.
- Baggio, P., Baratieri, M., Gasparella, A., Longo, G.A., 2008. Energy and environmental analysis of an innovative system based on municipal solid waste (MSW) pyrolysis and combined cycle. *Appl. Therm. Eng.* 28, 136-144.
- Bellomare, F., Rokni, M., 2013. Integration of a municipal solid waste gasification plant with solid oxide fuel cell and gas turbine. *Renew. Energ.* 55, 490-500.
- Bridgwater, A.V., 2012. Review of fast pyrolysis of biomass and product upgrading. *Biomass Bioenerg.* 38, 68-94.
- Buah, W.K., Cunliffe, A.M., Williams, P.T., 2007. Characterization of Products from the Pyrolysis of Municipal Solid Waste. *Process Saf. Environ.* 85, 450-457.
- Carrier, M., Loppinet-Serani, A., Denux, D., Lasnier, J.-M., Ham-Pichavant, F., Cansell, F., Aymonier, C., 2011. Thermogravimetric analysis as a new method to determine the lignocellulosic composition of biomass. *Biomass Bioenerg.* 35, 298-307.

- Cheng, H., Hu, Y., 2010. Municipal solid waste (MSW) as a renewable source of energy: Current and future practices in China. *Bioresource Technol.* 101, 3816-3824.
- Cozzani, V., Petarca, L., Tognotti, L., 1995. Devolatilization and pyrolysis of refuse derived fuels: characterization and kinetic modelling by a thermogravimetric and calorimetric approach. *Fuel*. 74, 903-912.
- Dimitrov, N., Kratofil Krehula, L., Ptiček Siročić, A., Hrnjak-Murđić, Z., 2013. Analysis of recycled PET bottles products by pyrolysis-gas chromatography. *Polym. Degrad. Stabil.* 98, 972-979.
- He, F., Yi, W., Bai, X., 2006. Investigation on caloric requirement of biomass pyrolysis using TG-DSC analyzer. *Energ. Convers. Manage.* 47, 2461-2469.
- Joshi, Y., Di Marcello, M., de Jong, W., 2015. Torrefaction: Mechanistic study of constituent transformations in herbaceous biomass. *J. Anal. Appl. Pyrol.* 115, 353-361.
- Mehrabian, R., Scharler, R., Obernberger, I., 2012. Effects of pyrolysis conditions on the heating rate in biomass particles and applicability of TGA kinetic parameters in particle thermal conversion modelling. *Fuel*. 93, 567-575.
- Miskolczi, N., Nagy, R., 2012. Hydrocarbons obtained by waste plastic pyrolysis: Comparative analysis of decomposition described by different kinetic models. *Fuel Process. Technol.* 104, 96-104.
- North Carolina Department of Environment and Natural Resources (NCDENR), 2010: North Carolina Solid Waste Annual Report, FY 2008-2009. Available online: <http://www.ncleg.net/documentsites/committees/ERC/ERC%20Reports%20Received/2010/Dept%20of%20Environment%20and%20Natural%20Resources/2010-Jan%20-%20Solid%20Waste%20Report%20FY2008-2009.pdf>
- Oyedun, A.O., Gebreegziabher, T., Ng, D.K.S., Hui, C.W., 2014a. Mixed-waste pyrolysis of biomass and plastics waste – A modelling approach to reduce energy usage. *Energy*. 75, 127-135.
- Oyedun, A.O., Tee, C.Z., Hanson, S., Hui, C.W., 2014b. Thermogravimetric analysis of the pyrolysis characteristics and kinetics of plastics and biomass blends. *Fuel Process. Technol.* 128, 471-481.
- Psomopoulos, C.S., Bourka, A., Themelis, N.J., 2009. Waste-to-energy: A review of the status and benefits in USA. *Waste Manage.* 29, 1718-1724.
- Sanchez-Silva, L., López-González, D., Villaseñor, J., Sánchez, P., Valverde, J.L., 2012. Thermogravimetric–mass spectrometric analysis of lignocellulosic and marine biomass pyrolysis. *Bioresource Technol.* 109, 163-172.

- Shadangi, K.P., Mohanty, K., 2014. Kinetic study and thermal analysis of the pyrolysis of non-edible oilseed powders by thermogravimetric and differential scanning calorimetric analysis. *Renew. Energ.* 63, 337-344.
- Singh, S., Wu, C., Williams, P.T., 2012. Pyrolysis of waste materials using TGA-MS and TGA-FTIR as complementary characterisation techniques. *J. Anal. Appl. Pyrol.* 94, 99-107.
- Sørnum, L., Grønli, M.G., Hustad, J.E., 2001. Pyrolysis characteristics and kinetics of municipal solid wastes. *Fuel.* 80, 1217-1227.
- U.S. Environmental Protection Agency (USEPA). 2014. Municipal Solid Waste Generation, Recycling, and Disposal in the United States: Facts and Figures for 2012. Available online: http://www3.epa.gov/epawaste/nonhaz/municipal/pubs/2012_msw_fs.pdf.
- Velghe, I., Carleer, R., Yperman, J., Schreurs, S., 2011. Study of the pyrolysis of municipal solid waste for the production of valuable products. *J. Anal. Appl. Pyrol.* 92, 366-375.
- Xue, Y., Zhou, S., Brown, R.C., Kelkar, A., Bai, X., 2015. Fast pyrolysis of biomass and waste plastic in a fluidized bed reactor. *Fuel.* 156, 40-46.
- Yang, H., Yan, R., Chen, H., Lee, D.H., Zheng, C., 2007. Characteristics of hemicellulose, cellulose and lignin pyrolysis. *Fuel.* 86, 1781-1788.
- Zheng, J., Jin, Y.-q., Chi, Y., Wen, J.-m., Jiang, X.-g., Ni, M.J., 2009. Pyrolysis characteristics of organic components of municipal solid waste at high heating rates. *Waste Manage.* 29, 1089-1094.
- Zhou, H., Long, Y., Meng, A., Li, Q., Zhang, Y., 2015a. Interactions of three municipal solid waste components during co-pyrolysis. *J. Anal. Appl. Pyrol.* 111, 265-271.
- Zhou, H., Long, Y., Meng, A., Li, Q., Zhang, Y., 2015b. Thermogravimetric characteristics of typical municipal solid waste fractions during co-pyrolysis. *Waste Manage.* 38, 194-200.

Figure Captions

Figure 1. Thermogravimetric characteristics during the pyrolysis of different MSW components at a heating rate of 10°C/min.

Figure 2. Calorimetric characteristics during the pyrolysis of different MSW components at a heating rate of 10°C/min.

Figure 3. Effect of heating rate on the pyrolysis rate during the pyrolysis of different MSW components.

Figure 4. Effects of temperature and heating rate on the pyrolytic reaction constants of different MSW components.

Figure 5. Mass spectra of H₂O, CO₂, CH₄ and H₂ during the pyrolysis of wood, paper, textile and PET plastic at a heating rate of 10°C/min.

Figure 6. Comparisons between the measured and predicted TGA and DSC curves for co-pyrolysis of the mixture of biomass and PET plastic at different mass fractions.

Figure 7. Total heat requirement of co-pyrolysis of the mixture of biomass and PET plastic at different mass fractions.

Figure 8. Wood and PET plastic mixtures of 1:1 mass ratio co-torrefied at different temperatures and times.

Figure 9. TGA and DTG curves during the pyrolysis of the mixture of 50% biomass and 50% plastic co-torrefied at different temperatures and times.

Figure 10. Heat flow and total heat requirement curves during the pyrolysis of the mixture of 50% biomass and 50% plastic co-torrefied at different temperatures and times.

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

	Paper	Textile(cotton)	Wood	Plastic (PET)
Proximate analysis (% by mass)				
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
Ultimate analysis (% by mass)				
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*	49.83	50.99	56.16	30.53
Sulfur	0.86	0.84	1.01	0.55

545 * calculated from the difference

Table 2. Total heat requirement (J/g) for the pyrolysis of individual MSW components and mixed biomass-plastic components as a function of temperature

Temperature (°C)	150	200	250	300	350	400	450	500
Wood	335.3	551.8	703.2	785.5	819.5	809.4	693.5	665.2
Paper	281.0	519.8	749.4	949.9	1290.8	1463.4	1701.5	2059.4
Textile (cotton)	340.1	712.8	1101.2	1541.8	1929.5	2066.7	2256.5	2483.2
Plastic (PET)	381.6	715.6	1040.1	1329	1566.4	1779.8	2109.4	2256.1
30% wood + 70% PET	359.6	645.3	905.2	1111.7	1272.7	1420.8	1581.3	1671.9
50% wood + 50% PET	330.2	583.4	797.3	938.5	1024.2	1077.1	1136.2	1138.0
70% wood+ 30% PET	310.3	492.1	626.7	693.8	714.9	692.9	584.3	455.0

Table 3. Activation energy and pre-exponential factors of reaction kinetics within the active pyrolysis temperature regime of individual MSW components at different heating rates

MSW component	Heating rate (°C/min)	k_0 (min ⁻¹)	E (KJ/mol)	Correlation coefficient (R ²)
Wood	10	2.46×10^2	41.47	0.93
	20	1.67×10^3	44.84	0.97
	40	3.88×10^3	48.15	0.97
	60	1.94×10^4	52.61	0.99
Textile	10	1.08×10^2	36.65	0.93
	20	6.46×10^3	52.52	0.94
	40	1.42×10^4	54.44	0.93
	60	3.17×10^4	56.41	0.91
Paper	10	2.20×10^3	50.01	0.94
	20	5.78×10^4	65.27	0.96
	40	2.91×10^5	68.49	0.97
	60	7.61×10^5	72.29	0.98
Plastic (PET)	10	9.43×10^{12}	181.86	0.95
	20	1.67×10^{13}	184.73	0.97
	40	1.35×10^{14}	196.36	0.98
	60	1.88×10^{16}	223.92	0.99

Table 4. Yield and fixed carbon content of co-torrefied 50%wood biomass and 50% PET plastic mixture

Torrefaction condition		Mass Yield (Wt. %)	Fixed Carbon (Wt. %)
Time (min)	Temperature (° C)		
Raw material	-	100	7.4
30	230	94.2	13.1
	250	90.3	16.6
	280	77.7	17.1
60	230	91.7	14.2
	250	86.5	16.8
	280	77.8	20.8

(A) TGA profile

(B) DTG profile

Fig. 1 Thermogravimetric characteristics during the pyrolysis of different MSW components at a heating rate of 10°C/min.

(A) Wood

(B) Paper

(C) Textile (cotton)

(D) Plastic (PET)

Fig. 2 Calorimetric characteristics during the pyrolysis of different MSW components at a heating rate of 10°C/min.

Fig. 3 Effect of heating rate on the pyrolysis rate during the pyrolysis of different MSW components.

(A) Paper

(B) Plastic (PET)

(C) Wood

(D) Textile (cotton)

Fig.4 Effects of temperature and heating rate on the pyrolytic reaction constants of different MSW components.

Fig. 5 Mass spectra of H₂O, CO₂, CH₄ and H₂ during the pyrolysis of wood, paper, textile and PET plastic at a heating rate of 10°C/min.

Fig. 6 Comparisons between the measured and predicted TGA and DSC curves for co-pyrolysis of the mixture of biomass and PET plastic at different mass fractions.

Fig. 7 Total heat requirement of co-pyrolysis of the mixture of biomass and PET plastic at different mass fractions.

Fig. 8 Wood and PET plastic mixtures of 1:1 mass ratio co-torrefied at different temperatures and times.

Fig. 9 TGA and DTG curves during the pyrolysis of the mixture of 50% biomass and 50% plastic co-torrefied at different temperatures and times.

Fig. 10 Heat flow and total heat requirement curves during the pyrolysis of the mixture of 50% biomass and 50% plastic co-torrefied at different temperatures and times.