Kinetic analysis of biomass/sorbent blends for gasification purposes

A.I Mabuda, N.S Mamphweli and E.L Meyer
University of Fort Hare, Institution of Technology, Alice, 5700
e-mail: amabuda@ufh.ac.za

Abstract. Biomass is one of the main renewable energy sources and coupled with a carbon dioxide adsorbent material such as calcium oxide sorbent it increases the biomass conversion efficiency during gasification. Kinetic study of materials is vital to the assessment of parameters including the feasibility, design, and scaling of industrial biomass conversion applications. This study aims to investigate the thermal degradation behavior of thermochemical conversion of biomass/sorbent blends in order to choose the ratio that result in higher conversion efficiency during gasification. Thermal stability is the stability of material to resist change in physical shape as its temperature changes. Thermogravimetric analysis (TGA) was employed to determine the thermal stability and kinetics of biomass and sorbent mixtures of pine wood, calcium oxide (CaO) and magnesium oxide (MgO), which will ultimately determine the gasification characteristics of the blends. A mixture of 75 % pine wood and 12.5 % CaO and 12.5 % MgO resulted in the highest thermal stability compared to others. For this reason this mixture was found to be the one suitable for gasification. The thermal analyses obtained for the different blends are presented and discussed in detail in this paper.

1   Introduction

Biomass is recognized as one of the major sources of renewable energy [1]. Biomass pyrolysis can be classified as a heterogeneous chemical reaction and can be affected by changes in reaction geometry and by interfacial diffusion of reactants and products [2, 3]. The progress of heterogeneous reactions could not be studied using the concentration of biomass components since these values may vary over time; the mentioned variation is a difference between homogeneous and heterogeneous reactions [4]. However, pyrolytic decompositions of biomass are best described considering independent parallel reactions, assuming the presence of pseudo-components [2].

Pyrolysis is a fundamental thermochemical conversion process that can be used to transform biomass directly into gaseous and liquid fuels. Pyrolysis is also an important step in combustion and gasification processes. The reaction dynamics and chemical kinetics of heterogeneous processes can be affected by three key elements [3]. In this regard, a thorough understanding of pyrolysis kinetics is vital to the assessment of items including the feasibility, design, and scaling of industrial biomass conversion applications [5, 6]. Table 1 presents a series of chemical reactions that occur during the conversion of biomass into useful products in a gasification system [7].

Table 1: Gasification reactions.

Reaction type	Heat of reaction	Equation
Oxidation reactions		
$C + O_2 \rightarrow CO_2$	-394 kJ/mol	(1)
$C + \frac{1}{2}O_2 \rightarrow CO$	-284 kJ/mol	(2)
$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$	-242 kJ/mol	(3)
$CH_4 + 2O_2 \leftrightarrow CO_2 + 2H_2O$	+803 kJ/mol	(4)
Reduction reactions		
$C + CO_2 \leftrightarrow 2CO$	+172 kJ/mol	(5)
$C + H_2O \leftrightarrow CO + H_2$	+131 kJ/mol	(6)
$C + 2H_2 \leftrightarrow CH_4$	+74.8 kJ/mol	(7)
$C + \frac{1}{2}O_2 \rightarrow CO$	-111 kJ/mol	(8)
Shift reaction		
$CO + H_2O \leftrightarrow CO_2 + H_2$	+41.2 kJ/mol	(9)
Methanization reaction		
$2CO + 2H_2 \rightarrow CH_4 + CO_2$	-247 kJ/mol	(10)

$CO + 3H_2 \leftrightarrow CH_4 + H_2O$	+206 kJ/mol	(11)
$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$	-165 kJ/mol	(12)
Steam reactions		
$CH_4 + H_2O \leftrightarrow CO + 2H_2$	+206 kJ/mol	(13)
$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2$	+36 kJ/mol	(14)

Thermogravimetric analysis (TGA) provides an excellent tool that may provide insight regarding the kinetics of heterogeneous reactions. However, it cannot be overstressed that the kinetic data obtained from a single thermo-analytical technique, does not provide the necessary and sufficient evidence to draw mechanistic conclusions about a solid state decomposition process [8]. The kinetic behavior of a given heterogeneous reaction system may change during the process and so it is possible that the complete reaction mechanism cannot be represented suitably by a single specific kinetic model [9].

The purpose of this paper is to evaluate the thermal stability of various biomass/sorbent blends using the TGA method and to determine kinetic parameters (activation energy, E and pre-exponential factor, A) using the model-free (Isoconversional) approach.

2   Methodology

TGA measurements were carried out with biomass and biomass/sorbent blends. The experiments were carried out in a nitrogen atmosphere with the flow rate maintained at 20 ml/min. Biomass (wood) was coarse ground to 250 μm and mixed with calcium oxide (CaO) and magnesium oxide (MgO). CaO and MgO powders were used without further preparation. The mixtures of biomass and sorbents are presented in Table 2.

Table 2: The mixture of wood, CaO and MgO materials

Method	Wood (%)	CaO (%)	MgO (%)	CaO.MgO (%)
I	75	12.5	12.5	25
II	90	5	5	10

The TGA measurements were conducted at different heating rates of 10 °C, 15 °C and 20 °C/min in a temperature range of 20 °C to 700 °C. The proximate and ultimate analysis of biomass is shown in Table 3. The kinetic parameters were determined using the model-free, Kissinger method.

Table 3: Proximate and ultimate analysis of wood

Proximate analysis	(wt. %)	Ultimate analysis	(wt. %)
Volatile matter	68	Carbon	47.5
Moisture content	8	Hydrogen	6.5
Fixed carbon	24	Nitrogen	0.1
Ash content	0.3	Oxygen[1]	45.9

[1]calculated by difference

2.1   Isoconversional methods

The majority of kinetic methods used in the area of thermal analysis considers the rate to be a function of only two variables, T and α [10]:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{15}$$

where $k(T)$ is the rate constant and $f(\alpha)$ is the reaction model. The temperature dependence of equation (15) is given by Arrhenius equation:

$$k(T) = Ae^{(-\frac{E}{RT})} \tag{16}$$

where T is the absolute temperature in K, R is the universal gas constant, A is the frequency factor, or pre-exponential, and E is the activation energy of the reaction. The extent of reaction, α, can be defined either as the mass fraction of biomass substrate that has decomposed or as the mass fraction of volatiles evolved and can be expressed as shown below:

$$\alpha = \frac{W_0 - W}{W_0 - W_f} \tag{17}$$

where W is the mass of substrate present at any time t, W_0 is the initial substrate mass, W_f is the final mass of solids (i.e., residue and unreacted substrate) remaining after the reaction.

The Kissinger method is a model free method, which allows obtaining the kinetic parameters of a solid-state reaction without knowing the reaction mechanism. Kissinger [12] developed a model-free, non-isothermal method with no need to calculate E for each conversion value in order to evaluate kinetic parameters. This method allows to obtain the value of the activation energy from a plot of Ln (β/T_m^2) against $1000/T_m$ for a series of experiments at different heating rates, β (°C/min), where T_m is the temperature peak of the DTG curve. The equation is the following:

$$\ln\left(\frac{\beta}{T_m^2}\right) = ln\left(\frac{AR}{E}\right) - \frac{E}{RT_m} \tag{18}$$

The activation energy can be calculated from the slope of the plot, which is equal to $-E/R$ and the pre-exponential factor from the intercept of the plot, which is equal to ln(AR/E).

3   Results and Discussions

Figure 1 shows the TGA curves of biomass and biomass/sorbent blends at the heating rate of 20 °C/min. The initial thermal degradation for all curves is due to water vaporization below 100 °C. This is then followed by a rapid weight loss due to devolatilisation, between the temperature range of 100 °C and 400 °C. After devolatilisation/pyrolysis of the biomass and biomass/sorbent samples, the remaining material consist mainly of char and carbonates, respectively. These data were limited to devolitilisation process up to 700 ºC, although the reactions were still taking place up to 900 ºC where the char and carbonates mass remains constants after 800 ° C. The small decomposition peak appear at temperatures 550 °C and 650 °C in the case of 25% CaO.MgO mixture, it can be attributed to the carbonation of $CaCO_3$, through which CaO can absorb the released CO_2 to form $CaCO_3$ product [13]. This figure shows that 25% CaO.MgO is the most thermally stable compared to other samples. This helps with the selection of the end use application, which helps to predict the performance of a material and improve its quality. Wood and 10% CaO.MgO blend decomposes by 7.5 and 8.55 %/°C after 600 °C respectively. Whereas 25% CaO.MgO blend loses weight at a low rate of 2.69 %/°C after this temperature. For this reason the 25% CaO.MgO sample was chosen for kinetic study and its results were compared with wood sample.
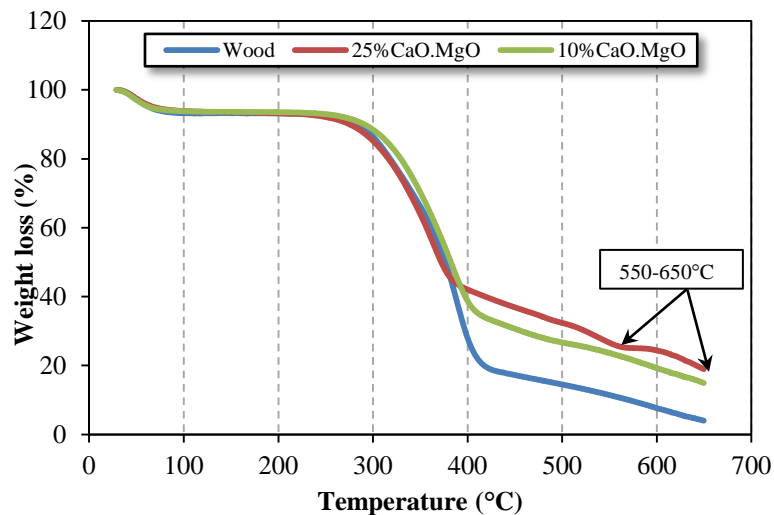
Figure 1: Thermal degradation of wood and blends at the heating rate of 20 °C/min.

Figures 2 shows the TGA curves of wood (solid lines) and wood with 25% CaO.MgO blend (dashed lines) at different heating rates of 10 °C/min, 15 °C/min and 20 °C/min, respectively. It is known that the heating rate affects both locations of the TGA curve and maximum decomposition rate [14]. As can be observed from both graphs, there is a shift in weight loss lines caused by decreased heating rate implying that the reaction is slowing down. At higher heating rates, individual weight losses are reached at lower temperatures. Again, during the measurements, at a lower heating rate, a larger instantaneous thermal energy is provided in the system and a longer time is required for the purge gas to reach equilibrium with the temperature of the furnace [15]. At a lower heating rate of 10 °C/min, 25% CaO.MgO blend shifted to higher temperature compared to wood. This means the temperature needed for this blend to decompose is 4.55 % higher than wood. Whereas the higher heating rate has a short reaction time and the temperature needed for the sample to decompose is lower. This also causes the maximum rate curve to shift to the right [16]. This can be a result of heat and mass transfer limitations. Which implies that the temperature in the furnace space can be a bit higher as the temperature of a particle and the rate of devolatilisation is higher than the release of volatiles [15]. It also implies that at a higher temperature the volatiles are released and are more likely to deposition reactions [17].
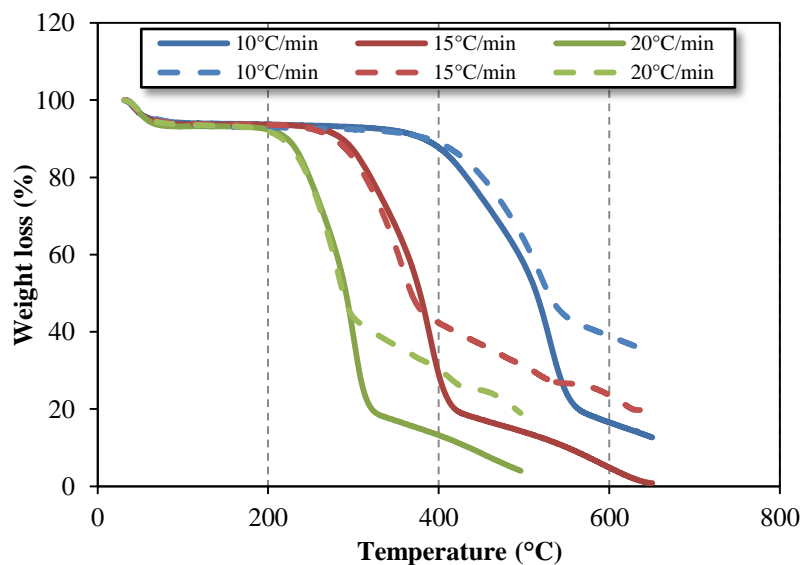

Figure 2: Thermal degradation of wood (solid lines) and wood with 25% CaO.MgO blend (dashed lines) at various heating rates

The kinetics parameters were obtained from model-free, non-isothermal TGA data and require a set of experimental tests at different heating rates. The heating rates were 10 °C/min, 15 °C/min and 20 °C/min as shown from Figure 2. Figure 3 shows the Kissinger plot of $\ln(\beta/T_m^2)$ versus $1000/T_m$ (K^{-1}) of the decomposition process for wood (blue plot) and 25% CaO.MgO blend (red plot) respectively. A linear fit to the data enabled the determination of E and A as per equation (18).

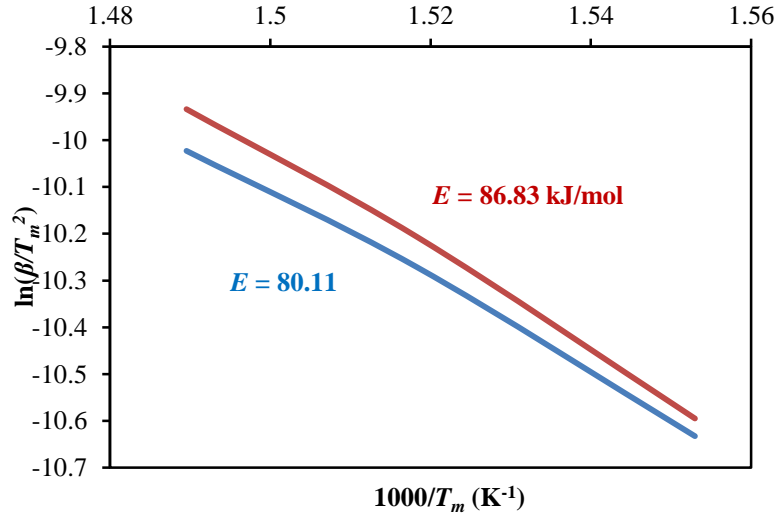
$E = 86.83 \text{ kJ/mol}$

$E = 80.11$

Figure 3: Plots of $\ln(\beta/T_m^2)$ versus $1000/T_m$ of wood sample (blue plot) and 25% CaO.MgO blend (red plot) for the heating rates of 10 °C/min, 15 °C/min and 20 °C/min

The results obtained from TGA were elaborated according to model-free method to calculate the kinetic parameters. The activation energy (E) and the pre-exponential factor (A) of wood and 25% CaO.MgO samples were calculated from Eq. (18) where T_m is a temperature which corresponds to the maximum weight loss peaks calculated from DTG curve. The peak temperatures were 370.9 °C, 385.6 °C, and 398.3 °C corresponding to 10 °C/min, 15 °C/min and 20°C/min heating rates, respectively. The correlation coefficient (R^2) for both wood and 25% CaO.MgO blend is 99.7%.

Table 4 presents the results for activation energy (E) and pre-exponential factor (A) obtained from this method. The activation energy obtained is 80.11 and 86.83 kJ/mol, and pre-exponential factor is 7.38 x 10^5 and 2.91 x 10^6 min^{-1} for wood and 25% CaO.MgO blend, respectively. This means that the reaction mechanism is not the same (8.39 % difference) for the decomposition process. The study [15] reported that the heating rate, the type of biomass tested and the atmosphere in which thermal degradation takes place, have significant effects on the thermal degradation rates and, therefore, on the activation energies. The results presented herein are in the agreement with the latter statement.

Table 4: Kinetic parameters (E and A) obtained by Kissinger method.

Samples	E (kJ/mol)	ΔE (%)	A (min^{-1})
Wood	80.11	—	7.38 x 10^5
25% CaO.MgO	86.83	8.39	2.91 x 10^6

4   Conclusions

There was a significant difference (59 %) in weight loss between the biomass and biomass with sorbent mixture (25% CaO.MgO) at higher temperature (400-650 °C), which implies that the wood with sorbents have a better thermal stability compared to pure wood. The activation energy (E) and the pre-exponential factor (A) for wood and 25% CaO.MgO blend were 80.11 and 86.83 kJ/mol and 7.38 x 10^5 and 2.91 x 10^6 min^{-1} respectively. The energy of the blend is 8.39 % higher than the biomass, which implies that the blend requires more energy to react and would thus gasify at higher

temperatures and release more energy than pure biomass materials. The released energy is due to the exothermic reaction whereby CaO absorbs CO_2 during the water-gas shift reaction in the gasifier. The resultant energy can be used by other endothermic reactions in the gasifier and for external use purposes.

5   References:

[1]   Bridgwater V., Meier D., Radlein D. *Organic Geochemistry* **30** (1999) 1479-1493.

[2]   Song Hu, Andreas Jess, Minhou Xu. *Fuel* **86** (2007) 2778–2788.

[3]   John E. White,W. James Catallo, Benjamin L. Legendre. *Journal of Analytical and Applied Pyrolysis* **91** (2011) 1–33.

[4]   Ozawa T. Bull *Chem Soc Jpn* 1965; **38:**1881–6.

[5]   Raveendran K., Ganesh A., Khilar K.C. *Fuel* **75** (1996) 987–998.

[6]   Sensoz S., Can M., Energy Sources. *Utilization, and Environmental Effects* **24** (2002) 347–355.

[7]   Ruiz, A. J., Juarez, C. M., Morales, P. M., Munoz, P., Mendivil, A. M. *Renewable and Sustainable Energy Reviews*, 18, (2013) pp. 174–183.

[8]   Vyazovkin S., Wight C.A. *International Reviews in Physical Chemistry* **17** (1998) 407–433.

[9]   Galwey A.K., Brown M.E. *Thermochimica Acta* **386** (2002) 91–98.

[10]   Vyazovkin S., Alan K. Burnham, José M. Criadoc, Luis A. Pérez-Maqueda, Popescu C., Sbirrazzuoli N. *Thermochimica Acta* **520** (2011) 1–19.

[11]   H.L. Friedman, Journal of Polymer Science. Part C: *Polymer Symposia* **6** (1964) 183–195.

[12]   Kissinger H., 1956. *Journal of Research of the National Bureau of Standards*, *Vol.***57**, No 4, pp. 217-221.

[13]   Biagini E., Barontini F., and Tognotti L 2006. *Ind. Eng. Chem. Res.,* **45** 4486–4493.

[14]   Slopiecka K., Bartocci P., Fantozzi F. *3rd International Conference on Applied Energy* - 16-18 May 2011 - Perugia, Italy, pages 1687-1698.

[15]   Gašparovič L., Koreňová Z., Jelemenský Ľ. *Chemical Papers* **64** (2) 174–181 (2010).

[16]   Quan C., Li A., Gao N., 2009. *Waste Management*, Vol.**29**, No 8, pp. 2353-236.

[17]   Bliek A., Van Poelje W. M., Van Swaaij W. P. M., van Beckum F. P. H., 1985. A*lChE Journal* (Vol. **31**, No. 10), pages 1666-1681.