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Pyrolysis and Char Burnout Characteristics of Cassava Peelings as Potential Energy Source

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Abstract

The pyrolysis behaviour, kinetics and char burnout of cassava peelings as a potential source of energy has been investigated using TGA. Four heating rates: 5, 10, 15 and 20oC/min were used to evaluate the kinetic parameters of the thermal decomposition process using iso-conversional non-isothermal method. An isothermal method was used to evaluate the burnout behaviour of char produced at 20oC/min by adopting the Arrhenius equation. During the pyrolysis process, it was observed that two distinct peaks were identified during hemicellulose decomposition which could be due to component complexity of agricultural waste products. The activation energy at 20% conversion was found to be 164 KJ/mol which is higher than what was observed between 30-50% conversions (151-154 KJ/mol). However, as the conversion increased from 60-90% the activation energy also increased from 162-290KJ/mol which suggests that the pyrolysis reaction progressed through multi step kinetic process. It was observed that the burnout of the chars was found to decrease with increase in heating rate up to the char produced at 15oC/min. However, further increase in the heating rate to 20oC/min during the pyrolysis process produced char with faster burnout profile. This may be due to higher porosity of the chars formed at that heating rate. It was also observed that as the heating rate increased from 5-15oC/min during pyrolysis, the activation energy of the resultant chars reduced. Again, higher activation energy was observed for the char produced at 20oC/min implying that highly porous char structure can diminish mass transfer limitations during char combustion. The pyrolysis and char combustion kinetics will be useful for modelling and the design of thermo-chemical cassava peelings conversion systems

Keywords: Biomass pyrolysis, heating rates, char burnout, kinetics

1. Introduction

The economic growth of any country depends largely on the availability of power supply in that country. Nigeria as one of the largest crude oil producing countries still has the problem of supplying constant electricity due to the challenges of the existing electricity generating sources (Oseni, 2011; Oyedepo, 2012; Olugbenga, 2013). Apparently, the use of alternative and renewable energy sources will help to alleviate these challenges. Biomass is one of the renewable energy options and has received significant attentions in the power sector as a renewable fuel. (Demirbas , 2005; Domenichini et al, 2011;). Though the potential of biomass to substitute oil is still not established, its development in Nigeria as an alternative source of fuel for electricity production is promising because of the abundance of biomass resources in the country. Thus, the understanding of the mechanisms during thermal conversion represents a crucial stage towards the optimum design of biomass energy systems. These studies are also important to understand the ignition, flame, combustion stability, and pollutants formation during biomass utilisation.

Nigeria has abundance of renewable energy resources which are not utilised. In fact, most of the wastes from agricultural products which are useful energy sources are wasted every year after harvest. One of such wastes is the cassava husk/peelings. Cassava is a crop in Nigeria which is widely cultivated in almost all the parts of the country for food. The crop has a thick husk which is usually peeled and used for other forms of food in some part of the country while others discard it as wastes. Most of the times, these underutilized residues are dumped on certain areas or burnt thereby causing environmental and health hazards. Studies have shown that cassava has the highest output of residues generated and it's estimated value is about 29 million metric tonnes (Agboro & Ogie, 2012). Many researchers have reviewed the potential of renewable energy resources in Nigeria with the aim of establishing the different renewable energy sources available in the country and the potential application of such resources (Olugasa et al, 2014; Iye & Bilsborrow, 2013; Mohammed, 2013; Simonya & Fasima, 2013) as well as the challenges of the existing electricity generating sources (Oseni, 2011; Oyedepo, 2012; Olugbenga, 2013) but have not investigated the energy values and combustibility of these biomass resources for power generation. Few studies have been carried out on the thermochemical characterisation and utilisation of a biomass waste to understand its potential for bio-oil production (Odetoye et al, 2013) and the pyrolysis kinetic of wood chips from Nigeria (Balogun et al, 2014). Till date, the pyrolysis behaviour, kinetics and char burnout characteristics of cassava peelings from Nigeria as a potential fuel for energy generation have not been investigated.

Pyrolysis of biomass is important because it is the first step in understanding the biomass combustion and gasification (Damartzis, et al, 2011). The knowledge of this process is essential in predicting the thermal decomposition behaviour of biomass fuel. The decomposition of biomass generally is a complex phenomenon due to the fact that different reactions take place as its decomposition from the solid state to gaseous and liquid products and then forming a solid product depending on the thermal environment and pyrolysis temperature. The pyrolysis temperature and heating rate are influenced by heat transfer from the gas to the biomass particle and within the biomass particle because it is a slow reaction. Hence, the pyrolysis behaviour is influenced by both heat transfer and chemical reaction (Burhenne et al, 2013). Due to the different components present in biomass, most researchers have analysed the decomposition of biomass as three separate components namely hemicellulose, cellulose and lignin. Hence the kinetics of these components have been studied separately as well (Burhenne et al, 2013; Wu et al, 2014). However, some have also studied the overall pyrolysis behaviour of biomass. In such cases, the overall kinetics of the pyrolysis has been investigated Seo et al, 2010. Several models are being used to determine the kinetic parameters of solid fuels during decomposition: model fitting and model free methods. Model free non-isothermal methods are used to determine the kinetic parameters because they are simple and more errors are avoided (Liu et al, 2013) and provide more accurate results (Balogun et al, 2014). The model-free method is based on the assumption that the kinetics of the reactions does not depend on the heating rate (Damartzis, et al, 2011).. One of the commonly used model-free methods for the determination of kinetic parameters of solid decomposition based on TGA analysis is the Flynn–Wall–Ozawa's (FWO) model which use the correlation of the heating rate of the samples, the activation energy and the inverse temperature.

Char combustion is an important aspect of solid fuel combustion because it is the rate limiting step. Secondly, it determines the level of unburned carbon in the fly ash. Incomplete combustion causes decrease in combustion efficiency of the boiler, has adverse effect on heat transfer equipment and electrostatic precipitator operation. It also reduces the suitability of the fly for use as by-products and hence, the need to investigate the burnout characteristics of the char produced from the cassava peelings. Therefore, this work investigates the pyrolysis characteristics of the fuel in terms of the kinetics of the pyrolysis and the combustion reactivity of the resultant char

2. Materials and Methodology

2.1 Sample collection, Preparation and properties

Cassava peelings were collected from farmland after harvesting and sun dried for 5 days. The dried samples were pulverised and sieved. Particle size used for this experiment is 125-250 µm.

2.2 TGA pyrolysis test

Pyrolysis tests were carried out using TA instrument Q600 with N_2 flow of 100ml/l. About 5-10 mg of samples were analysed at different heating rates of 5, 10, 15 and 20°C/min. the sample was first heated from ambient temperature to 105°C to remove moisture, kept isothermal for 5 minutes and then heated to 850°C and kept at that temperature for 10 minutes to remove all volatiles. However, for the proximate analysis, the heating rate used was 150°C/min which is the maximum achievable heating rate of the TGA used. This was to ensure that all volatiles were removed. From the pyrolysis data, the rate of pyrolysis and the kinetics parameters were calculated using global decomposition kinetic equations and iso-conventional methods.

$$\frac{dx}{dt} = Aexp(-\frac{E}{RT})\int (x) \qquad (1)$$

Where dx/dt is the rate of conversion, E is the activation energy (J/mol), A is the pre-exponential factor, R is the universal gas constant, T is temperature (K), x is the extent of conversion and f(x) is the reaction model which is a function of the extent of conversion.

For non-isothermal experiment with different heating rates, where the heating rate,β = dT/dt, the reaction rate is:

$$\frac{dx}{dT} = \frac{A}{\beta}\exp\left(-\frac{E}{RT}\right).f(x) \qquad (2)$$

The method used to determine the kinetic parameters in this work is the Flynn–Wall–Ozawa's (FWO) method. The method is based on Boyle's approximation (Boyles 1965)

$$log\ p(x) \cong -2.315 + 0.457x \qquad (3)$$

The final form of the FWO equation is given as

$$log\ \beta = log\frac{EA}{g(x)R} - 2.315 - 0.457\frac{E}{RT} \qquad (4)$$

By carrying out TGA analysis at different heating rates, the temperatures at different conversions are noted. A plot of log β against 1/T gives a line with a slope. The activation energy can be calculated using equation (5). Then the activation energy can be obtained.

$$slope = -0.457\frac{E}{R} \qquad (5)$$

2.3 TGA measurement of char reactivity

For the char burnout tests, raw sample was devolatilised using the procedure in 2.2. Then the temperature was ramped down to 425^{o}C and gas atmosphere was switched to air to burnout the char. From the produced char burnout profiles, two quantitative measures of reactivity were obtained, the times to different burnout levels and the apparent first order rate constant (K) of char burnout. The TGA combustion data between 5 and 95% burnout levels were used to calculate the rate constant (k), based on the following equation:

$$\frac{dx}{dt} = k(1 - x) \qquad (6)$$

Where t is time and x= (1-C/C_0) is the fractional weight conversion, with C as the remaining carbon mass and C_0 as the original carbon mass (Le Manquais et al, 2012). By integration, the solution of equation (6) subject to the initial condition α=0 at t=0 then yields

$$-\ln(1 - x) = kt \qquad (7)$$

The rate constant, k, can then be obtained as the gradient of the linear relationship between the natural log of (1-x) and reaction time t. Subsequently, by plotting lnK vs 1/T for different pyrolysis temperatures, the values of the activation energy (E) and the pre-exponential factor (A) can be estimated from the slope and intercept of an Arrhenius plot using equation 8.

$$lnk = lnA - \frac{E}{RT} \qquad (8)$$

3. Results

3.1 Biomass characterization

The characterisation comprises of proximate and ultimate analysis. The proximate analysis is used to determine the moisture content, volatile matter yield, the fixed carbon content and the ash content of the fuel. The ultimate analysis gives information on the organic carbon content, nitrogen, hydrogen and oxygen contents. Cassava peelings used in this work has 76.6wt% volatile matter content on dry basis. The high amount of volatile matter strongly influences its combustion behaviour and suggests good potential of the feedstock for energy production by pyrolysis and gasification (Damartzis, et al, 2011; Chutia et al, 2013). It has fixed carbon content of 20.5wt % and ash content of 2.9wt% on dry basis as presented in Table 1.

Table 1 Proximate and Ultimate Analysis of Biomass

Proximate Analysis		Ultimate Analysis	
Parameters	Value (%)	Parameters	Value (%)
Moisture (ar)	7.0	C (db)	42.4
Volatile matter (daf)	76.6	H (db)	6.0
Fixed carbon (daf)	20.5	N (db)	1.1
Ash (db)	2.9		

ar =as received, daf =dry and ash free , db =dry basis

3.2 Pyrolysis characteristics

The TGA curves obtained for the thermal decomposition of the biomass at the different heating rates are presented in Figure 1. Like typical thermal decomposition profiles of lignocellulose biomass, there is an early stage of decomposition which is due to moisture evaporation at temperatures less than 150^{o}C. The major weight loss was then observed at temperatures between 150^{o}C-400^{o}C which corresponds to decomposition of hemicellulose and cellulose. The pyrolysis was completed at about 600^{o}C depending on the heating rate, resulting in evolution of gases and leading to formation of char (Balogun et al, 2014; Burhenne et al, 2013). However, there are two distinctive regions observed in the major weight loss TGA/DTG curve. The first region which occurred from 150-250^{o}C is typical of hemicellulose decomposition because of its less stable polymeric structure (Burhenne et al, 2013). Two distinct peaks were identified during hemicellulose decomposition which could be due to component complexity of agricultural products. Meanwhile, cellulose decomposition occurred from 250-400^{o}C. Cellulose has higher thermal stability because of its good ordered structure with a long polymer of glucose without any branches (Chen, et al, 2013; Liu et al, 2011). The tail end represents lignin which decomposes over a long period of time up to 600^{o}C possibly due to further cracking of some organic species from primary reactions or decomposition of formerly produced intermediates (Liu et al, 2013; Skodras et al, 2007). The decomposition temperatures of the hemicellulose, cellulose and lignin vary slight in different biomass materials because their chemical structures, their proportion in different biomass parts and their thermal stability differ (Lee et at, 2013). Nevertheless, the range of decomposition temperatures of this sample is in agreement with other biomass samples (Lapuerta et al, 2007; Wang, et al, 2012).

3.3 The effect of heating rate on pyrolysis characteristics

The influence of heating rate pyrolysis characteristics of the biomass sample is observed in Figures 1and 2. The peak temperature for weight loss was observed to increase slightly with increase in heating rate in Figure 1. Figure 2 presents the derivative weight loss. It was observed that increasing the heating rate influenced the temperature range of the stages of decomposition. Three temperatures were recorded to give a better understanding of the pyrolysis process. The onset temperature (T_a) which describes the commencement of the pyrolysis process was shifted to higher temperature with increase in heating rate. The offset temperature (T_o) which describes the end of the process was also shifted to higher temperatures. These shifts could be due to heat transfer limitation at high heating rates (Balogun et al, 2014). The maximum temperature (T_{max}) is the temperature at which maximum weight loss was observed. At 5°C/min, the maximum rate of pyrolysis was 2.7 %/min while 5.5, 8.6 and 11.5 %/min were obtained at the heating rate of 10, 15 and 20°C/min respectively.

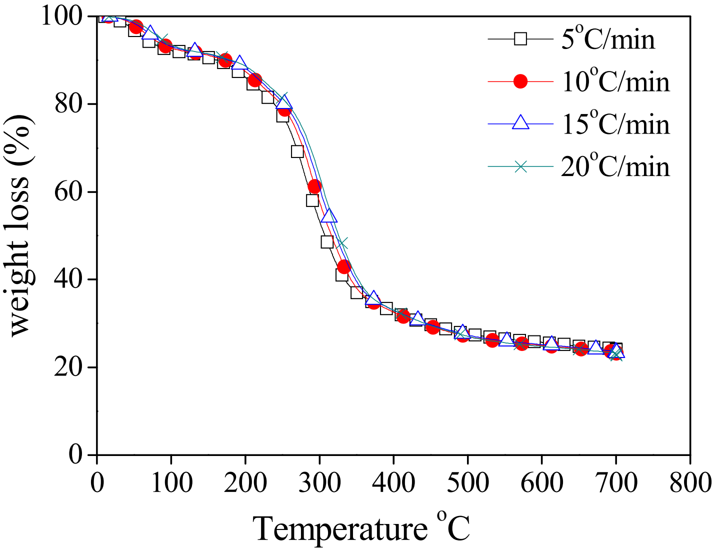

Figure 1. The Effect of Heating Rate on Weight Loss of KSV.

The increase in maximum rate of pyrolysis and the increase in temperatures at such rates can be due to the fact that biomass has an heterogeneous structure and possess a number of constituents and these constituents give individual decomposition their characteristic peaks in definite temperature ranges in the pyrolysis process (Ounas et al, 2011). From Table 2, it can be seen that the conversion at the maximum mass loss (α_{max}) also increased with increase in heating. It was also observed that at heating rate of 5°C/min, the α_{max} conversion achieved was 36% but increased to 38, 49 and 51% at 10, 15 and 20°C/min respectively. Also, the effect of heating rate on volatile matter and char yields are presented in Table 2. The yield of volatile matters increased from 72- 75 % on dry basis while the residual char yield decreased slightly from 24 % to 23 %. The higher volatile yields have been described as a result of heat flux in the high heating regime which reduces the viscosity of the melted solid and intensify the volatile forming reactions (Damartzi et al, 2011). This was observed in Table 1 where the 76.6 % of volatiles were obtained at the 150°C/min. Also, it was observed that the decomposition curve shifted slightly to the right as the heating rate increased. The shift of TGA curves at higher heating rates is due to different heat transfer and kinetic rates delaying the sample decomposition (Seo et al, 2010).

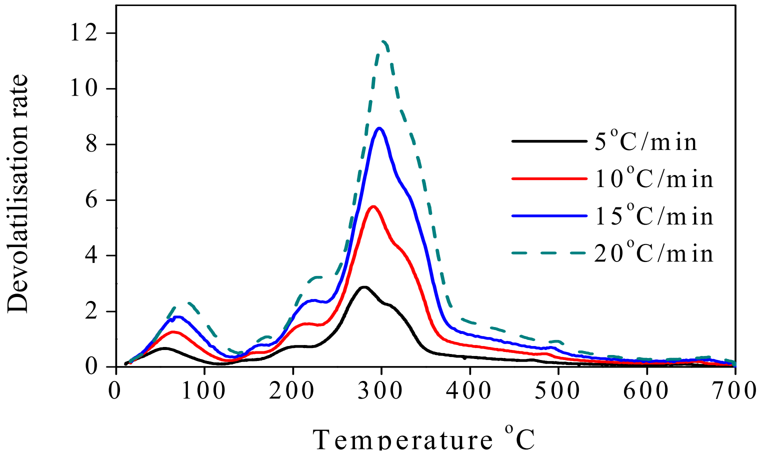

Figure 2. Effect of Heating Rate on the Pyrolysis Rate of KSV

Table 2. Influence of Heating Rate on Pyrolysis Characteristics

Heating rate (°C/min)	T_a (°C)	T_{max}	T_o (°C)	R_{max} (%/min)	α_{max}	Volatile yields (% db)	Char yield (% db)
5	160	274	350	2.7	36	72.9	23.9
10	162	285	363	5.6	38	74.1	23.2
15	164	292	372	8.4	49	74.4	23.2
20	170	298	382	11.5	51	75.2	22.7

3.4 Determination of kinetic parameters

From the TGA data, the extent of conversion (x) during the decomposition of the biomass was calculated using equation (2). At different conversions with the different heating rates, the corresponding temperatures were derived. Conversion values between 20% and 90% were used for the calculation of the kinetic parameters. In Figure 3, iso-conversion linear plots of logβ vs 1/T were derived using equation 4 and 5 and subsequently the kinetic parameters were obtained at the different conversion levels. The kinetic parameters were obtained from the slope of the appropriate plot and the results are presented in Table 3. There were high values of R^2 for all the conversions applied which implied that there was strong correlation and low errors were associated with the determination of the kinetic parameters. The activation energies, pre-exponential and R^2 values are presented in Table 3. In figure 4, it was also observed that the activation energies (E) increased with increase in conversion. Other researchers have also observed similar increase of E values with increase in conversion during biomass pyrolysis. The properties of the different biomass could play a key role in the variation of apparent activation energy in the pyrolysis process (Gai et al, 2013) especially for agricultural products where the growth period of the biomass and the harvesting times vary. In the range of conversion between 0.2-0.9, the activation energy of cassava peeling increased from 151-290 KJ/mol. Similar range of activation energies have been obtained during the pyrolysis of other agricultural wastes (Chen et al, 2013). An increasing dependence of E on conversion is an indication of the occurrence of a multi-step reaction (Gai et al, 2013). The degree of polymerisation of these reactions has been observed to be the possible reason for the variation in E values as decomposition progresses (Balogun, 2014).

Table 3. Kinetic Parameters of Cassava Peelings at Different Conversions

% conversion	E (KJ/mol	A min^{-1}	R^2
20	164	3.25×10^{18}	0.996
30	151.9	4.36×10^{16}	0.992
40	151.2	4.65×10^{15}	0.991
50	153.5	1.75×10^{16}	0.999
60	161.5	5.67×10^{16}	0.998
70	169.9	1.59×10^{17}	0.999
80	203.0	6.29×10^{19}	0.997
90	289.5	9.41×10^{24}	0.983

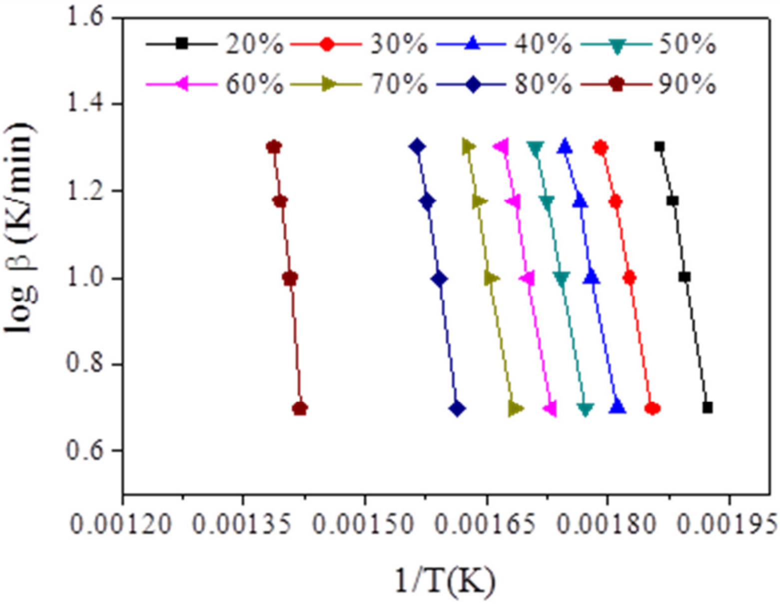

Figure 3. Estimation of Pyrolysis Activation Energy of Cassava Peelings using FWO Method at Different

Conversions.

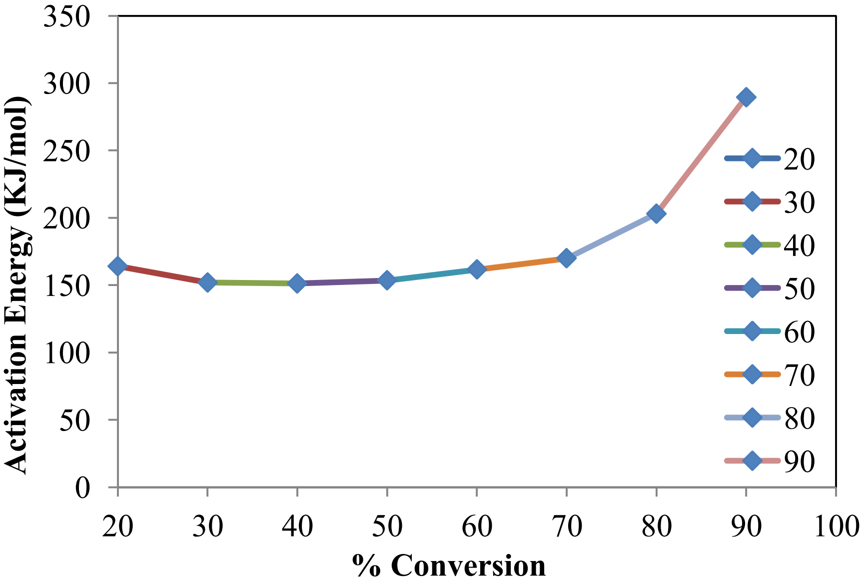

Figure 4 Activation Energies as a Function of Different Conversions

3.5 Char combustion analysis

Figure 5 presents the TGA burnout profiles of the chars produced at the different heating rates. There was variation in reactivity which may be due to morphological differences due to different heating rate during the pyrolysis process. It was observed that the burnout of the chars was found to decrease with increase in heating rate up to the char produced at 15°C/min. However, the char produced at 20°C/min burnt off much faster than the char produced at 15°C/min and was burning similar to chars produced at 5 and 10°C/min. Presumably, during the pyrolysis process, the surface texture of the char produced at 20°C/min coarsens and the internal texture of the fibre bundles becomes sparse (Okumura et al, 2009). Highly porous chars structures formed during the pyrolysis process will give easy access to oxygen into the char surface for combustion. Additionally, high heating rate during pyrolysis also results in disordered carbon structure in the residual char which will lead to larger number of active sites available for combustion (Wormat et al, 1995). This could be plausible reason for the combustion reactivity of the char produced at 20°C/min. From Table 4, it was observed that a higher heating rate decreased the activation energies confirming the influence of heating rate on the burnout characteristics of the chars produced. Again, the activation energy of the char produce at 20°C/min was found to be higher than what was obtained for the other chars implying that highly porous char structure can diminish mass transfer limitations during char combustion, depending on the catalytic contributions of its inherent mineral matter (Le Manquais et al, 2009).

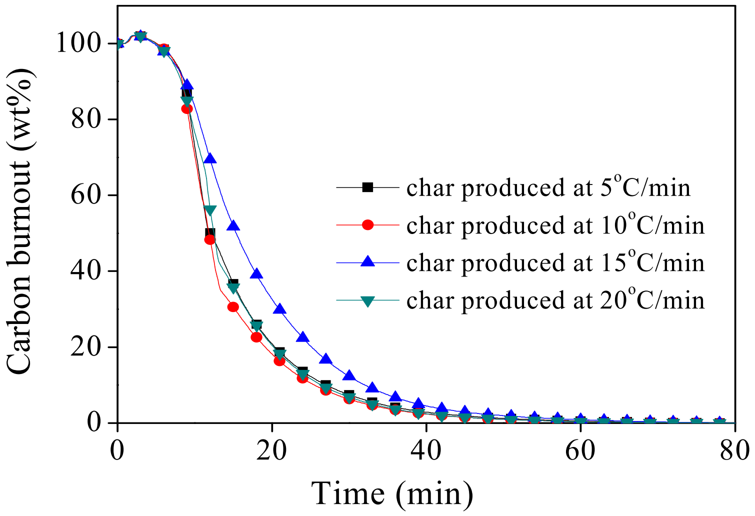

Figure 5. TGA Carbon Burnout Profile at 400°C of KSV Chars Produced at Different Heating Rate

Table 4. Kinetic Parameters during Char Combustion

Heating rate (^{o}C/min)	E (KJ/mol)	A (min^{-1})	R^2
5	104.4	6.2×10^7	0.987
10	102.6	4.5×10^7	0.974
15	101.4	3.4×10^7	0.100
20	105.6	3.0×10^7	0.978

4 Conclusions

The effect of heating rate on the pyrolysis of characteristics of cassava peelings and combustion reactivity of the resultant chars has been investigated using TGA and the following conclusions have been drawn:

- The high volatile matter (VM) and fixed carbon (FC) content of the raw material will provide easy ignition and gasification of cassava peelings and this will make it a potential source of renewable energy.
- The apparent activation energy of pyrolysis varied between approximately 151 and 290 kJ/mol as a function of conversion.
- The burnout reactivity showed that higher heating rate will favour the combustion characteristics of the chars. The apparent activation of the chars during combustion also varied between 101 and 105KJ/mol
- The kinetic data will be useful to model, design and develop combustion systems for cassava peelings

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