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Analysis of Pyrolysis Kinetic and Energy Content of Agricultural and Forest Waste

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Abstract:
Selected agricultural and forest wastes included rice husk, coconut husk, cashewnut shell, eucalyptus, pine and mangrove were used for thermal characterization. The studied materials have heating value between 13 and 23 kJ/kg, such that the biomass material can be used as a fuel by directly burning, but their energy content is lower as compared to coal and other fossil fuels. The energy content of the biomass material can be improved through pyrolysis process for the mentioned materials, the cashew nut shell had higher energy content than other biomass material due to its high hydrogen to carbon ratio and low oxygen to carbon ratio. Thermochemical characteristic depicted high degradation at a heating rate of 10 K/min. All studied materials except mangrove and pine, maximum degradation occurred at 5 K/min. The reactivity of coconut husk was highest whilst cashew nut shell had the least reactivity. The activation energy for cashew nut shell obtained was 336.41 kJ/mole and the activation energy of the other biomass ranged between 220 and 130 kJ/mol. The coconut husk, pine, eucalyptus and rice husk are more reactive than mangrove and cashewnut shell.

Keywords:
Agricultural Waste; Forest Waste; Pyrolysis; Thermogravimetric Analysis

1. INTRODUCTION

Tanzania depends mainly on agricultural sector for the economy, employing over 80% of the population [1]. The agricultural activities generate a considerable amount of waste, which can be harnessed for energy production. Wilson, et al. reported that over 12,604 million tons of agricultural waste and 1.2 million cubic meters of forest waste are generated annually [2].

The untreated agricultural and forest waste are not good for energy production, since they contain moisture content of about 30%, and a calorific value of less than 10 MJ/kg with a low bulk density of 160 kg/m3, which cause a storage problem [3]. When directly burnt in boilers, they generate residues that could lead to high disposal costs and pose environmental problem [4]. An advanced thermal technology is required to harness energy with the intimacy of minimizing disposal cost and environmental pollution.

The thermal technologies require knowledge of thermal behavior of biomass before application by simulating a pyrolysis process within the TGA. Thermo-gravimetric analysis (TGA) is one of the techniques that are used to study the thermal behavior of solid fuels. The TGA shall assist to determine kinetic parameters from decomposition process by evoking the Kissingers method [5].

The Kissinger's method has been used by different researchers to determined kinetic parameters, during thermal degradation of a material. Slopiecka et al. [6] studied the Kissinger method to determine kinetic parameters of poplar wood, the values of activation energy and pre-exponential factor obtained were consistent and in good agreement with that obtained by model free method. Yan and Wu in [7] observed that Kissinger's method gave higher fitting degree than other methods during determination of kinetic parameters of wheat straw lignin.

The Kissingers method is independent on reaction mechanism for determination of activation energy, however the determination of the frequency factor assumes first order reaction mechanism [8]. In this method, the peak temperature (Tmax) is used to determine the activation energy (Ea), whilst the thermal decomposition rate is measured at different heating rate through a sequence of experiments.

In the TGA, the pyrolysis rate is expressed by using Arrhenius Eq. (1), k is the rate constant, which depends on temperature.

$$k = A\exp(-E_a/RT) \tag{1}$$

Here T is the absolute temperature, Ea is the activation energy, A is the pre exponential factor, R is the gas constant.

This study focused on the analysis of pyrolysis kinetic through thermal degradation and the effects of elemental composition on energy content of the selected biomass materials.

2. METHODOLOGY

Six samples were used in this study, three were from agricultural waste; rice husk, coconut husk and cashew-nut shells. The other three were from forest waste; these are from eucalyptus, pine and mangrove.

The experiments were divided into two steps; the first step was to study the characteristics of the samples by using proximate, ultimate analysis and calorific value by using bomb calorimeter. The second step was to study the thermo-degradation and heat of pyrolysis by using thermo-gravimetric analyzer (TGA).

The proximate analysis of the sample were carried out according to ASTMD 3172 method and ultimate analysis was done according to ASTMD 3176 and the HHV was obtained by ASTM D2015.

The thermo-gravimetric analyzer used in this study was NETZSCH STA 409 PC Luxx, the schematic arrangement of the apparatus is shown in **Figure 1** . Prior to thermo-gravimetric experiments, biomass samples were grounded to small particles (<1 mm) and then oven dried at 105°C to a constant weight for removing the moisture. Thereafter a 30 mg sample was heated under inert nitrogen (99.95% purity) condition at constant heating rate from room temperature to 1273 K. The heating rates used during thermogravimentric analysis were 5, 10, 20, 40 K/min. At the end of experiment the furnace was cooled to ambient temperature still providing a nitrogen purge gas flow.

3. RESULTS AND DISCUSSION

The properties of six biomass samples are listed in **Table 1** and **Table 2** , the properties described the higher heating value, proximate and ultimate analysis. The data revealed that the materials have high content of volatiles, carbon, oxygen and hydrogen. The relative amount of nitrogen is minor. This is typical composition of biomass as reported by [2] and [9]. Forest wastes contain more volatiles than agricultural waste with the exceptional of cashewnut shell. The oxygen content of forest waste is higher

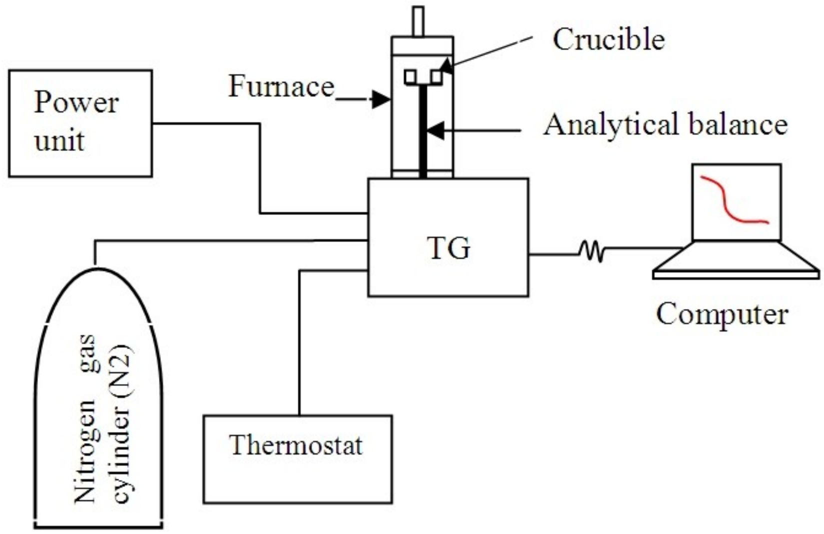

Figure 1. **Schematic sketch for thermo-gravimetric analyzer**

Table 1. **PROXIMATE ANALYSIS OF BIOMASS MATERIALS**

Proximate analysis						
	CcH	RH	CnS	EU	PN	MG
MC(wt%)	5.43	8.20	2.10	6.50	9.00	7.50
VM(wt%)	61.15	51.10	84.60	81.50	76.60	73.50
FC(%)	29.70	14.40	11.50	11.00	13.30	12.00
ASH(wt%)	3.72	26.30	1.80	0.50	1.10	7.00

than that of agricultural waste. Cashew nut shells contain higher energy content, whereas rice husk has lower energy content than other materials. The energy content of agricultural and forest waste is higher compared to municipal solid waste. The average high heating value of agricultural and forest is about 17 MJ/kg, while municipal solid waste is about 11 MJ/kg [10].

The energy content of the material depends on ash content, hydrogen to carbon (H/C) and oxygen to carbon ratio (O/C). One of the possible reasons of the lower energy content of rice husk is due to high ash content, since it has H/C and O/C almost the same as other biomass materials as shown in **Table 2** .

The biomass materials exhibit high H/C (Hydrogen to carbon ratio) and high O/C (Oxygen to carbon ratio) as compared to coal, the H/C of lignite, bituminous and anthracite are 0.1, 0.06-0.08 and less 0.05 respectively, the corresponding O/C for the same type of coal are 0.4, 0.1 and less 0.1 [11, 12], the findings for the selected agricultural and forest waste are shown in **Figure 2** .

Figure 2 is similar to Van Krevelen diagram but this represents only biomass materials and it has two vertical axes. The left vertical axis represent H/C axis and the right axis is HHV axis. Both vertical axes are drawn with a common horizontal O/C axis. The data for H/C are represented by makers without filling and pale in color, whereas the data for HHV are represented by bolded black markers.

The material that has high H/C and high O/C exhibits low energy content [8]. The rice husk (RH) represented by square makers has H/C of 0.13 and HHV of 13.24 MJ/kg, which is smaller than other biomass material since it has high H/C and high O/C. The large value of HHV of 22.83 MJ/kg for Cashew nut shell (CnS) in **Table 2** could be mainly due to high H/C of 0.12 and smaller O/C of 0.59 as shown in **Figure 2** .

Table 2. **ULTIMATE AND HHV OF BIOMASS MATERIALS**

Proximate analysis						
	CcH	RH	CnS	EU	PN	MG
C (wt%)	50.29	35.60	56.90	50.00	50.5	48.00
H (wt%)	5.05	4.50	7.10	6.10	6.78	5.80
N (wt%)	0.45	0.19	0.46	0.20	0.40	0.13
O (wt%)	39.63	33.40	33.65	43.50	42.32	41.50
H/C	0.1	0.13	0.12	0.12	0.13	0.12
O/C	0.79	0.94	0.59	0.87	0.84	0.86
HHV (MJ/kg)	17.35	13.24	22.83	17.76	16.50	16.90

Where: MC=Moisture content, VM=Volatile matter, FC=Fixed carbon, HHV=Higher heating value, CcH=Coconut husk; RH=Rice husk; CnS=Cashewnut shell; EU=Eucalyptus; PN=Pine; MG=Mangrove.

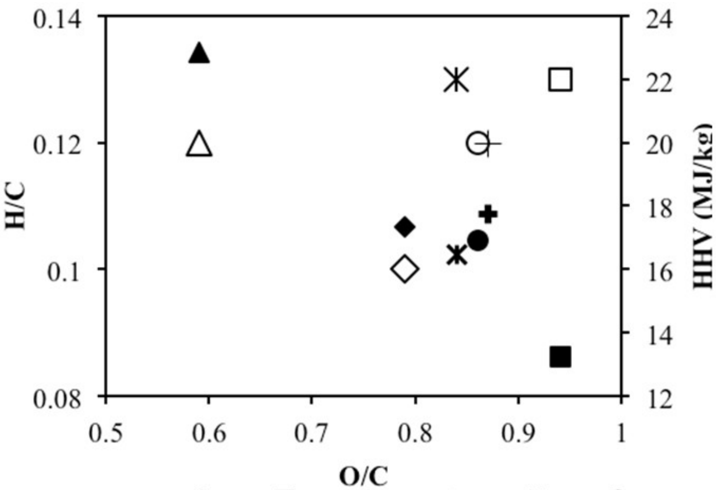

Figure 2. **Classification of biomass by H/C and HHV v/s O/C**

The results in Figure 2 reveal that the biomass material that contains high O/C content exhibit low energy content, this also was reported by Demirbas in [13].

The thermogravimetric analysis curves for each sample at heating rate 5, 10, 20 and 40 K/min are shown in Figure 3 . The curves of biomass samples form a depression kink at temperature about 500 K, this is due to moisture removal, but the cashew-nut shell does not have the kink.

High degradation of all biomass materials is observed between 500 and 900 K, at this temperature range volatiles are released, in this temperature range, the thermal decomposion is dominated by the decomposition of hemicellulose and cellulose presented in the sample [14]. Low degradation is observed at temperature above 900 K, which is the char degradation [15, 16].

Table 3 and Table 4 show the volatile and char released at different heating rates. The volatile release is high for cashew-nut shell at each heating rate, whereas the rice husk has low volatile release. The high degradation of the biomass material was observed at heating rate of 10 K/min, except for mangrove and pine, the high degradation was observed at heating rate of 5 and 20 K/min respectively. The differences of the heating rate for degradation are due to their physical and chemical characteristics of biomass materials [10]. The results of TG are contrary to the study of Zang et al. [17] on the effect of heating rate on wire

Table 3. **VOLATILE RELEASE DURING THERMOGRAMETRIC ANALYSIS**

Heating rate (K/min)	5	10	20	40
Rice husk (wt%)	75.46	78.63	72.76	78.09
Cashew nut shell (wt%)	85.69	99.19	96.98	92.06
Coconut husk (wt%)	82.10	86.34	85.61	83.34
Eucalyptus (wt%)	79.93	93.34	90.05	88.13
Mangrove (wt%)	88.74	76.31	84.32	77.90
Pine (wt%)	90.67	80.41	91.46	90.62

Table 4. **CHAR RELEASED DURING THERMOGRAMETRIC ANALYSIS**

Heating rate (K/min	5	10	20	40
Rice husk (wt%)	17.77	13.82	19.89	15.49
Cashew nut shell (wt%)	14.31	0.81	3.02	7.94
Coconut husk (wt%)	10.69	3.91	5.99	8.67
Eucalyptus (wt%)	16.20	1.01	2.80	4.41
Mangrove (wt%)	0.13	14.57	6.34	13.29
Pine (wt%)	1.15	11.63	0.83	1.65

mesh reactor. They observed that the heating rate from 0.6 K/min to 100 K/min did not show significant variation of the char yield. However the extremely high heating rate of 261600 K/min gave high decrease in yield of biochar. But Demirbas in [18] shows that the char yield does not depend only of heating rate, it also depends on particle size of the sample and temperature of pyrolysis. The char increases by increases the particle size of sample. High tempreature, smaller particles and high heating rate decrease the char yield [18].

Figure 3 shows the thermogravimetric analysis of the biomass material at different heating rate. The high residue observed in agricultural waste was highest in rice husk 19.89% at 20 K/min, this also was revealed in [2] and the lowest residue 0.81% was cashew nut shell at 10 K/min, this also was observed by Tsamba in [5]. Where highest char in forest waste was 16.2% at 5 K/min in eucalyptus and lowest was 0.13 K/min at 5 K/min in mangrove.

The forest waste are suitable for bio-oil production and agricultural waste are suitable for production of syngas, with exception of cashew-nut shells this has been revealed in **Table 3** and **Table 4** that forest waste produces high volatiles, whereas agricultural waste contains high char. The char acts as a catalyst during pyrolysis by cracking the bio-oil [19]. Therefore, from the TG curves it can be observed that cashew-nut shell is most suitable for production bio-oil since it contains high volatiles and rice husk is suitable for production of syngas since it contains high char and the suitable operating heating rate is 10 K/min.

The DTG curves of agricultural and forest wastes are shown in **Figure 4** , the curves are drawn at different heating rate, the heating rate of 5, 10, 20 and 40 K/min. The peaks are observed to move toward the right hand side as the heating rate increases.

Generally, DTG has three visible peaks, the peak below 450 K is due to moisture release and the other two peaks are observed at temperature between 450 and 700 K, the first peak is for hemicellulose degradation and the second peak is for cellulose degradation, but these peaks overlap. The hemicellulose appears as shoulder on the left and cellulose is associated with the peak [20], this is observed on coconut husk, eucalyptus, mangrove and pine. The cashew nut shell and rice husks behave differently; they contain peak on the left and the shoulder on the right, Tsamba in [5] stated that the peak is hemicellulose and the shoulder is cellulose. The lignin degradation is considered to be slow over a broad temperature range

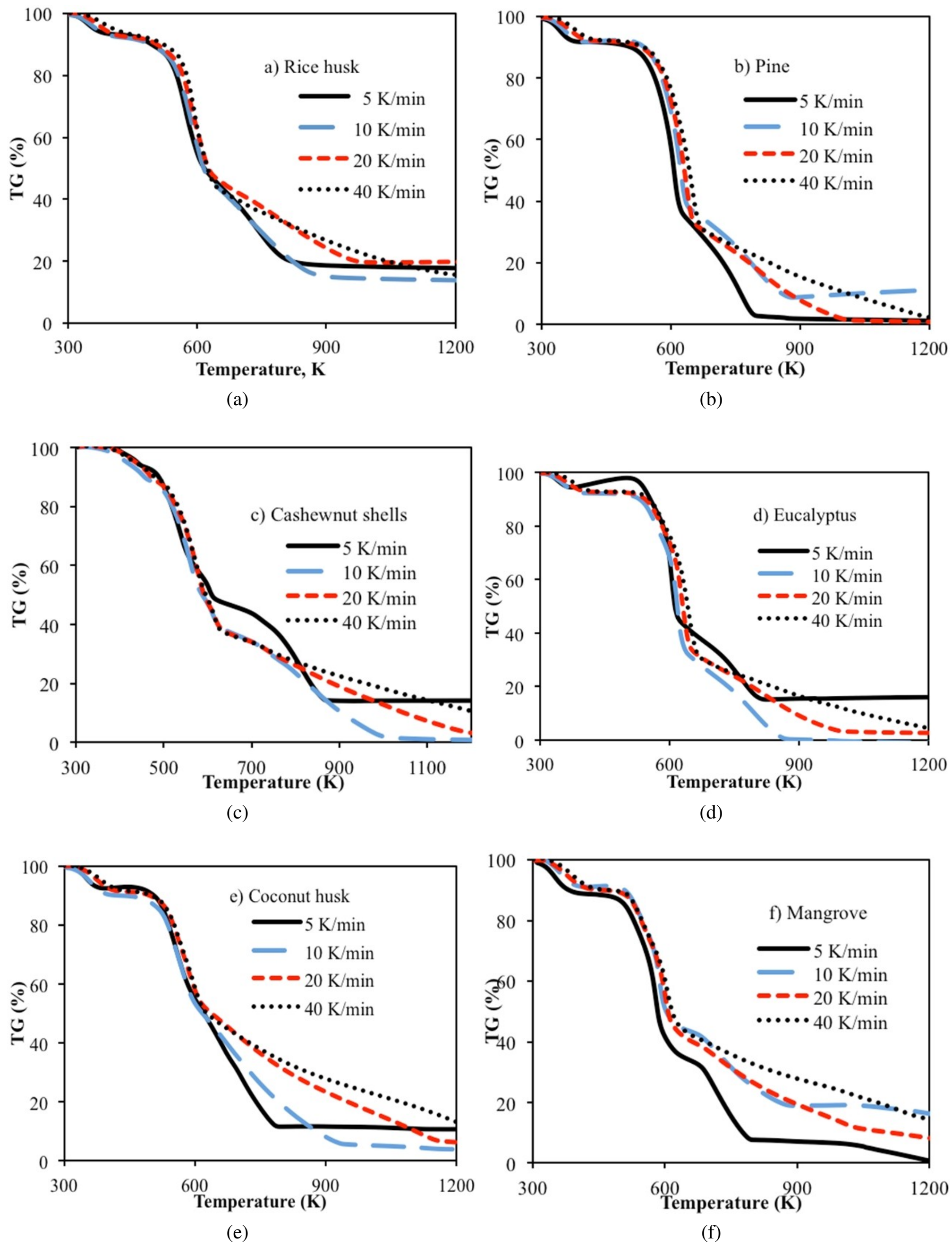

Figure 3. **Thermo-gravimetric analysis of agricultural and forest waste**

between 500 and 800 K for all biomass materials [10, 16].

The kinetic parameters of agricultural and forest waste are shown in **Table 5** . The values of activation energy (Ea) and pre-exponential factor were obtained by using Kissinger's method. The biomass degradation was assumed to be first order reaction. Few literatures have established the kinetic parameters, the activation energy for cashew nut shell obtained was 336.41 kJ/mole and the one reported in [2] was 293.48 kJ/mol, the values reported in [5] range between 140 and 170 kJ/mol. The activation energy of the other biomass ranged between 220 and 130 kJ/mol. These values are comparable to those reported by Di

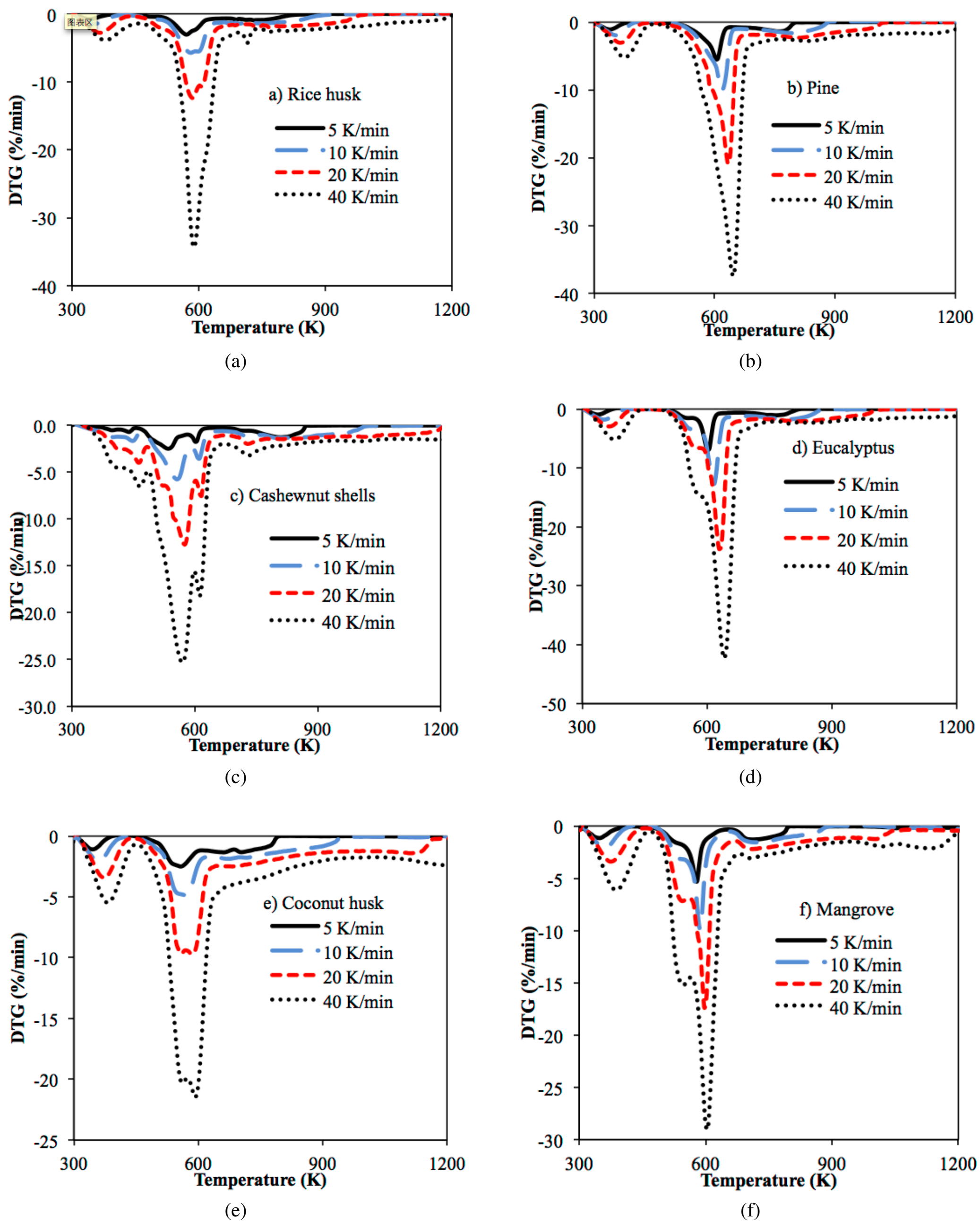

Figure 4. **Differential thermogravimetric analysis of agricultural and forest waste**

Blasi [10].

In essence, low activation energy are more reactive since it requires small amount of energy to make the material to react, and those with high activation energy need high energy for reaction. The coconut husk, pine, eucalyptus and rice husk are more reactive than mangrove and cashew nut shell.

The agricultural and forest waste are potential energy resources. Their energy content depends on their chemical composition. the cashew nut shell exhibited high energy content since it had high H/C ratio with relatively low O/C ratio, whereas rice husk exhibited low energy content, because it had high H/C and relatively high O/C, this concluded that oxygen content tend to decrease energy content of biomass

Table 5. **KINETIC PARAMETERS OF BIOMASS MATERIALS**

Biomass material	E_a(kJ/mole)	A(s^{-1})
Cashewnut shell	336.411	7.262E+28
Rice husk	180.075	2.401E+27
Coconut husk	138.153	2.563E+12
Eucalyptus	157.576	1.132E+13
Mangrove	216.966	1.516E+19
Pine	152.446	3.420E+12

materials.

The thermal degradation revealed that high volatiles were released from cashew nut shell, eucalyptus and pine so these biomass materials are proper for production of bio-oil through pyrolysis. High char and little amount of volatile released from rice husk were observed. Therefore rice husk is the preferable material for syngas production, since char is acting as a catalyst during gasification [21].

The determination of the kinetic parameters provides information to simulate pyrolysis mechanism which will assist in the design of improved reactor system.

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References

[1] A. M. Mshandete *et al.*, “Biofuels in tanzania: status, opportunities and challenges,” *Journal of Applied Biosciences*, vol. 40, pp. 2677–2705, 2011.

[2] L. Wilson, W. Yang, W. Blasiak, G. R. John, and C. F. Mhilu, “Thermal characterization of tropical biomass feedstocks,” *Energy Conversion and Management*, vol. 52, no. 1, pp. 191–198, 2011.

[3] S. P. P. Board, “Wood chips for pulp production.”

[4] A. Szogs and L. Wilson, “A system of innovation?: Biomass digestion technology in tanzania,” *Technology in Society*, vol. 30, no. 1, pp. 94–103, 2008.

[5] A. J. Tsamba, “Fundamental study of two selected tropical biomasses for energy: coconut and cashew nut shells,” 2008.

[6] F. F. K. Slopiecka, P. Bartocci, “Thermogravimetric analysis and kinetic study of poplar wood pyrolysis,” in *Third International Conference on Applied Energy*, pp. 1687–1698, 2011.

[7] Q. Yang and S. Wu, “Thermogravimetric characteristics of wheat straw lignin,” *Cellulose Chemistry & Technology*, vol. 43, no. 4, p. 133, 2009.

[8] P. S. S. Ledakowica, “Kinetics of biomass thermal decomposition,” *chem.pap.*, vol. 56, no. 6, pp. 378–381, 2002.

[9] K. Raveendran, A. Ganesh, and K. C. Khilar, “Influence of mineral matter on biomass pyrolysis characteristics,” *Fuel*, vol. 74, no. 12, pp. 1812–1822, 1995.

[10] V. Nasserzadeh, J. Swithenbank, D. Scott, and B. Jones, “Design optimization of a large municipal solid waste incinerator,” *Waste Management*, vol. 11, no. 4, pp. 249–261, 1991.

[11] P. Basu, *Biomass gasification and pyrolysis: practical design and theory*. Academic press, 2010.

[12] T. Bridgeman, J. Jones, I. Shield, and P. Williams, “Torrefaction of reed canary grass, wheat straw and willow to enhance solid fuel qualities and combustion properties,” *Fuel*, vol. 87, no. 6, pp. 844–856, 2008.

[13] A. Demirbas and G. Arin, “An overview of biomass pyrolysis,” *Energy sources*, vol. 24, no. 5, pp. 471–482, 2002.

[14] J. Reina, E. Velo, and L. Puigjaner, “Thermogravimetric study of the pyrolysis of waste wood,” *Thermochimica acta*, vol. 320, no. 1, pp. 161–167, 1998.

[15] M. G. Grønli, “A theoretical and experimental study of the thermal degradation of biomass,” 1996.

[16] L. J. L. Gasprovic, Z. Korenova, “Kinetic study of wood chips decomposition by tga,” in *36th International Conference of Slovak Society of Chemical Engineering*, 2009.

[17] Z. Zhang, S. Yani, M. Zhu, J. Li, and D. Zhang, “Effect of temperature and heating rate in pyrolysis on the yield, structure and oxidation reactivity of pine sawdust biochar,”

[18] A. Demirbas, “Effects of temperature and particle size on bio-char yield from pyrolysis of agricultural residues,” *Journal of Analytical and Applied Pyrolysis*, vol. 72, no. 2, pp. 243–248, 2004.

[19] M. Van de Velden, J. Baeyens, and I. Boukis, “Modeling cfb biomass pyrolysis reactors,” *Biomass and Bioenergy*, vol. 32, no. 2, pp. 128–139, 2008.

[20] C. Di Blasi, “Modeling chemical and physical processes of wood and biomass pyrolysis,” *Progress in Energy and Combustion Science*, vol. 34, no. 1, pp. 47–90, 2008.

[21] A. Demirbas, *Bio Refineries for Biomass Upgrading Facilities*. Springer, 2010.