NON-ISOTHERMAL KINETIC STUDIES OF TRIPLOCHITON SCLEROXYLON (AFRICAN WHITE WOOD) SAWDUST USING THERMOGRVIMETRY

[1]M.A. SOKOTO, [2]L.G. HASSAN, [3]M.G. LIMAN

[1,2,3]Department of Pure and Applied Chemistry, Usmanu Danfodiyo University, Sokoto
E-mail: [1]abdullahimuhammadsokoto@gmail.com

Abstract - The Triplochiton scleroxylon (African white wood) sawdust obtained from Nigeria was evaluated for its biofuels potential and its kinetic degradation behavior using thermogravimetric technique. The decomposition of the sawdust was carried out in nitrogen atmosphere with a flow rate of 10cm3min-1 from ambient temperature to 900ºC. The results of the thermal profile shows that an active and passive pyrolysis occurred between the temperatures of 200 and 400oC with lower heating rates and between 200-800oC with high heating rate The kinetic parameters such as activation energy, pre-exponential factor and reaction order were determined using Friedman (FD), Kissinger-Akahira-Sunose (KAS), and Flynn-Wall-Ozawa (FWO) methods. The average apparent activation energy values of 126.42, 126.47 and 129.83 kJmol-1 were calculated using FD, KAS, and FWO models respectively. The activation energy values obtained were depended on conversion, which is an evidence of multi-steps kinetic processes during the pyrolytic degradation of the sawdust. The kinetic data would be of immense benefit to model, design and develop thermo-chemical system for the conversion of the sawdust to fuel.

I. INTRODUCTION

Triplochiton scleroxylon is a tropical tree widely processed for timber in the West African countries. It's a soft wood characterized with whitish to pale yellow heartwood. The tree acquired numerous trade names, it is known as "obeche", 'wawa' and 'samba' in Nigeria, Ghana and Côte d'Ivoire respectively (Orwa et al., 2009). Processing of Triplochiton scleroxylon timber logs into marketable sizes generate tons of residues by which the sawdust being the major component. Although the sawdust is locally used for heat generation, large portion of it gets into waste stream (Diji et al, 2013). Heap of this refuse create nuisance into the environment as well as increasing the waste management problem. Thus, ways of combating these challenges were proffered and more are still being developed. Several researchers had reported the biofuels potential of sawdust through biological processes, Diji et al., (2013); Bagudo et al., (2011); Ogunleye and Awogbemi, (2007). Thermo-chemical approach for the conversion of sawdust to fuel has not been extensively studied especially in Nigeria. Thus, to broaden the application of this residue as well as to improve on its current usage; knowledge of its thermal properties and kinetic decomposition is paramount especially in large scale application. Pyrolysis process is perceived t to have great promise as a means for converting biomass into chemicals and fuels (Balat, 2008). The techniques have received much attention nowadays for being an attractive means of getting rid of waste materials through an environmentally friendly decomposition. Hu et al., (2008) and Vuthaluru (2004) had reported the pyrolysis conversion of animal and plant residues and refuses, such as lignocelluloses materials and plastic wastes to other environment friendly end-use products. Biomass pyrolysis can be described as the direct thermal decomposition of the organic matrix in the absence of oxygen to obtain an array of solid, liquid, and gas products. This method has been used for commercial production of a wide range of fuels, solvents, chemicals, and other products from biomass feedstocks (Yaman, 2004). The present work was aimed to study the proximate and ultimate compositions and kinetic decomposition pattern of obeche sawdust.

II. MATERIALS AND METHODS

The Triplochiton scleroxylon sawdust was obtained from wood seller market popularly known as 'kara' in Sokoto State, Nigeria. The collected sample was air dried and sieved through a 20mm pores size mesh, and then kept in an air tight plastic container. Proximate and ultimate analyses of the sawdust were determined in accordance with AOACS method of analyses. Vario Micro Elemental Analyzer, Parr 6300 bomb Calorimeter, and Inductive coupled plasma-atomic emission spectrophotometer (ICP-DRE, PS-3000 UV Leeman Labs inc) were used for determination of CHNS, gross calorific value and trace metal content respectively. The pyrolysis experiment was performed using TGA analyzer; (Shimadzu DTG-60) under nitrogen atmosphere at 100ml min-1 flow rate at different heating rates (5, 10, 15, 20, 30, and 40ºC min-1) from ambient temperature to 900ºC. Some iso-conversional kinetic models were used to determine the kinetics and thermodynamic parameters of the sawdust degradation according to procedure reported by White et al.. (2011)

Kinetics Modeling

Pyrolysis degradation of polymeric substrates in solid state can be described by general expression for reaction rate constant which is mathematically expressed as:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (1)$$

Where is the reaction rate, k (T) denotes dependence of rate on temperature, is the rate dependence on the model, T denotes the absolute temperature and t, the time. The residual weight (α) is defined in terms of change in mass of the sample as:

$$\alpha = \frac{W_i - W_t}{W_i - W_f} \quad (2)$$

where Wi, Wt and Wf are initial mass of the sample, mass at a given time and final weight of the sample at the end of reaction respectively. According to Barneto et al., (2011), the kinetic rates are based on the Arrhenius equation which can be expressed as:

$$k = A\exp\left(-\frac{E}{RT}\right) \quad (3)$$

where A, is the pre-exponential factor, E is the activation energy, R is the gas constant and T, temperature in Kelvin. Combination of eqns. 1 and 3 gives:

$$\frac{d\alpha}{dt} = A\exp\left(-\frac{E}{RT}\right)f(\alpha) \quad (4)$$

at a controlled temperature and constant heating rate constant. The rearrangement of equation (4) gives:

$$\frac{d\alpha}{dT} = \frac{A}{\beta}\exp\left(-\frac{E}{RT}\right)f(\alpha) \quad (5)$$

Integration of equation (5) resulted to::

$$g(\alpha) = \int_0^{\alpha}\frac{d\alpha}{f(\alpha)} = \frac{A}{\beta}\int_0^{T}\exp\left(-\frac{E}{RT}\right)dT \quad (6)$$

Where g(α) is the integral form of the reaction model or conversion dependant f (α). The right hand side (6) has no exact analytical solution. According to White et al., (2011), numerous approximations can be used to solve the right side of equation. This formed the basis upon which various model equations were derived.

III. RESULTS AND DISCUSSION

Moisture content is a parameter that contributes to low heating value and low thermal efficiency of a feedstock as well as prone to energy loss during storage due to decomposition (Mckendry, 2002). The moisture content of the Triplochiton scleroxylon sawdust (Table 1) is comparably high than the value reported for pine wood sawdust (11.26wt %). The substrate analyzed has high percentage of volatile matter, which indicates the potential of the feedstock as a good blending material in co-firing process. Calorific value measures the heating quality of biomass fuel, and also reflects the heat energy to be liberated when biomass material used as source of heat. High calorific value indicates the potentials of the biomass as good source of energy. Nitrogen was not detected in Triplochiton scleroxylon sawdust. This implies decomposition of Triplochiton scleroxylon sawdust may not results in NOx emission and perhaps sulphur emission would be negligible due low percentage of sulphur content in the sawdust.

Table 1: Proximate composition of Triplochiton scleroxylon and Values from Literature

Sample name	Moisture (%)	Ash	Volatile matter (db%)	Fixed carbon (db%)	Source
Obeche sawdust	23.83 ± 0.21	0.92 ± 0.55	97.72 ± 0.12	1.36	Present study
Pine wood	11.26	0.61	75.32	12.81	Xiaoli et al., 2013
Pine wood Sawdust	9.4	0.5	73.40	6.70	Amutio et al., 2012
Pinus insignis sawdust	-	0.22	83.74	16.04	Olazar et al., 2001

The relative percentages of CHNSO obtained from the sawdust were C (40.843). H (5.951). N (0.0), S (0.045) O (52.241). The carbon (%) obtained in the present study is lower than the value reported for pine wood sawdust (49.33%). The percentage hydrogen in the present study were similar to the value reported for pine wood sawdust (5.54%) (Amutio et al., 2012) Ash content is an index of inorganic constituents in a matter. High ash content showed the likelihood of high concentration of the trace elements. The ash content of the sawdust (Table 1) is low which implies it may have less concentration of trace elements. The concentration of trace (mg/kg) in the obeche sawdust were: Mg (899), Ca (2044), Ni (<1), Mn (5), V (<1), Fe (<1), Zn (29), Al (2), Cr (<1), P (662), Na (368) K (1567) Pb (<1), Co (<1) Trace element has catalytic

activity during chemical reactions, thus these elements may influence the thermal decomposition process

3.1 Thermograms Characterization

It is evident from the thermograms (Figure 1) that, there are three stages which indicate moisture removal, active and passive pyrolysis stages. The minor peak observed between the temperature range of 100-150oC signifies moisture released. The major stages of thermal decomposition (active and passive) occurred between the temperatures of 200 and 400oC with lower heating rates and between 200-800oC with high heating rate. Maximum decomposition of the sawdust occurred at 345oC with the total mass lost due to volatilization of 87wt%. The mass lost observed for the volatilization of the sawdust was lower than that for the decomposition of sugarcane bagasse (90.8wt %), but higher than values reported for corn stover (80.3wt%) and corn cob (82.7wt%) (Aboyede et al., 2012).

The maximum decomposition temperature for the analyzed sample corresponds to the value reported for cellulose decomposition (Chen et al., 2013). Also the results obtained from this study are in agreement with decomposition pattern of pine wood sawdust reported by Xiaoli et al. (2013). The decomposition profile of the obeche sawdust follow similar pattern with that of sugarcane baggasse (Aboyede et al., 2013). The similarities in decomposition could be due possession of similar active compounds. The potential of sugarcane bagasse as feedstock for green fuel has extensively study, thus the obeche sawdust perhaps could be a viable feed for fuel production owing to its comparable decomposition with potentially identified biomass feedstock.

3.2. Effect of Heating Rate

The heating rate influences the DTG curve positions, maximum decomposition rate and location of maximum Tm peaks. Figure 1 indicates that increase in heating rates shifts the peak temperature to higher value without changing thermal profile of decomposition except at 40oC min-1. The temperature shift may probably be due to increased thermal lag at a given temperature. High heating rate implies the substrate attained the set temperature at shorter time (Vamvuka et al, 2003). Also, the temperature shift could be as result of decrease in heat transfer efficiency with high heating rates. It was reported that low heating rates leads a gradual and better heat transfer to the inner parts of biomass particles during heating (Idris et al., 2010; Damartzis et al., 2011). Kim et al. (2013) also reported that the maximum rate of decomposition increase with an increase in heating rate because of increase in thermal energy.

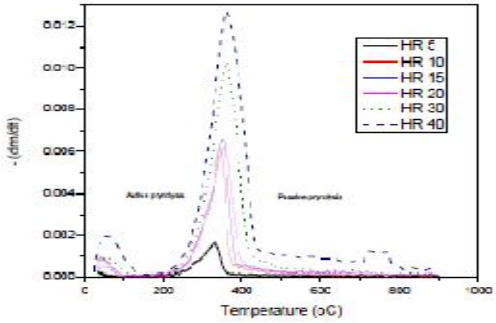


Figure 1: DTG curve for Triplochiton scleroxylon sawdust with different heating rates

3.3 Kinetics of the Thermal Decomposition

The kinetic parameters such as activation energy, pre-exponential factor and reaction order were determined using different Friedman (FD), Kissinger-Akahira-Sunose (KAS), and Flynn-Wall-Ozawa (FWO) kinetics model. The average activation energy values of 126.42, 126.47 and 129.83 kJmol-1 were calculated using FD, KAS, and FWO models respectively (Table 2). The apparent activation energy values obtained were depended on conversion, which is an evidence of multi-steps kinetic processes during the pyrolytic degradation of the sawdust.

Table 2: Values of Activation Energy derived from FD, KAS and FWO models at different Conversion and their Correlation Coefficient Values (R2)

	FRIEDMAN		KAS		FWO	
Conversion	E(kJ)	R^2	E(kJ)	R^2	Ea(kJ)	R^2
0.05	114.8282	0.96701	97.10901	0.96242	100.6563	0.96785
0.10	144.5043	0.99671	122.9127	0.99142	125.6377	0.99247
0.15	140.6335	0.99624	137.9401	0.99497	140.1253	0.99554
0.20	140.029	0.99756	133.8135	0.99694	136.3759	0.99728
0.25	147.1381	0.9999	134.7352	0.99871	137.4135	0.99885
0.30	151.1693	0.99917	136.4619	0.99915	139.1775	0.99925
0.35	155.441	0.9991	141.101	0.99931	143.6908	0.99939
0.40	147.3544	0.99544	141.612	0.99897	144.2716	0.99912
0.45	140.9666	0.98792	140.6279	0.99724	143.4266	0.99763
0.50	130.7789	0.97736	136.9859	0.9955	140.0419	0.99616
0.55	118.1793	0.96251	132.805	0.99378	136.1501	0.99472
0.60	105.3983	0.94076	127.7672	0.98957	131.4403	0.99118
0.65	92.23309	0.90846	119.3684	0.98049	123.5503	0.98365
0.70	89.31166	0.89693	114.2683	0.97662	118.7895	0.98055
0.75	88.98096	0.85393	105.2257	0.964	111.2645	0.97034
0.80	115.8328	0.65615	99.71142	0.90612	105.2848	0.92221
Average	126.4237		126.4653		129.831	

Table 2 portrayed the values of activation energy at mass conversion ranging from 0.05 to 0.8. The values signify that the activation energy varies at different fractional conversions which illustrate that the thermal degradation of the sawdust proceeds through a complex multi-step mechanism (Vyasovkin et al., 2011). Degradation of polymeric substrates (such as biomass) by thermal process involves various homolytic dissociation, chain sessions and complex reactions that are difficult to analyze separately; hence the activation energies at the designated mass conversions are the average values of reactions at each point in the mass conversion. The values of activation energy increases with increasing conversion from 0.05 to 0.4 using KAS method, while from 0.45 to 0.8 conversions the values of activation energy decreases with increasing conversion. Values of activation energy using Friedman method were constant through conversion from 0.05 to 0.1and almost similar for conversion from 15 to 30%; then decreases energy value is noticeable with increasing conversion from 35- 75%. FWO method showed no clear trend of the activation energy value from 5-45% conversion, but the activation energy values increases with increases in conversion from 50-80% conversion. The KAS and FWO models unlike fitting method provide apparent activation energies as a function of mass loss without any assumptions of reaction order or mechanism. The overall activation energy of the whole process evaluated using the arithmetic mean reveled consistency in the activation energies values of the kinetic methods employed which infer the likelihood of the method to give a reliable kinetics of the data. Higher value of activation energy implies more difficult of a reaction occurs. The activation energy signifies the minimum required energy to start a reaction, hence the lower the activation energy values the likelihood of the reaction to proceed at faster rate. The calculate values of activation energy obtained from this study were moderately low.

3.4 Kinetic Parameters

The values of pre-exponential factor, order, entropy, enthalpy and free energy are presented in Table 3. These thermodynamic parameters probably proffer the feasibility, orderliness and the mechanism of the reaction. Although, in a thermal degradation system heat energy supplied to reactants is used for dissociating bonds of reactants. Enthalpy change of a chemical reaction reflects the heat absorbed or released in the chemical bond dissociation under constant pressure The enthalpy change values obtained using eqn 16, implies the degradation of the sample proceed via endothermic process at lower heating rates which is also maintained throughout the process. The enthalpy values increase with increase in heating rate. As the temperature rose, more thermal energy was supplied to the samples, resulting in the dissociation of the stronger chemical bond (Kim et al, 2010). Change of entropies values shown in Table 5 had negative values, indicating that the degree of disorder of products formed through bond dissociations was lower than that of initial reactants. However, the negative change of entropies values implies formation of the active complex that can be characterized by high degree of arrangement (Vlaev et al., 2003).

Table 3: Kinetic parameters of Obeche sawdust

Heating rates(°C/min)	5	10	15	20	30	40
Kinetics parameters						
A(S^{-1})	609214.7	1.15E+08	1.19E+08	10569242	1.38E+08	35255636
ΔH (J)	92005.53	116221.5	115408.8	102689.2	114740.3	106460.7
ΔG (JS^{-1})	181959.4	181132.4	180683.3	181088.2	180454.2	179434.4
ΔS(JS^{-1})	-148.382	-105.005	-104.731	-124.945	-103.641	-115.021
Order (n)	3.8					

The pre-exponential factor (A) measures the frequency of the occurrence of situation that may lead the products formation. Most of the values obtained are within the range of 108-1014 S-1 reported for decomposition of solid substrate (Galewy, 2000).

CONCLUSIONS

A pyrolysis study of Triplochiton scleroxylon sawdust was carried out via thermogravimetric technique in inert atmosphere at different heating rates. The data generated were modeled using Friedman, KAS and FWO methods for the prediction of kinetic parameters. The overall values of activation energy obtained from the three models were similar. Although the values vary with the degree of conversion which signifies the thermal degradation of the sawdust sample proceed via multi-steps kinetics. The comparison of activation energy values based on the degree of conversion had shown an agreement between the values obtained from KAS and FWO methods. The compositional analyses of the feedstock reveled low ash content and high caloric value. The kinetic data would be useful to model, design and develop thermo-chemical system for Triplochiton scleroxylon sawdust. However, the results of this

study had provided an insightful idea that could be useful for application of sawdust as a feedstock for generation of energy.

REFERENCE

[1] Aboyade, A. Johann O. G., F., Carrier M., Edson L. M., Johannes H. K. (2013) Thermogravimetric Study of the Pyrolysis Characteristics and Kinetics of Coal Blends with Corn and Sugarcane Residues Fuel Processing Technology 106 :310-320

[2] Amutio, Maider, Gartzen Lopez, Roberto Aguado, Maite Artetxe, Javier Bilbao, Martin Olazar(2012) Kinetic study of Lignocellulosic Biomass Oxidative Pyrolysis Fuel 95: 305 - 311

[3] Bagudo, B.U, Garba, B. , Dangoggo, S. M. and Hassan, L.G. (2011) The Qualitative Evaluation of Biogas Samples Generated from Selected Organic Wastes; Scholars Research Library. Archives of Applied Science Research,3(5):549-555

[4] Balat, M. (2008): Mechanisms of Thermochemical Biomass Conversion Processes. Part 1: Reactions of Pyrolysis, Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 30:7, 620-635,

[5] Barneto, A.G., Carmona, J.A., Alfonso, J.E.M., Serrano, R.S.(2010) Simulation of the Thermogravimetry Analysis of three non-Wood Pulps. Bioresour. Technol ; 101: 3220 - 3229

[6] Chen, D., Zheng, Y, and Zhu, X. (2013):In-depth Investigation on the Pyrolysis Kinetics of Raw Biomass. Part I: Kinetic analysis for the Drying and Devolatilization Stages. Bioresource Technolo 131 : 40 - 46

[7] Damartzis, T., Vamvuka, D.,Sfakiotakis, S., and Zabaniotou, A., (2011). Thermal Degradation Studies and Kinetic Modeling of Cardoon (Cynara cardunculus) Pyrolysis using Thermogravimetric Analysis. Bioresour. Technol. 102, 6230 - 6238.

[8] Diji, C.J., Ekpo, D.D, and Adadu C.A (2013): Design of a Biomass Power Plant for a Major Commercial Cluster in Ibadan, Nigeria. The International Journal of Engineering and Science 2(4):23-29.

[9] Galwey, A.K., (2000) Structure and Order in Thermal Dehydrations of Crystalline Solids, Thermochimica Acta: 355 :181- 238

[10] Hu, S., Xiang, J., Sun, L. S., Xu, M. H., Qiu, J. R., and Fu, P. (2008). Characterization of Char from rapid Pyrolysis of Rice Husk. Fuel Process. Technol. 89:1096 -105.

[11] Idris SS, Rahman NA, Ismail K, Alias AB, Rashid ZA, and Aris MJ.(2010). Investigation on Thermochemical Behaviour of Low Rank Malaysian Coal, Oil Palm Biomass and their Blends during Pyrolysis via Thermogravimetric Analysis (TGA) Bioresource Technology. ,101(12):4584 - 4592

[12] Kim, Y.S; Kim, Y.S and Kim, S.H.(2010): Investigation of Thermodynamic Parameters in Thermal decomposition of Plastic Waste-Waste Lube Oil Compound. Journal of Environ. Sci. 44: 5313 - 5317.

[13] Mckendry, P. (20002) Energy Production from Biomass (part I): Overview of Biomass. Bioresource Technology; 83: 37-46

[14] Ogunleye I.O and Awogbemi O, (2007). Determination of thermo-physical properties of eight varieties of sawdust". Journal of Research in Engineering, 2(4): 8 - 14.

[15] Olazar, M, Aguado, R., San Jose´, M. J. and Bilbao J(2001). Kinetic study of fast pyrolysis of sawdust in a conical spouted bed reactor in the range 400–500°C. Journal of chemical technology and biotechnology,76: 469-476

[16] Orwa C, Mutua, A., Kindt R , Jamnadass R, Anthony, S. (2009). Agroforestree Database:a tree reference and selection guide version 4.0 (http://www.worldagroforestry.org/sites/treedbs/treedatabases.asp)

[17] Vamvuka, D.,Kakaras, E., Kastanaki E., Grammelis, P., (2003). Pyrolysis characteristics and kinetics of biomass residuals mixtures with lignite. Fuel 82: 1949-1960

[18] Vlaev, L.T, Markovska, I.G and Lyubchev, L.A.(2003).Non-isothermal Kinetic pyrolysis of Rice Husk.Thermochimica Acta 406:1-7

[19] Vuthaluru, H. B. (2004). Investigations into the pyrolytic behaviour of coal/biomass blends using thermogravimetric analysis. Bioresour. Technol. 92:187–195.

[20] Vyasovkin, S; Burnham, A.K; Criado, J.M; Perez-Maqueda, L.A; Popescu, C. and Sbirrazzuoli, N.(2011).ICTAC Kinetics Committee Recommendation for Performing kinetic Computation on thermal Analysis Data.Thermochimica Acta: 520:1-19

[21] White, J.E., Catallo, W.J. and Legendre, B.L., (2011). Biomass Pyrolysis Kinetics: A Comparative Critical Review with relevant Agricultural Residue case Studies. J. Anal. Appl. Pyrolysis 91, 1–33.

[22] Xiaoli, G., Xu, M, Lixian L., Cheng, L., Kanghua C. and Zhongzheng L. (2013) TG-FTIR Analysis of Pine Sawdust Pyrolytic Kinetics Cellulose Chem. Technol., 47 (1-2), 31-35

[23] Yaman, S. (2004). Pyrolysis of Biomass to Produce Fuels and Chemical Feedstocks. Energy Conversion and Management 45:651- 671

★★★