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Abstract
Energy flow analysis and thermal degradation of municipal solid waste was carried out using differential scanning calorimetry and thermo-gravimetric analyzer at heating rates of 10 K/min, 20 K/min, 30 K/min and 40 K/min in a nitrogen atmosphere and temperatures between 308 K and 1273 K. The activation energy (E_a) is the energy barrier which must be overcome for reaction to occur. Thermal degradation behavior experiments show that the municipal solid waste is less reactive than biomass or coal with activation energy ranging between 205.9 to 260.6kJ/mol. These value are higher than typical wood activation energy which ranges between 50 and 180kJ/mol and coal with a range between 30 and 90 kJ/mol. These value of activation energy can be improved by pretreatment of municipal solid waste.

Keywords: *Municipal Solid Waste, Thermal behavior, Thermo-gravimetric analyzer*

1 INTRODUCTION

The generation of municipal solid waste in cities in developing countries has been in the increase due to city growth. Cities are facing a challenge in solid waste management due to complex composition of waste and poor effective waste handling methods. The challenges include such as difficult of recycling into useful material, poor management of biodegradable waste and inefficient waste management infrstructure (Henry *et al.*, 2006, Kuo *et al.*, 2008). The increase of this wastes may lead to environment degradation if not appropriately managed (Johari *et al.*, 2012).
Waste to energy options are better way in managing waste and solving the energy crisis . Cities from developing countries are facing energy crisis where as solutions to waste handling could contribute to availability of energy. Recovery of energy from waste is a problem due to diverse nature of thermal characteristics of the waste (Belgiorno *et al.*, 2003). Some of the thermal characteristics in mention include calorific values, chemical composition, thermal degradation behavior and chemical kinetics . This work contribute to availing the same and compare these with those from biomass and sub-bituminous coal.

2 MATERIAL AND METHODS

2.1 Random sampling

The sampling of material was based on ASTM D5231 for random sampling. Due to un existence of trucks for collecting waste from domestic premises and other waste generating centres, the waste were collected by using push carts, bicycles, wheelbarrows and donkey carts. The waste was randomly collected within the city from collecting points of Sakina, Kaloleni and central market. These were classified to plastics, glass, paper, food wastes and metals.
The noncombustible component was separated from the others and samples of the remaing waste were availed for laboratory analysis. In order to get accurately waste composition for analysis the average weight of about 200kg of municipal solid waste were used. The heap of 200kg from each collecting point of Sakina, Kaloleni and Central market wastes were thoroughly mixed using shovels and spade, then the mixed portion of sample of about 8kg were packed to an airtight polythene bag for laboratory analysis.

2.2 Proximate and ultimate analysis study

The samples were subjected to standards test methods of proximate and ultimate analysis in accordance to ASTMD 3172 and ASTMD 3176 respectively.

2.3 Thermal degradation analysis study

The thermal degradation analysis were studied under inert condition using a thermo gravimetric analyzer type NETZSCH STA 409 PC Luxx connected to power unit 230 V, 16 A. High purity nitrogen, 99.95% used as carrier gas was controlled by a gas flow meter and fed into the thermo gravimetric analyzer at a flow rate of 60 ml/min and a pressure of 0.5 bar. A STA 409 PC Luxx, proteus software was utilized to acquire storage and analyse the data in a computer. The samples used in TGA were shredded into smaller pieces of approximately 30mm, mixed and grounded to a grinding machine to less than 1mm size. The a sample of 30±0.1 mg with average particle size less than 1mm was loaded to crucible and subjected into furnace and heated from 308 to 1273 K at heating rate of 10 K/min, 20 K/min, 30 K/min and 40 K/min. The calculated thermo-gravimetric output from proteus software was obtained as thermal decomposition profile; thermo-gravimetric (TG), differential thermo-gravimetric (DTG) and differential scanning calorimetry (DSC) curves.

Heat released and absorbed by municipal solid waste degradating sample was determined by using differential scanning calorimetry curves. The DSC monitors heat associated with phase changes and chemical reactions as a function of temperature. The heat was determined by integrating of the area between the baseline and the curve. The kinetic parameters of the representative samples were determined from the Kissinger's method (Ledakowicz and Stolarek, 2003).The method deploy the thermal degradation of municipal solid waste under non isothermal condition (Sonobe and Worasuwannarak, 2008) and the rate constant for the process is expressed by Arrhenius Equation (1)

$$k = A\,exp\left(-E_a/_{RT}\right) \qquad (1)$$

where, k is the rate constant, which is temperature dependent, A the pre-exponential factor, E_a the activation energy, R the universal gas constant and T is the absolute temperature. The reacted fraction x is determined by

$$x = \left(w_0 - w_t\right)/\left(w_0 - w_\infty\right) \qquad (2)$$

where, x is the reacted fraction, w_0 the initial mass, w_t the mass remaining after time t, w_∞ the final mass. f(x) the algebraic function depending on the reaction mechanism. Then,

$$dx/_{dt} = Af(x)\,exp\left(-E_a/_{RT}\right) \qquad (3)$$

The temperature rise at a constant heating rate (β), is expressed as in Equation 4.

$$\beta = dT/_{dt} \qquad (4)$$

Equation 5 is the differentiation of Equation 3

$$d^2x/_{dt^2} = \left\{E_a\beta/_{RT^2} + Af'(x)\,exp\left(-E_a/_{RT}\right)\right\} dx/_{dt} \qquad (5)$$

The maximum rate occurs at a temperature T_{peak}, approximations at T_{peak} condition yield Equation 6.

$$\ln\left(\beta/_{T^2_{peak}}\right) = \ln\left(AR/_{E_a}\right) - \left(E_a/_{RT_{peak}}\right) \qquad (6)$$

Equation 6 is a straight line graph, of $\ln(\beta/T^2_{peak})$ v/s $(1/T_{peak})$, The line slope is E_a/R and the intercept on the vertical axis is $\ln(AR/E_a)$, which are used to determined the values of E_a and A. The fractional pyrolysis of municipal solid waste component is obtained by taking the ratio of the change mass of municipal solid waste component at time t and total reactive mass of a sample as shown in Equation 2. The activation energy (E_a) is the energy barrier which must be overcome for reaction to occur. Activation energy tells on how quickly the reaction occurs. This means if the activation energy is high the reaction will go slowly but if the activation energy is lower, the reaction goes quickly. The pre exponential factor shows an empirical relationship between temperature and rate coefficient. It depends on how often molecule collide and how properly oriented when they collide when all concentrations are 1 mol/l.

3 RESULTS AND DISCUSSION

3.1 Proximate and Ultimate analysis

The results of proximate and ultimate analysis are shown in Table 1. The moisture content of the municipal solid waste as received ranges between 55.70 and 63.99 wt%, which is more than 50 wt% of the total weight of the sample. This high moisture content is prohibitive for combustion process as it raises the ignition temperature. At the same time, it reduces the heating value of the fuel (Muthuraman *et al.*, 2010), typical proximate analysis of biomass gives the results shown in Table 2. The volatiles released on dry basis of municipal solid waste for Kaloleni, Sakina and Central market are 74.43, 84.00 and 78.30 wt%, repectively, whilst the volatile matter contained in pure biomass such as forest residue, oak wood, and pine are 79.9, 78.1 and 83.1 %wt respectively (Vassilev *et al.*, 2010). Generally, fuels that contains high volatile, have low fixed carbon, the case is the same to municipal solid waste from Kaloleni with fixed carbon of about 17.41 wt%. The advantage of high volatile and low fixed carbon is rapid burning of a fuel, while a fuel with low volatile and high fixed carbon has low combustion rate (McKendry, 2002). The high value of volatile matter and low fixed carbon of municipal solid waste shows that the municipal solid waste is highly reactive if the moisture contents are controlled. The ash content of the sampled municipal solid waste range between 8.16 to 13.48 wt.%, which is small, this is advantage to waste management and environment because it offers the possibility of having small quantity of heavy metals, salts, chlorine and inorganic pollutant to the bottom ash (Lam *et al.*, 2010). The ultimate analysis of the municipal solid waste shows that the concentration of phosphorus and chlorine are negligible while the carbon and hydrogen content were above 50% and 5% respectively. The oxygen content was about 34%. Sulfur is about 0.29%, this is low compared to values from of bituminous coal at 1.1 wt% (Nakao *et al.*, 2006).

Table 1: Proximate and Ultimate analysis of municipal solid waste.

			Proximate analysis				
Location	**Moisture as received (wt%)**	**Volatile Dry basis (wt%)**	**Ash Dry basis (wt. %)**	**Fixed carbon Dry basis (wt. %)**	**HHV (MJ/kg)**		
Kaloleni	59.67	74.43	8.16	17.41	11.90		
Sakina	63.99	84.00	10.00	6.00	11.37		
Central market	55.70	78.30	13.48	8.22	12.76		
			Ultimate analysis				
Location	**C (wt. %)**	**H (wt. %)**	**O (wt. %.)**	**N (wt. %)**	**S (wt. %)**	**Cl (wt. %)**	**P (wt. %)**
Kaloleni	55.57	5.34	34.88	2.09	0.31	0.04	0.10
Sakina	55.70	5.29	34.27	2.13	0.22	0.07	0.13
Central Market	53.20	5.24	34.71	2.86	0.37	0.04	0.11

Table 2: Proximate and Ultimate analysis of typical biomass materials and coal.

			Proximate analysis		
	Moisture (Wet basis)	**Volatiles**	**Ash**	**Fixed carbon**	**Source**
Biomass					
Coffee husk	10.0	78.5	2.4	23.1	(Tang *et al.*, 2014)
Rice husk	10.4	62.95	18.5	13.4	(Yusof *et al.*, 2008)
Rice husk	9.45	70.6	17.09	12.31	(Wilson *et al.*, 2010)
Coal					
Bituminous coal	3.21	37.65	25.44	33.7	(Mashingo *et al.*, 2014)

			Ultimate analysis			
Biomass	**C (wt. %)**	**H (wt. %)**	**O (wt. %.)**	**N (wt. %)**	**S (wt. %)**	**Source**
Coffee husk	47.5	6.4	43.7	-	-	(Tang *et al.*, 2014)
Rice husk	37.9	5.2	27.7	0.14	0.61	(Yusof *et al.*, 2008)
Rice husk	50.45	6.58	41.46	1.49	0.23	(Wilson *et al.*, 2010)
Coal						
Bituminous coal	81.01	5.79	10.46	1.71	1.39	(Mashingo *et al.*, 2014)

Table 3: Characteristic property summary

	Moisture temperature(K)			**Hemicellulose temperature (K)**			**Cellulose temperature(K)**		
Material	Onset	Peak	Offset	Onset	Peak	Offset	Onset	Peak	Offset
Rice husk	313.1	356.8	423	423	575.8	643	643	694.9	773
Time (s)		336			1596			2334	
Coffee husk	313	371	471	471	590.9	753	753	960.2	1013
Time (s)		442.2			1670.4			3919.8	
Municipal solid waste	313	356.2	408.9	408.9	556.8	660	660	748.7	913
Time (s)	480			1462.3				2634	
Coal	313	390.4	423	650	693.1	710		No peak	
Time (s)		312			1121			2442s at >1121.1K	

Where

Onset temperature is the temperature that the studied region is started.
Peak temperature is the temperature where the maximum degradation is taking place
Offset temperature is the temperature in which degradation from the identified region is ending.

The municipal solid waste calorific value is about 12 MJ/kg, this value is smaller than average biomass heating value of about 17 MJ/kg (Heylighen, 2001). The energy content of MSW can be improved by pre-treating the municipal solid waste so as to reduce oxygen content, since oxygen in fuel reduces the energy content of a fuel (McKendry, 2002). Alternatively, the municipal solid waste can be co-fired with coal for improving energy content (Li *et al.*, 2004, Sami *et al.*, 2001).

3.2 Thermogravimetric analysis

The municipal solid waste from the collecting points degraded to 75 to 85 %wt in the thermogravimetric analyser as shown in Figure 1. The municipal solid waste from Central market degraded to 85 %wt, while the Kaloleni degraded to 75 %wt. The residue formed is between 25 and 15 wt%. The residue contains fixed carbon and ash, the high residue is observed at municipal solid waste from Kaloleni 25 wt% and the lowest residue is observed at municipal solid waste from Central market and Sakina 15 wt%. this value is also supported the value obtained during proximate analysis. The char can be used as a fuel, but municipal solid waste that have high ash content hinder the combustion of char due to the layer of ash formed on the surface to inhibit the diffusion of oxygen into the char (Himawanto *et al.*, 2013). Compared with biomass and coal, Figure 2 the municipal solid waste has less ash contents, Figure 3 and Figure 4 show that all the samples have 3 majour peak, the moisture, hemicellulose and cellulose degradation peak. The degradation of each sample are different from each other. The values related to the degradation are shown in Table 3.

The values show that the rice husk is less reactive than others, this can be shown by looking the duration in which it degrade to its first peak after 336 seconds while coffee husk reach its first peak after 442.2 seconds. coal is highly reactive than others it react after 312 seconds, at 693.1K there is apeak which shows that the maximum devolatilization of coal.

3.3 Differential thermal gravimetric

Figure 3 shows the derivative of thermo-gravimetric analysis (DTG), which has four visible regions; these are moisture release region, lignocellulocis degradation region, plastic degradation region and char pyrolysis region (Lai *et al.*, 2011). The moisture release region is ranging between 303 and 423K. Lignocellulocic degradation region ranges between 423 and 643K, at this region volatile matters are released, the region corresponds to pyrolysis of lignocelulosic biomass. The plastic degradation ranges between 643 and 913 K and the char pyrolysis region ranges between 913 and 1273.

The same identified regions were also observed by Lai et al.(2011).

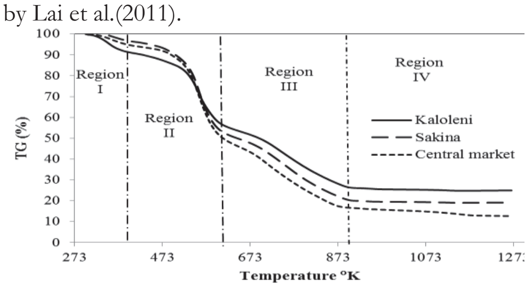

Figure 1: TG of Municipal solid waste

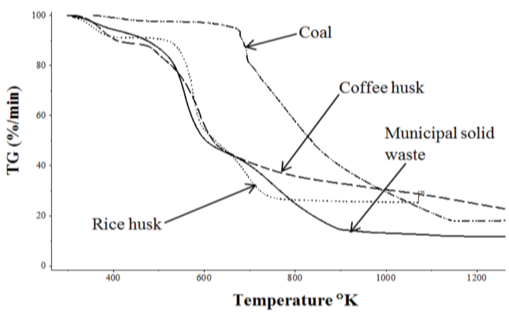

Figure 2 : TG of various biomass, Municipal solid waste and coal

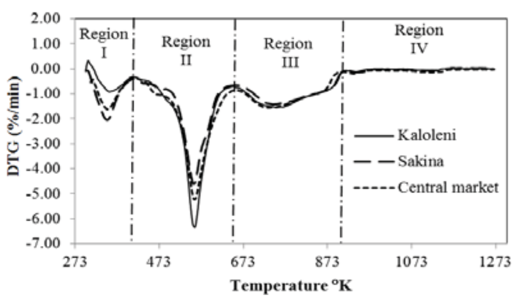

Figure 3: DTG of municipal solid waste

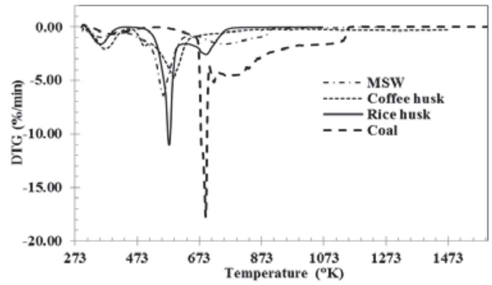

Figure 4: DTG of various biomass, MSW and Coal

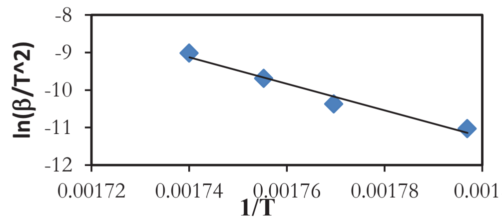

Figure 5: Determination of kinetic parameter of Arusha municipal solid waste.

3.4 Chemical Kinetics

DTG curves at different heating rate were used to develop individual Figure 5, which was used to calculate the activation energy (E_a) and pre exponential factor (A), as given in Table 4. The activation energy of MSW ranges between 205.934 kJ/mol and 260.60kJ/mol. This value is higher than that of biomass and coal which range between 50 and 180 kJ/mol and 30 and 90 kJ/mol respectively. This shows that MSW need high energy to react as compared to biomass and coal. The reactivity of MSW can be increased by reducing the non combustible (Biswas, 2011).

Table 4: Activation energy and Pre-exponential factor of municipal solid waste

Location	**E_a (kJ/mol)**	**A (s^{-1})**	**Source**
Kaloleni	258.680	9.142×10^{23}	
Sakina	205.934	8.977×10^{18}	Original research
Central Market	260.60	1.186×10^{28}	
Biomass			
Rice husk	166.5		(Belgiorno *et al.*, 2003)
Coffee husk	161	2.33×10^{6}	(Wilson, 2010)
Coal			
Bituminous coal	105–130		(Álvarez *et al.*, 1995)

3.5 Differential scanning calorimetry

The differential scanning calorimetry (DSC) curves shown in Figure 4, reveal an endothermicity between 303 and 423, this is due to evaporation of moisture. The temperature range of 423 to 1273 K the process undergoes exothermic reaction due to the devolatilization of the municipal solid waste and plastic pyrolysis. The energy absorbed due to evaporation of moisture by waste from Kaloleni, Sakina and Central market collecting points were 0.11 MJ/kg, 0.2 MJ/kg and 0.15 MJ/kg respectively, whilst energy released from the same respective collection points were -7.6 MJ/kg, -8.3 MJ/kg and-8.5 MJ/kg in respective manner. The energy released in the DSC by municipal solid waste was lower than that from biomass which is at 9.6 MJ/kg and coal which is at 13.49 MJ/kg.

The energy release results from bomb calorimeter experiments shows that municipal solid waste contains 12MJ/kg while energy released results from DSC shows that MSW ranges from 7.6MJ/kg to 8.5MJ/kg. The energy released from bomb calorimeter is the energy containing in a MSW in dry basis. The mass of dry 1 kg of MSW is equivalent to about 1.63kg of the mass of net MSW. This is because the 63% of moisture is taken out during bomb calorimetry. The moisture of 0.63kg require 1.411 MJ/kg of dry MSW. This energy ultimately should be obtained from the 12 MJ/kg. The balance 10.6 MJ/kg is the energy that one would recover per kg of dry MSW from the MSW energy conversion.

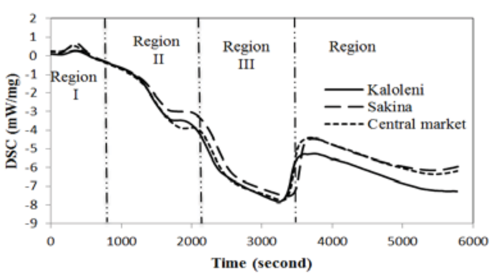

Figure 6: DSC of Arusha Municipal solid waste sites.

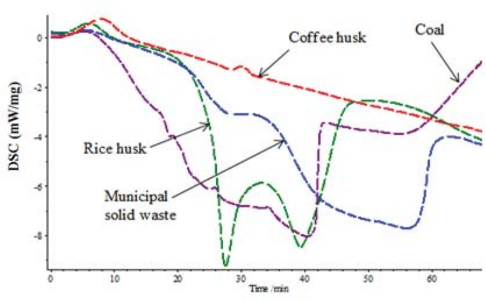

Figure 7: DSC of typical biomass, MSW and coal.

4 CONCLUSION

This paper finding related to municipal solid waste characterization of a typical developing country city.

- The proximate analysis of municipal solid waste show that, the waste contain more than 50% and 5% of carbon and hydrogen respectively.
- This contribute to the calorific value of the material.
- The ultimate analysis shows that the average amount of nitrogen, sulphur, chlorine and phosphorus are small.
- The energy content of waste is about 12MJ/kg which is about 30% of energy contained in coal and 60% of energy contained in biomass.
- The activation energy from municipal solid waste range from 205.9 to 260.6 kJ/mol the corresponding value for biomass is 167.4 kJ/mol while for coal it is 105–130 kJ/mol.
- For every kg of dry MSW, energy recovery of 10.6 MJ/kg is expected to be realized.

5 LIST OF ABBREVIATION

ASTM	American Standard Test and Methods
COSTECH	Commission for Science and Technology
DSC	Differential scanning calorimetry
DTG	Differential thermal gravimetric
HHV	Higher heating values
MSW	Municipal solid waste
NM AIST	Nelson Mandela African Institute of Science and Technology
TG	Thermal gravimetric analysis
UDSM	University of Dar es Salaam

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