

Kinetic Study of the Thermal Decomposition for Mixed Municipal Solid Waste Using Thermogravimetric Analysis

Nzioka Antony Mutua¹, Alunda Benard Ouma², Odero Shirley Atieno³

¹Department of Environmental and Energy Engineering, Kyungpook National University, Republic of Korea

²Department of Mining and Mineral Processing Engineering, Taita Taveta University, Kenya

³World Food Programme, Kenya

Article Info

Article history:

Received May 30th, 2017

Revised Aug 20th, 2017

Accepted Oct 18th, 2017

Keyword:

Thermal decomposition

Temperature

Municipal solid waste

ANOVA

Composition

Activation Energy

ABSTRACT

Thermal conversion of wastes is one of the perspectivesolution to ‘municipal solid waste’ problem. Thermal conversion process entails thermal decomposition of material with an increase in temperature. This experimental analysis investigated thermal decomposition of municipal solid waste using the thermogravimetric technique. The objective of the analysis was to analyze the changes in kinetic characteristics with changes in the composition of content in sample waste and temperature. Sample waste analyzed consisted of plant organic waste, paper, plastics, wood and inert substance. Proximate and elemental analyses were determined and calorific values determined experimentally using bomb calorimeter. Thermogravimetric curves were derived using thermogravimetric analyzer (TGA) at different temperature rates. Activation energy and preexponential factor were derived using Flynn-WallOzawa, KissingerAkahiraSunose and Kissinger model equations. Additional statistical analyses of variance using ANOVA was conducted for the different sets of composition analyzed. Results showed kinetic parameter values for different model free models used in analysis as well as the level of variance in activation energies for different composition of waste and temperature rates used.

Corresponding Author:

Nzioka Antony Mutua

Department of Environmental and Energy Engineering,

Kyungpook National University,

Daehak-ro 80, Buk-gu, College of Engineering, Daegu, 41566, Republic of Korea

Email: manymutua@knu.ac.kr

1. Background

There are different solutions proposed by researchers seeking to reduce the adverse effects of accumulating municipal solid wastes (MSW) in countries with developing and emerging economies. One of the perspective solutions is thermal conversion processes which may such processes such as pyrolysis, waste-to-energy, aerobic/anaerobic conversion processes among others [1]–[4]. Previous research showed that recycling and conversion of MSW with high moisture content to refuse derived fuel is feasible and may require minimal treatment [1],[5],[6].

Thermal decomposition process may provide sufficient information so as to understand the thermal conversion process. Thermogravimetric analysis is one of the perspective methods of studying the thermal decomposition process of any material including MSW. Some researchers have presented valuable data related to the thermogravimetric analysis of the MSW [7]–[9]. Research presented in the publications mentioned above focussed on the kinetic characteristics of the components or a combination of components in the MSW. It is, in our opinion, of utmost importance to study the sample material (i.e. MSW) with all the components combined.

Therefore, the objectives of this research are to study the thermal decomposition of MSW, derive the kinetic characteristics as well as study the effect of changes in the composition of MSW on the kinetic characteristics of the thermal decomposition process.

2. Materials and methods

2.1. Materials

Sample MSW consisted of plant wastes, shredded plastics and paper and wood chips. In this research, we used combustible materials and excluded all possible inert materials (glass, soil, metals etc.) We prepared two sets of samples as shown in Table 1 based on other references [5], [10], [11]. The particle size of sample MSW was <20 mm recommended by Athanaopolous [12], and reference [13] provided mathematical formulation for determining the particle size of our sample MSW. The sample MSW used in this research was prepared on as received basis. We conducted this experimental study based on the workflow presented in Figure 1.

We prepared sample MSW and used approximately 200 g. We dried the sample MSW at a temperature of 80°C for 24 hours. We used ASTM E955 – 88 standards to determine ash content on “dry material” basis [14].

Table 1. Composition of the sample MSW used in the experimental study

Mixing proportion, (% weight basis) for “as received” MSW		
Component	Set 1	Set 2
Plant wastes	73	52
Shredded paper	11	21
Shredded plastics	11	21
wood	5	6
Proximate analysis		
Ash content, (%)	6 ∞ 12	10 ∞ 12
*Moisture content, (%)	55 ∞ 56	35 ∞ 38
*Bulk Density, (kg/m ³)	85 ∞ 109	60 ∞ 76

Remark:

Mixing proportion provided in this table is based on previous research [5]

* - “as received” basis

References [4], [5] provided formula for calculating the bulk density for “as-received” MSW. We calculated the gross calorific values using bomb calorimeter (plain-jacket oxygen bomb-type, Parr Instrument Company-USA). Calorific standard (Benzoic acid pellets) used were in accordance with Parr Instrument Company’s (USA) specification. We calculated appropriate corrections from the “after-combustion” remains of the bomb calorimeter: these corrections are specified in the analytical equipment’s manual. Net calorific values were determined using empirical formulas provided by Ilinkh [15] as well as ASTM E955-88 standards [14]. The formula (1) was suggested by Ilinkh while (2) by ASTM E955 – 88 standards. Calorific values were converted to MJ/kg SI unit. The formulas for calculating the net calorific values are shown below:

$$Q_N = 4600 - 4A - 51.85X \quad (1)$$

$$Q_N = \frac{[100 - (X + A)]Q_g}{100} \quad (2)$$

In the formulas above, Q_g , Q_N represent gross and net calorific values respectively (MJ/kg) while variables A , X represent ash content and moisture content shown in Table 1. We calculated the gross calorific values on “dry material” basis and the net calorific values on “as received” basis.

We analysed the thermal decomposition process using TGA-50 supplied by Shimadzu Scientific (USA) equipped with the thermal analysis workstation (Shimadzu TA-60WS). We reduced the particle size of the sample MSW and prepared pellets using laboratory press machine and a roundshape tablet press(4 mm diameter). TGA analysis was conducted up to 900°C (1173 K) for four different temperature rates (5, 10, 20 and 50 K/min) under inert conditions sustained using argon gas (gas flowrate=10 ml/min).

3. Thermal decomposition theory and calculation

General formula used to describe reaction kinetics (i.e. thermal decomposition process) can be written as follows [16]:

$$\frac{dc}{dt} = k(T) f(c) \tag{3}$$

From the equation above, function $k(T)$ represents the rate constant which conforms with the Arrhenius law. We may express the rate constant as follows:

$$k(T) = Ae^{\frac{-E}{RT}} \tag{4}$$

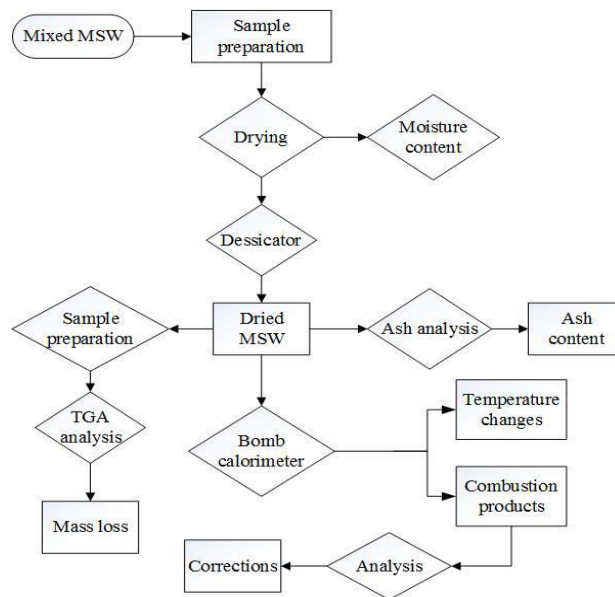


Figure 1. Experimental analysis workflow

where variable E represent the activation energy (kJ/mol), R - universal gas constant (j/mol K), A - pre-exponential factor (/min) and T - temperature (K). We might justify (3) by assuming that the sample MSW would undergo complex decomposition process generating volatile substances and char [16]. Therefore, we may determine the degree of conversion (c) using the following expression [17]:

$$c = \frac{m_{t-start} - m_{t-i}}{m_{t-start} - m_{t-final}} \quad (5)$$

where variables $m_{t-start}$, $m_{t-final}$, m_{t-i} represent initial, final and mass at the time (i). If we assume that our reaction is first-order ($n=1$), then (3) may be rewritten as follows:

$$\frac{dc}{dt} = (1-c)^n A e^{\frac{-E}{RT}} \quad (6)$$

Formula (6) corresponds to isothermal conditions. Thermogravimetric analysis is conducted under non-isothermal conditions whereby the actual temperature is expressed as a function of heating rates. Therefore, we will rewrite (6) to satisfy the non-isothermal conditions as follows [16]:

$$\frac{dc}{dT} = (1-c)^n \frac{A}{\beta} e^{\frac{-E}{RT}} \quad (7)$$

From the formula above, β represents the rate of heating (K/min) that we will use in thermogravimetric analysis.

In this study, we will use several non-isothermal model equations, namely: Kissinger, Kissinger – Akahira – Sunose and Flynn – Wall – Ozawa. The Kissinger model equation can be described as follows[18]:

$$\ln\left(\frac{\beta}{T_m^2}\right) = \ln\left(\frac{AR}{E}\right) - \frac{E}{RT_m} \quad (8)$$

From the formula above, variable T_m represent the peak temperature (K) where $dm_{t-i}/dt = 0$. We may calculate the activation energy by plotting a graph of $\ln(\beta/T_m^2)$ versus $1000/T_m$. The Kissinger – Akahira – Sunose model equation can be expressed as follows:

$$\ln\left(\frac{\beta}{T_{\alpha(i)}^2}\right) = \ln\left(\frac{A_{\alpha(i)}R}{E_{\alpha(i)}g[\alpha(i)]}\right) - \frac{E_{\alpha(i)}}{RT_{\alpha(i)}} \quad (9)$$

We can calculate the activation energy using model equation (9) mentioned above by plotting a graph of $\ln(\beta/T_{\alpha(i)}^2)$ versus $1000/T_{\alpha(i)}$. From formula (9) variable $E_{\alpha(i)}$, $T_{\alpha(i)}$ represent activation energy and temperature at conversion value $\alpha(i)$ respectively. Santos et al. [17] provided precise formulation and explanation of the integral function $g[\alpha(i)]$. The final model that we will use in our study (Flynn – Wall – Ozawa) can be expressed as follows:

$$\ln(\beta) = \ln\left(\frac{A_{\alpha(i)}E_{\alpha(i)}}{Rg[\alpha(i)]}\right) - 5.331 - 1.052 \frac{E_{\alpha(i)}}{RT_{\alpha(i)}} \quad (10)$$

From formula (10) we can determine activation energy from the graphical dependence of $\ln(\beta)$ versus $1000/T_{\alpha(i)}$. In this experiment, we will analyse the level of variance for our samples (i.e set 1 and 2). We will use one-way ANOVA analysis for the activation energy values obtained for all the model equation used. The following conditions were considered for the one-way ANOVA test:

- Levene test of variance
- Actual power analysis
- Tukey range test
- Number of Tests = 5

4. Results and discussion

4.1. Gross and net calorific value

Table 2 shows the gross and net calorific values of the mixed MSW. Experimental and empirical results showed that the mixed MSW with low plant wastes content (MSW set 2) had higher calorific value than that with high plant wastes content (i.e. MSW set 1). We obtained these calorific values without including the soil content. Soil, just like many inert compounds, are bound to have an adverse effect the calorific values of MSW since a significant amount of heat may be used in the oxidation /formation of other compounds from the inert substances. Our preliminary analysis coupled with previous research supported our conclusion [19]. The net calorific values calculated using the empirical formulas chose did not differ significantly.

Table 2. Calorific values for mixed MSW

Gross calorific values, MJ/kg		
	Set 1	Set 2
Q_g	14.5 ± 0.5	16.9 ± 1.2
Net calorific values, MJ/kg		
Ilinykh (2013)	6.1 ± 0.15	10 ± 0.3
ASTM E955 (2009)	5.1 ± 0.3	8.6 ± 0.25

4.2. Thermal decomposition

Thermal decomposition process was analyzed from the temperature of 300 K to 1073 K. Decomposition reaction showed similar decomposition characteristics for all the temperature rates. These decomposition characteristics were in three stages, namely: dehydration; fast decomposition of high molecular substances such as cellulose, lignin, etc. and subsequent and slow degradation of lower molecular compounds with the formation of char. Dehydration phase ended at a temperature range of 500 – 568 K for MSW set 1 and 495 – 560 K for MSW set 2. The second phase characterising the fast degradation process of high molecular compounds ended at a temperature range of 788 – 872 K for MSW set 1. The final stage began from the temperatures mentioned above till 1173 K. Solid residue for MSW was between 6 – 10% for MSW set 1 and 11 - 12 for MSW set 2 which corresponds to the values obtained from the proximate analysis. Preliminary analysis indicated that the presence of impurities such as inert substances might lead to the formation of anomalous/irregular decomposition behaviour of the MSW.

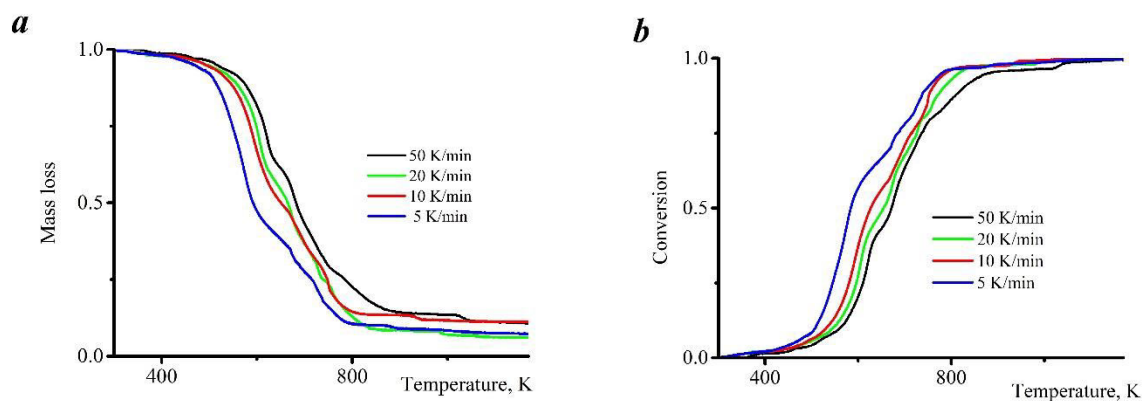


Figure 2. TGA mass loss and conversion curves for MSW set 1. Graph a: TGA mass loss and b: conversion curves.

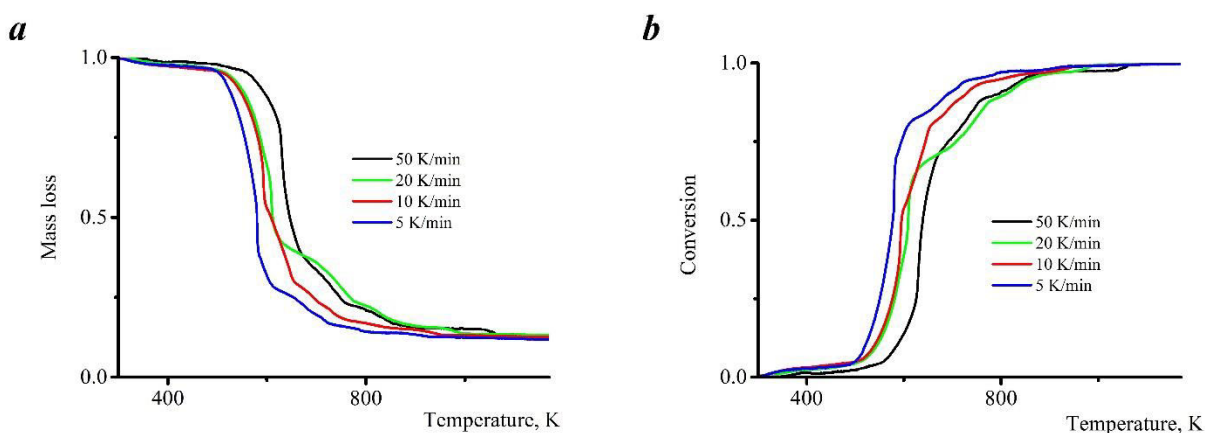


Figure 3. TGA mass loss and conversion curves for MSW set 2: Fig. a - TGA mass loss and b - conversion curves

4.3. Kinetic study and statistical analysis

We derived the linear regression equations for conversion values ranging from 0.1 to 0.8 for Kissinger – Akahira – Sunose / Flynn – Wall – Ozawa model equations and Kissinger Model equations to determine the activation energy values. From the Kissinger model equation, the activation energy values for MSW set 2 were higher than those of MSW set 1: MSW set 2 had a mean activation value of 122.5 kJ/mol while MSW set 1 had 135.6 kJ/mol.

From Kissinger – Akahira – Sunose model equation, the activation energy values ranged from 76 – 90 kJ/mol for MSW set 1 and 78 – 105 kJ/mol for MSW set 2. From the Flynn – Wall – Ozawa model equation, the activation energy values ranged from 75 – 96 kJ/mol for MSW set 1 and 83 – 109 kJ/mol for MSW set 2. From these two model equation, it is evident that MSW set 2 had the average activation energy greater than MSW set 1. This result is in contrast with the values we obtained using the Kissinger model equation.

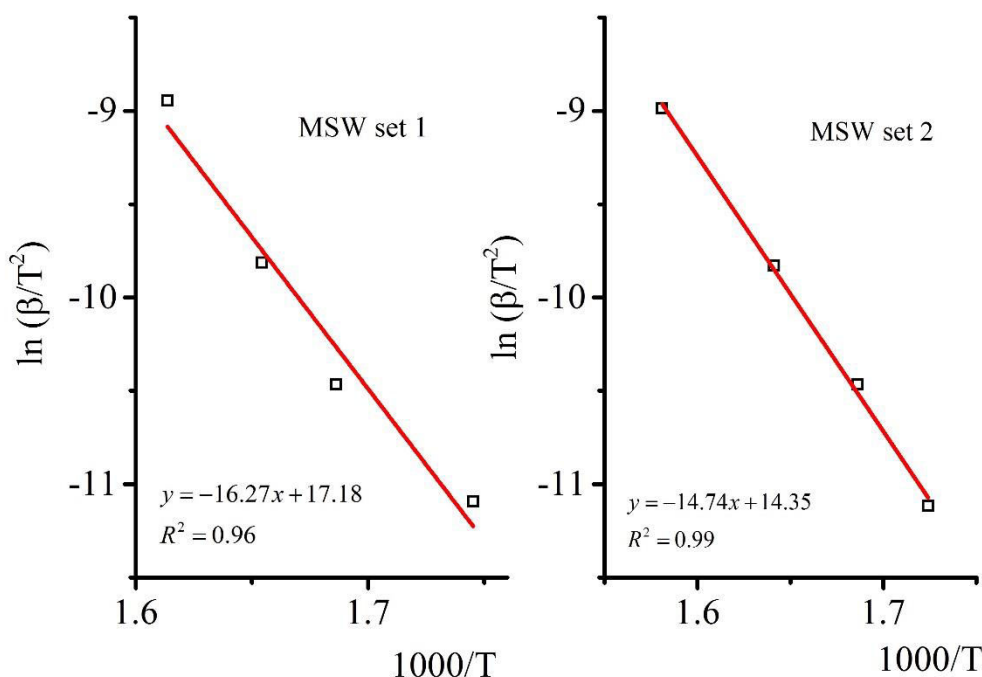


Figure 4. Graphicplots derived using the Kissinger model equation for MSW set 1 and 2

We conducted preliminary thermal decomposition analysis of MSW with inert substances (soil) with the objective of investigating the feasibility of correlating the differences between activation energy values and the organic plant wastes composition. Even though we might correlate such differences with the composition of organic plant wastes in this experimental study, the irregular characteristics of the thermal decomposition of MSW+inert substances from our preliminary analysis with MSW did not support our theory.

Table 3. Linear regression equations derived using Kissinger – Akahira – Sunose model equation

	MSW Set 1			MSW set 2		
	$y = ax + b$	R^2	E	$y = ax + b$	R^2	E
0.1	$y = -10.84x + 10.9$	0.95	90	$y = -9.51x + 7.58$	0.94	78.9
0.15	$y = -9.95x + 7.97$	0.95	83	$y = -9.25x + 6.55$	0.93	76.9
0.2	$y = -9.7x + 7.02$	0.92	80.6	$y = -9.14x + 5.97$	0.93	76.1
0.25	$y = -9.78x + 6.8$	0.93	81.4	$y = -9.4x + 6.15$	0.93	78.2
0.3	$y = -10.26x + 7.34$	0.92	85.4	$y = -10.18x + 7.28$	0.94	84.8
0.35	$y = -11.06x + 8.44$	0.93	91.2	$y = -10.96x + 8.43$	0.95	91.2
0.4	$y = -11x + 8.06$	0.91	91.5	$y = -11.9x + 9.8$	0.97	98.9
0.45	$y = -8.43x + 3.43$	0.93	67.9	$y = -12.58x + 10.72$	0.99	104.3
0.5	$y = -8.42x + 3.14$	0.93	69.8	$y = -12.58x + 10.72$	0.99	104.5
0.55	$y = -8.3x + 2.62$	0.9	68.8	$y = -12.57x + 10.6$	0.97	104.8
0.6	$y = -9.17x + 3.61$	0.87	76.4	$y = -11.2x + 8.14$	0.91	92.9

Table 4. Linear regression equations derived using Flynn – Wall – Ozawa model equation

	MSW set 1			MSW set 2		
	$y = ax + b$	R^2	E	$y = ax + b$	R^2	E
0.1	$y = -12.12x + 25.45$	0.96	95.6	$y = -10.61x + 22.2$	0.96	83.6
0.15	$y = -11.05x + 25.6$	0.93	87.5	$y = -10.4x + 21.23$	0.94	82.1
0.2	$y = -10.84x + 21.7$	0.92	85.7	$y = -10.3x + 20.69$	0.96	81.6
0.25	$y = -10.93x + 21.53$	0.92	86.5	$y = -10.58x + 20.9$	0.96	83.7
0.3	$y = -11.43x + 22.1$	0.92	90.4	$y = -11.37x + 22$	0.96	90
0.35	$y = -12.24x + 23.2$	0.93	96.7	$y = -12.16x + 23.21$	0.97	96.2
0.4	$y = -12.2x + 22.86$	0.94	96.5	$y = -13.1x + 24.61$	0.98	103.5
0.45	$y = -10.6x + 19.84$	0.96	83.8	$y = -13.66x + 25.44$	0.99	107.6
0.5	$y = -9.67x + 18$	0.95	76.2	$y = -13.8x + 25.54$	0.99	109.4
0.55	$y = -9.55x + 17.53$	0.91	75.2	$y = -13.8x + 25.4$	0.97	98

We conducted one-way ANOVA test analysis so as to determine the level of similarity/variance between MSW set 1 and 2. ANOVA test for all the cases and model equations showed significant differences between MSW set 2 and MSW set 1

5. Conclusion

We investigated the thermal decomposition of MSW, and the following conclusions would be made:

1. Calorific values of MSW set 2 were higher than that of MSW set 1. We could attribute these differences to the composition of MSW.
2. Net calorific values calculated empirically exhibited some similarity
3. The thermal decomposition process for MSW showed similar decomposition characteristics
4. Activation energy values derived using Kissinger model ranged from 135 kJ/mol for MSW set 1 and 122 kJ/mol for MSW set 2.
5. Activation energy using Kissinger – Akahira – Sunose model equation ranged from 76 – 90 kJ/mol for MSW set 1 and 78 – 105 kJ/mol for MSW set 2. MSW set 2 had an average activation energy value greater than that of MSW set 1
6. Activation energy using Flynn – Wall - Ozawa model equation ranged from 75 – 96 kJ/mol for MSW set 1 and 83 – 109 kJ/mol. MSW set 2 had an average activation energy value greater than that of MSW set 1
7. Measurement of variance showed a significant difference in activation energy values.

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