Kinetics Properties and Thermal Behavior of Pine Sawdust and Municipal Solid Waste

Abstract

Waste resulting from economic activities has been an integral part of every human society. Effective waste management is considered to be consistent with improved quality of life through removal of potential hazards of uncontrolled disposal. Recent years has witnessed a number of sustainable energy recovery technologies developed to divert solid waste destined for landfills. Waste management is a global problem and therefore development of energy recovery technologies and at the same time serving dual purpose in its reduction has become a priority in recent years. The present study reports kinetics properties and thermal behavior of pine sawdust and municipal solid waste (MSW) using thermogravimetric analysis (TGA) and thus providing theoretical basis for development of energy recovery technologies. Results of this study have shown that the activation energy of both MSW and pine sawdust varies with temperature. The analysis of pine sawdust shows that it has activation energy (E_a) values of 26.19 kJ/mol., 87.46 kJ/mol. and 54.46 kJ/mol. At respective temperature ranges between 350 – 400K, 550 – 650K and 700 800K. MSW has activation energy between 72.91kJ/mol. and 139.1 kJ/mol. at temperature ranges between 700 – 900K and 500 – 600K respectively. The estimated value of pre-exponential factor for pine sawdust was determined to have the values of 2.46 x 10^4, 1.6 x 10^{10} and 5.32 x 10^{16} (s^{-1}) with temperature ranges between 350 – 400K, 550 – 650K and 700 800K respectively. Municipal solid waste has the values of 3.01 x 10^{12} and 7.31 x 10^3 (s^{-1}) with a temperature range of 500 – 600K and 700 – 900K respectively. From these findings, it has been determined that MSW and pine sawdust available in Arusha and Kilimanjaro possess a potential for energy recovery.

Keywords: Municipal solid waste (MSW), Pine sawdust, thermogravimetry (TG), differential thermogravimetry (DTG), differential scanning calorimetry (DSC)

1. INTRODUCTION

The sustainable economic development of any country is usually accompanied with energy demand increases and environment degradation challenges (Wolfram *et al.*, 2012; Kichonge *et al.*, 2014; Ahmed *et al.*, 2017). As economic sectors grows the energy demand and waste generation in cities rises primarily influenced by population growth, changing life styles and thus rapid urbanization (Tsamba *et al.*, 2006; Chiemchaisri and Visvanathan, 2008; Gentil *et al.*, 2009; Omari *et al.*, 2014). Inappropriate waste management strategies and insufficient energy supply contributes to poor life quality in cities (Kuo *et al.*, 2008; Johari *et al.*, 2012; Kichonge *et al.*, 2015) as a result of uncontrolled greenhouse gases (GHGs) emission to the atmosphere among others (Noor *et al.*, 2013). Municipal solid waste (MSW) uncontrolled burning results in emissions of gases such as methane and carbon dioxide and therefore considered as among major climate change contributors (Chiemchaisri and Visvanathan, 2008; Kothari *et al.*, 2010; Udomsri *et al.*, 2011). Then again, the emissions of GHGs such as carbon dioxide, methane and nitrous oxide from uncontrolled agricultural activities are considered to be among climate change contributors (Cole *et al.*, 1997; Smith *et al.*, 2007).

The primary sources of energy for many years has been from fossil fuels, which are fast depleted and contributed to the global warming (Ryu, 2010; Shahsavari and Akbari, 2018). There is a need for a sustainable source of renewable energy to replace fossil fuels as global energy demand is continuously increasing in parallel with population increase and industrial development. The biogenic fraction of municipal solid waste and forest waste are renewable in nature and therefore they can be used to mitigate energy and environmental challenges (Varol *et al.*, 2010; Mohammed *et al.*, 2013). Conversion of waste to energy is one among methods in waste management while mitigating energy challenges (Barbieri *et al.*, 2016). Renewable waste materials from MSW and agriculture activities such as pine sawdust are convertible to useful energy forms through waste to energy routes for sustainable development. Compared to fossil fuels pine sawdust and MSW due to their nature can reduces equivalent CO_2, SO_2 and NO_X emissions (Baxter, 2005; Shahsavari and Akbari, 2018).

The abundant pine sawdust and municipal solid wastes and their renewable nature are encouraging their utilization as the source of sustainable renewable energy (Varol *et al.*, 2010; Hossain *et al.*, 2014; Pandey *et al.*, 2016b). Pine sawdust and municipal solid wastes need to be processed so as to upgrade its fuel quality for energy recovery (Chaula *et al.*, 2014b). There are many ways of energy recovery from pine sawdust and municipal wastes, but the common one being physical treatment such as making pellets, thermal treatment such as combustion, pyrolysis, and gasification (Chen *et al.*, 2016). Biological treatment such as fermentation and anaerobic digestion (Sharholy *et al.*, 2008). The municipal solid waste contains a big portion of biomass materials such as food, wood, and paper (Pandey *et al.*, 2016a). The knowledge of thermal degradation is essential for predicting the pyrolysis behavior of municipal solid waste and pine sawdust materials (Johari *et al.*, 2012). The characterization makes easier to optimize their utilization and gives essential information in designing the suitable energy recovery technologies for their disposal (Sonobe and Worasuwannarak, 2008; Clarke and Preto, 2011). Thermal degradation of pine sawdust and municipal solid waste pose a big challenge due to their nature and composition (Belgiorno *et al.*, 2003). The chemical reactions that take place during their degradation and chemical kinetics used to estimate the potentiality for energy recovery (Chaula *et al.*, 2014a). Thermal degradation values such as activation energy, frequency factor, rate of reaction, calorific values, differential scanning calorimetry and differential thermal gravimetric can be determined by using thermogravimetric analysis (TGA) (Chen *et al.*, 2014; Mhilu, 2014; Mishra and Mohanty, 2018). TGA is considered as the simplest and the most effective method to analyze the burning profile of a fuels as compared to others (Sanchez et al., 2009; Yorulmaz and Atimtay, 2009). The purpose of this study was therefore to determine and analyze the kinetics properties and thermal behavior of pine sawdust and MSW available in Arusha and Kilimanjaro using TGA and therefore to provide a theoretical basis for making use of their properties and characteristics so to turn them into sustainable energy resources.

2. MATERIAL AND METHODS

2.1. Material Sampling and Collection

Municipal solid waste and the pine sawdust collected from various saw mills in Arusha & Kilimanjaro were used. Different equipment and standard test methods were adopted in order to determine and analyze thermal degradation. The airtight polythine bags were used for quality assurance and safety of samples transport from source to laboratory for analysis.

2.2. Municipal waste collection

The sampling of municipal solid waste material was based on ASTM D5231-03. The method for random sampling for determination of the composition of unprocessed municipal solid waste (ASTM, 2003; Gidarakos *et al.*, 2006). The waste was randomly collected and categorized to plastic, paper, food, and non-combustibles. The combustible components were collected for laboratory analysis.

2.3. Pine sawdust collection

The pine sawdust samples obtained from sawmills were natural dried and collected for laboratory analysis.

2.4. Thermal Degradation Analysis Study

The experiments for the pyrolysis of wastes were performed by using thermo-gravimetric analyzer type NETZSCH STA 409 PC L_{uxx}. Then samples collected as per municipal waste and pine sawdust sampling paragraphs above were grounded to small particles of 1mm and oven dried at 378K to constant weight. Then a sample of 30±0.1 mg of wastes with an average particle size less than 1mm was loaded to the crucible and subjected into the furnace and heated. These samples mass are small and therefore it is assumed that the thermal degradation within the sample is negligible (Dirion *et al.*, 2008).

The thermal gravimetric analyzer connected to PC installed with proteus software for data acquisition, storage and analysis. The thermal gravimetric analyzer is used to measure the quantity of mass change due to physical and chemical reactions; it is combined the heat flux differential scanning calorimetry which determines the physical and chemical reactions associated with thermal effect. The profile curves of thermogravimetry (TG), differential thermogravimetry (DTG) and differential scanning calorimetry (DSC) were obtained from Proteus software (Wilson *et al.*, 2011).

2.4.1. Municipal solid wastes thermal degradation analysis

The municipal solid waste samples and subjected to heat at temperature ranges vary from 308 to 1273K and heating rate of 10K/min. The calculated thermo-gravimetric from Proteus software was obtained and recorded.

2.4.2. Thermal degradation analysis of pine sawdust

The pine sawdust samples were subjected to heat at temperature ranges from 308 to 973K with a heating rate of 10K/min. The calculated thermo-gravimetric output from Proteus software was obtained and recorded.

2.5. Kinetic parameters analysis

The method deployed to determine Kinetic parameter was Coasts-Red fern methods equation (1). It is used as a standard method for studying the thermal degradation of pine sawdust and municipal solid waste under non-isothermal condition (Amutio *et al.*, 2012; Farrokh *et al.*, 2019). The Coasts-Red fern method used to calculate the kinetic parameters of first-order reaction (Coats and Redfern, 1964; Tsamba *et al.*, 2006).

$$\ln\left[\frac{-\ln(1-x)}{T^2}\right]=\left[\frac{AR}{\beta E_a}\left(1-\frac{2RT}{E_a}\right)\right]-\frac{E_a}{RT} \qquad (1)$$

Using the known heating rate, the line graph of $\ln\left[\left(-\ln\left(1-\alpha\right)\right)/T^2\right]$ versus 1/T understudied material will be a straight-line graph. The slope and intercept of the line graphs were used to calculate the kinetic parameters (Lai *et al.*, 2011; Tan *et al.*, 2019).

Since the value of $\frac{2RT}{E_a} << 1$ that can be neglected, the interception on the vertical axis is $\left(AR/\beta E_a\right)$ and the slope line is E_a/R can be used to determine the values of E_a and A.

The constant heating rate (β) is expressed as shown in Equation 2.

$$\beta = dT/dt \qquad (2)$$

The rate constant for the process is expressed by Arrhenius Equation 3.

$$k = A\exp\left(-E_a/RT\right) \qquad (3)$$

Where: k is the rate constant which depends on the temperature

A is the pre-exponential factor (S^{-1})

E$_a$ is the activation energy (kJ/mol)

R is the universal gas constant $(8.3142\,kJmol^{-1}K^{-1})$ and

T is the temperature (K)

$$\frac{dx}{dt}=k\,f(x) \qquad (4)$$

$f(x)$ Algebraic function depending on reaction mechanism

$$\frac{dx}{dt}=Af(x)exp\left(-E_a/RT\right) \qquad (5)$$

Degree of conversion x

$$x=\left(w_0-w_t\right)/\left(w_0-w_\infty\right) \qquad (6)$$

Where:

w_o Initial mass

w_t The mass remaining at time t

w_∞ The final mass remaining

3. RESULTS AND DISCUSSION

3.1. TG Analysis of Municipal Solid Waste and Pine Sawdust

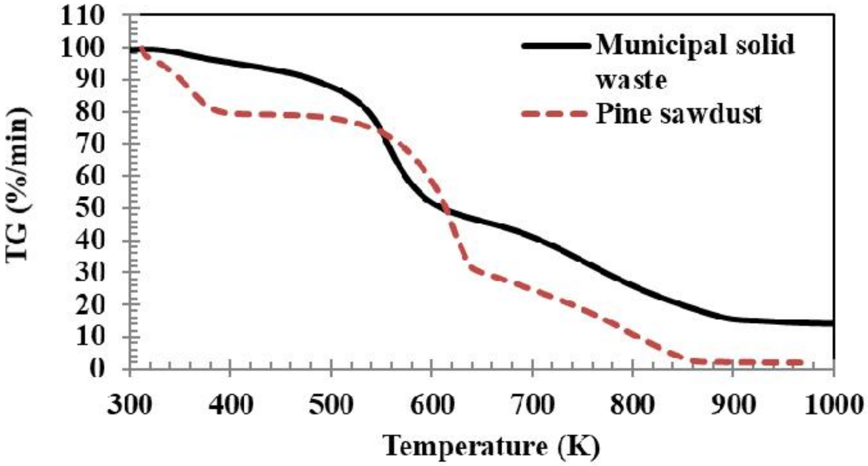

Figure 1: TG Curves of Municipal solid waste and Pine sawdust

Table 1: TG results of Municipal solid waste and pine sawdust

S/N	Material	Moisture release	Volatile release	Remaining Char& Ash
1	Municipal solid waste	3.6	80.8	15.6
2	Pine sawdust	18.9	77.5	3.6

The thermo-gravimetric analysis results were shown in Figure 1 and Table 1. The value of ash remaining in pine sawdust is much less compared to municipal solid waste. The big amount of moisture released at 378K from pine sawdust (18%) shows that there are much moisture contents in pine sawdust than in municipal solid waste. There is also slightly more volatiles in municipal solid waste than in pine sawdust. The value of ash remaining is higher in municipal solid waste than in pine sawdust shows that there are many mineral components in municipal solid waste than in pine sawdust (Quina *et al.*, 2018).

3.2. DTG analysis of municipal solid waste and pine sawdust

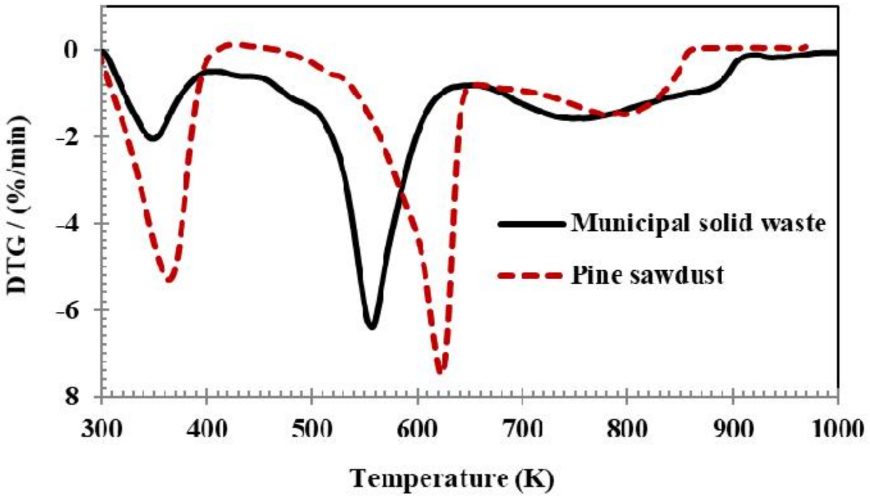

Figure 2: DTG of municipal solid waste and pine sawdust

Figure 2 shows the derivative of thermo-gravimetric analysis (DTG), for municipal solid waste and pine sawdust. The municipal solid waste curve shows that the degradation derived in four shoulders. The first shoulder is the degradation of moisture, this is ranging from 303K to 423K, and the second shoulder is the lignocellulose degradation which ranges between 423 and 643K. The third shoulder ranges between 643 and 913K shows the degradation of plastics and hemicellulose materials (Quina *et al.*, 2018). There is very small char pyrolysis in pine sawdust curve since it has a very little char remaining in the reaction, Figure 1 and Figure 2 (Lai *et al.*, 2011). The degradation of plastic and hemicellulose materials are overlapping in municipal solid waste degradation while the degradation of hemicellulose in pine sawdust is clearly defined in Figure 2. The char pyrolysis falls in 4th shoulder ranges between 913 and 1273K.

3.3. DSC Analysis of Municipal Solid Waste and Pine Sawdust

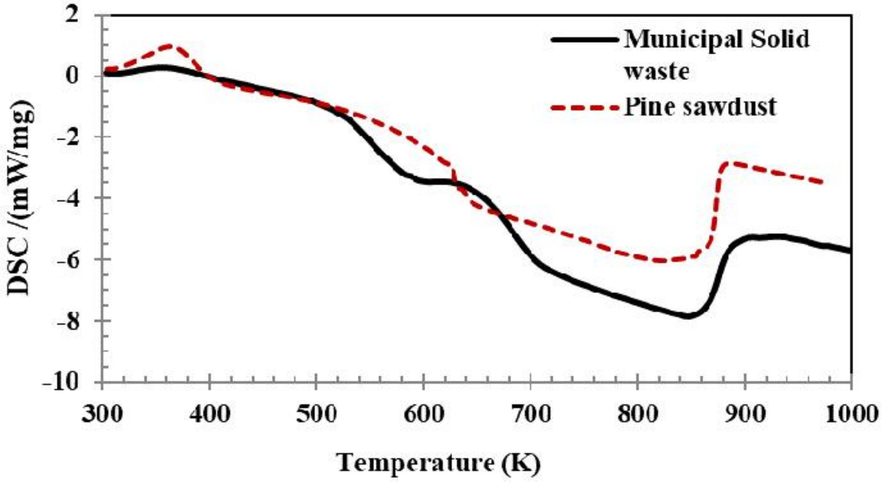

Figure 3: DSC from Municipal Solid Waste and Pine Sawdust

Figure 3 shows the differential scanning calorimetry curves. All curves show that there are endothermic reactions during its initial stage of degradation. The temperature range between 300 and 370K, this is due to the release of moisture. The pine sawdust curve is higher than a municipal solid waste curve. The value of this moisture is clearly seen in the TG and DTG curves (Figure 1 and Figure 2). The energy used to release moisture from pine sawdust is higher than that used in municipal solid waste. The structure of pine sawdust is so that the moisture is entrained in its cell walls and for that case, it requires more energy to remove moisture from pine sawdust than in municipal solid waste (Wilson *et al.*, 2011). An energy release result due to differential scanning calorimetry (DSC) of municipal solid waste has energy quantity ranging from 7.6 to 8.5MJ/kg. Compared to the energy found from bomb calorimetry about 12MJ/kg. The energy amount found in DSC is low. The energy found during bomb calorimetry is the energy determined from dry MSW pellets. The energy found during DSC is the energy remaining after drying MSW. The energy to dry MSW that make the difference between the two. The energy released due to DSC of pine sawdust has the energy value of 15.1 MJ/kg.

3.4. Kinetic parameters of municipal solid waste

The value from the TGA curve of MSW obtained and put into coats Red-fern method give the value as shown in Figure 4.

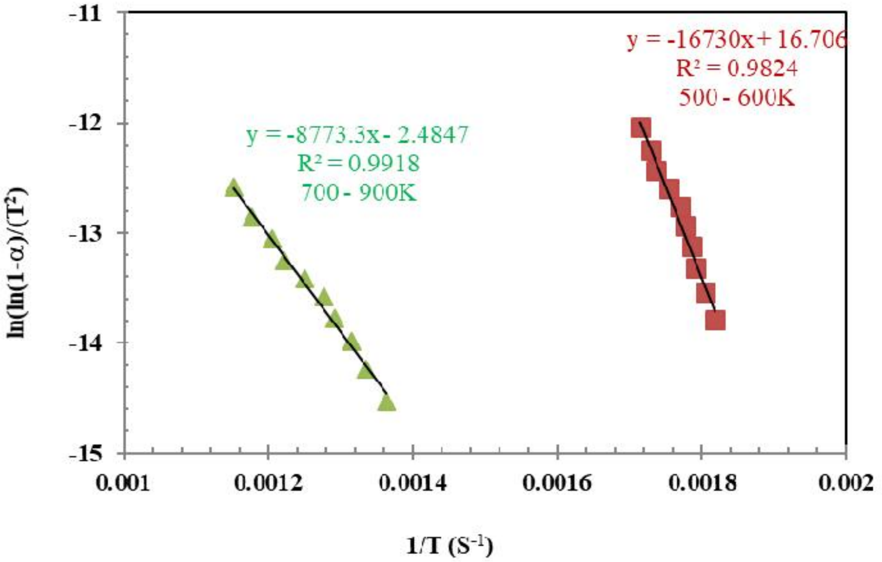

Figure 4: Determination of kinetic parameter of Municipal solid waste

The kinetic parameters of municipal solid waste are shown in two curves. The kinetic parameter at high-temperature peak and at the low-temperature peak as shown in Figure 4 and Table 2. The kinetic parameter graphs show the values of Pre-exponential factor (A) for municipal solid waste as 3.01 x 10^{12} and 7.31 x 10^{3} (S^{-1}) for low and high temperature respectively. The value of E_a for municipal solid waste is 72.91 and 139.1 kJ/mol. for low and high temperature respectively.

3.5. Kinetic parameters of pine sawdust

The value from the TGA curve of pine sawdust obtained and insert into Coats Redfern method gives the value as shown in Figure 5.

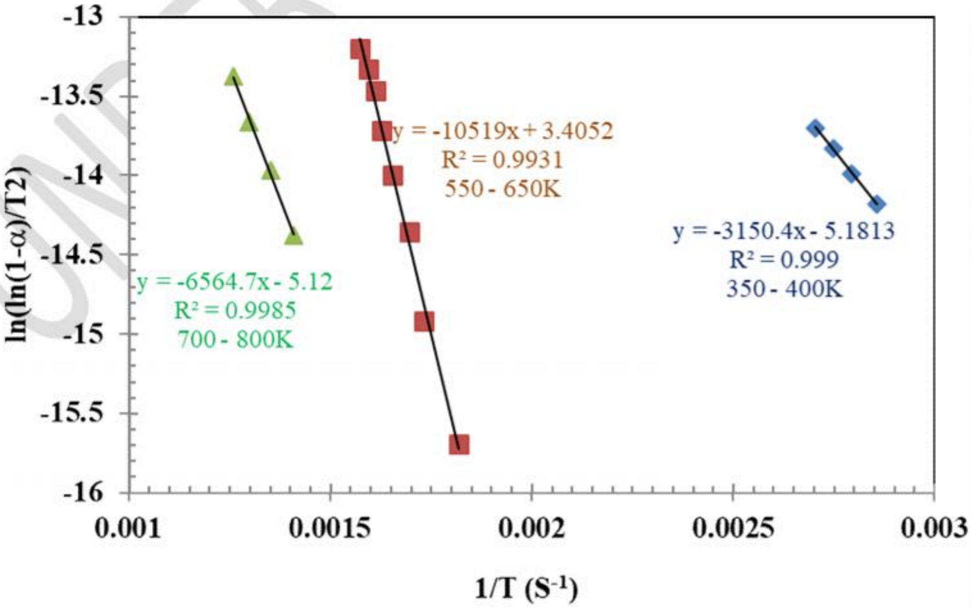

Figure 5: Determination of the kinetic parameter of pine sawdust

The pine sawdust kinetic parameters as shown in Figure 5 in three curves, the degradation of hemicellulose at low-temperature peak and of cellulose at high-temperature peak. The results tabulated in Table 2 show that the activation energy E_a ranging from 26.19 to 87.46 kJ/mol. The value of pre-exponential factor increases from 2.46 x 10^4, 1.6 x 10^{10} and 5.32 x 10^{16} (S^{-1}) with a respective increase in the temperature range of 350 – 400K, 550 – 600K and 700 – 800K.

Table 2: Activation energy and Pre-exponential factor of municipal solid waste and pine sawdust

Type of waste	Temperature (K)	Activation energy (kJ/mole)	Pre-exponential factor (s^{-1})
Municipal solid waste	500 – 600	139.1	3.01 x 10^{12}
	700 – 900	72.91	7.31 x 10^3
Pine sawdust	350 – 400	26.19	2.46 x 10^4
	550 – 600	87.46	1.6 x 10^{10}
	700 – 800	54.58	5.32 x 10^{16}

4. CONCLUSION

From the results obtained in this study, it can be concluded that the activation energy of both MSW and pine sawdust varies with temperature. The determined energy recovery from dry MSW was 10.6 MJ/kg while energy recovery from dry pine sawdust was 15.1 MJ/kg. Differential scanning calorimetry (DSC) shows that at the beginning the reactions are endothermic due to the release of moisture from the samples and thereafter moisture released the reactions undergo exothermic reaction. The analysis of pine sawdust shows that it has activation energy (Ea) values of 26.19 kJ/mol., 87.46 kJ/mol. and 54.46 kJ/mol. with respective temperature ranges between 350 – 400K, 550 – 650K and 700 800K while MSW activation energy was determined in between 72.91kJ/mol. and 139.1 kJ/mol. with temperature ranges between 700 – 900K and 500 – 600K respectively. The estimated value of pre-exponential factor for pine sawdust was 2.46 x 104, 1.6 x 1010 and 5.32 x 1016 (s-1) at temperature ranges between 350 – 400K, 550 – 650K and 700 800K respectively while that for MSW was 3.01 x 1012 and 7.31 x 103 (s-1) at a temperature ranges of 500 – 600K and 700 – 900K respectively. The conclusion drawn from this study show promising potential for energy recovery from both MSW and pine sawdust available in Arusha and Kilimanjaro.

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