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Kinetic Analysis of Thermal Stability and Activation Energies of Agricultural Waste Residues Using Flynn-Wall-Ozawa and Coats-Redfern Models

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Abstract

The objective of the study was to determine the thermal degradation mechanisms and apparent activation energies of agro waste residues using thermo gravimetric analysis. Thermal degradation behaviors of corncob (CCF), rice hull (RHF), walnut shell (WSF) and oil palm (OPF) fibrous wastes under N₂ atmosphere were evaluated to derive their kinetic parameters at various heating rates of 5, 10, 20 and 40°C/min. Kinetic parameters were calculated using Flynn-Wall-Ozawa (F.W.O) and Coats Redfern models. The thermo gravimetric analysis (TGA) results showed that activation energies of the fibers varied significantly with the extent of degradation indicating a multistage mechanism involving a variety of compounds. Higher heating rate affected not only the temperature of maximum weight loss, but also the activation energies and degradation conversions of the agro fibers during decomposition. Activation energies of the agro waste residues decomposition appeared to peak around 40-50% conversion. The apparent activation energies (E_a) of the agro waste residues according to (F.W.O) and Coats Redfern models was found to be in the range between 184.74/183.87 kJ/mol for rice hull, 184.18/180.73 kJ/mol for walnut shell, 162.37/161.33 kJ/mol for corncob and 141.64/140.54 kJ/mol for oil palm fiber.

Keywords: Apparent activation energy, Thermal stability, Agro-residues, Thermo gravimetric analysis, Flynn-Wall-Ozawa, Coats Redfer

Introduction

Nowadays, it is not enough for products to meet technical and economical requirements, it is also important that they have sustainable characteristics. This necessity motivates academic and industrial researches to develop innovative solutions, which can be noted from the large number of technical papers investigating the

use of agro-industrial residues as raw materials for producing energy, biofuels, and composites (Kumar *et al.* 2008; White *et al.* 2011). A further example found in the technical literature about the uses of agro waste feedstock is the production of composites, regarded as promising materials that can replace petrochemical based composites (Lv *et al.* 2010).

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Agro-industry is an economic sector that generates immense amounts of agro residues. This renewable biomass usually comes from non-edible plants or parts of them (Goyal *et al.* 2008). Agro residues find applications in the automotive, packaging and building industries. Agro residues are composed of lignocellulosics and as such they are subjected to thermal degradation during composites production (Zhang *et al.* 2010). Therefore, understanding the thermal degradation characteristics of these agro resources will help in the design and application of composites. Slopicka *et al.* (2012) examined the kinetic study of the decomposition of poplar wood by a comparison of Kissinger and FWO methods with a good agreement value 153.92 kJ/mol and 158 kJ/mol. Corradini *et al.* (2009) studied the activation energy of several cotton fibers with thermogravimetric analysis (TGA) and Flynn-Wall-Ozawa method, and it was 150 kJ/mol. They concluded that these methods were efficient for the description of the degradation mechanism of solid state reactions.

Nada and Hassan, (2000) investigated cellulose and some cellulose derivatives and obtained their activation energies of 53-182 kJ/mol. Kinetic analysis of the dynamic TGA data can offer an estimation of activation energy as a function of the conversion rate and can also predict the degradation time in an isothermal mode (White *et al.*, 2011).

The objective of the study was to determine the thermal degradation mechanisms and apparent activation energies of agro waste residues using the models approach analyses.

Materials and methods

Materials: The corncob fiber was obtained from Mt. Pulaski Products, LLC Mt. Pulaski, IL, USA. The rice hull fiber was supplied by Rice Hull Specialty Products, Stuttgart, AR, USA. The walnut shell fiber was obtained from Composition Materials Co. CT, USA. Samples

were oven dried at 105 °C for 24 h. The samples were of 60 to 100 mesh particle size. The fibers were used as supplied by the manufacturers. The oil palm fiber (OPF) was collected from the rural farmers of Ebonyi State, Nigeria. The fibers were soaked in hot water with detergent for three days in order to remove the residual oil and other impurities. The fibers were dried in the sun for one week to obtain a dry mass and bagged in black polythene. A 40-mesh Wiley grinder was used to reduce the fiber particle prior to TG analysis.

Methods Thermogravimetric analysis: The thermal stability of agro fibers was investigated using a thermal gravimetric analyzer (SDT Q600, TA Inst.). 5-10mg of sample was weighed in a platinum pan and operated under a continuous flux of nitrogen (60ml/min). Under dynamic analysis, all of the samples were heated from room temperature to 500°C with 5, 10, 20 and 40°C/min ramp; under isothermal conditions (Sathasivam and Haris 2012; Elkhaoulani *et al.* 2013)

Kinetic modeling: The isoconversional Flynn-Wall-Ozawa method is an integral method, which leads to $-E_a/R$ from the slope of the line determined by plotting $\log \beta$ against $1/T$ at any certain conversion rate (Flynn and Wall 1966). The modified Coats-Redfern method is a multiple-heating rate application of the Coats-Redfern equation (Coats and Redfern 1964). Plotting the left-hand side for each heating rate against $1/T$ at that heating rate gives a family of straight lines of slope $-E_a/R$.

Activation energy of thermal decomposition: To evaluate activation energy, Flynn-Wall-Ozawa and Coats-Redfern expressions were used as follows (Yao *et al.* 2008):

Flynn Wall Ozawa expression (Yao *et al.* 2008)

$$\ln(\beta_i) = \ln(A_a E_a / R g(\alpha)) - 5.331 - 1.052 E_a / RT_{ai} \dots\dots\dots(i)$$

where $g(\alpha)$ is constant at a given value of conversion. The subscripts i and α denotes given value of heating rate and given value of

conversion, respectively. The activation energy E_a is calculated from the slope - $1.052E_a/R$.

Coats Redfern expression (Yao *et al.* 2008):

$$\ln(\beta/T^2) = \ln(K_0R/E_g(x)) - E_a/RT \quad \text{.....(ii)}$$

where, E_a = activation energy of thermal decomposition, R = gas constant, β = heating rate, and T = absolute temperature. For activation energy (E_a), a linear relationship between $\log \beta$ and $1/T$, $\log \beta/T^2$ and $1/T$ at selected fraction of thermal decomposition was displayed and E_a was then evaluated from the slope. The selected fraction ranged from 0.05 to 0.5 and the resulting values of the activation energy for each fraction were compared.

Results and discussion

Thermal stability of agro fibers and weight loss of agro fibers: The weight loss as a function of temperature for the four studied agro fibers and their derivatives are shown in Figs. 1(a and b). The oil palm fiber degradation initiated earlier starting from 150°C and there are three major degradation peaks in the derived weight loss curve, 210°C (43%), 275°C (42%) and 360°C (52.5%). By contrast, rice hull fiber had its degradation occurring from above 250°C and there are three major degradation peaks in the derived weight loss curve, 310°C (60%), 350°C (50%) and 410°C (10%). Corn cob fiber degradation started from below 200°C with two major degradation peaks in the derived weight loss curve, 300°C (48%) and 350°C (80%). Walnut shell fiber degradation started very close to 250°C with two major degradation peaks in the derived weight loss curve, 270°C (38%) and 350°C (60%). Walnut shell fiber degradation started very close to 250°C with two major degradation peaks in the derived weight loss curve, 270°C (38%) and 350°C (60%).

From the results obtained it could be said that rice hull agro residue has better thermal stability as evidenced by the higher activation energies of 184.74 and 183.87 kJ/mol according to FWO and Coats Redfern models. This could be attributable to the chemical composition of the rice hull agro residues, which according to Yao *et al.* (2008) contained a higher silica content.

Degradation kinetics and activation energy of agro fibers

To obtain activation energy of thermal decomposition, the data obtained were converted to a $\log \beta$ and $1/T$, $\ln(\beta/T^2)$ and $1/T$ as presented in Tables 1-4. Figs. 2 (a and b) show the activation energy of thermal decomposition as a function of conversion rate using F-W-O and Coats Redfern models. Figs. 3(a, b, c and d) Fig. 4(a, b, c and d) represent the isoconversional curves of corncob, rice hull, walnut shell and oil palm fibers by FWO and Coats Redfern models respectively. Because decomposition at the early stage was affected by the moisture, the fixed conversions (α) were selected from 0.05 to 0.5. The activation energy for each (α) was calculated from the slope of each straight line. It was found that as thermal decomposition proceeded in the rice hull fiber, the activation energy increased from (175 kJ/mol) at 5% conversion decreased steeply at 30 % conversion and it then increased to (194 kJ/mol) at 50% conversion. This finding is similar to the result obtained by Alwani *et al.* (2014). The activation energy of thermal decomposition for corncob fiber increased from (147 kJ/mol) at 5 % conversion and increased linearly to (177 kJ/mol) at 50 % conversion. The activation energy of thermal decomposition for walnut shell fiber increased from (179 kJ/mol) at 5 % conversion, experienced a reduction between 10 to 20 % conversion and thereafter increased to (179 kJ/mol) at 50 % conversion.

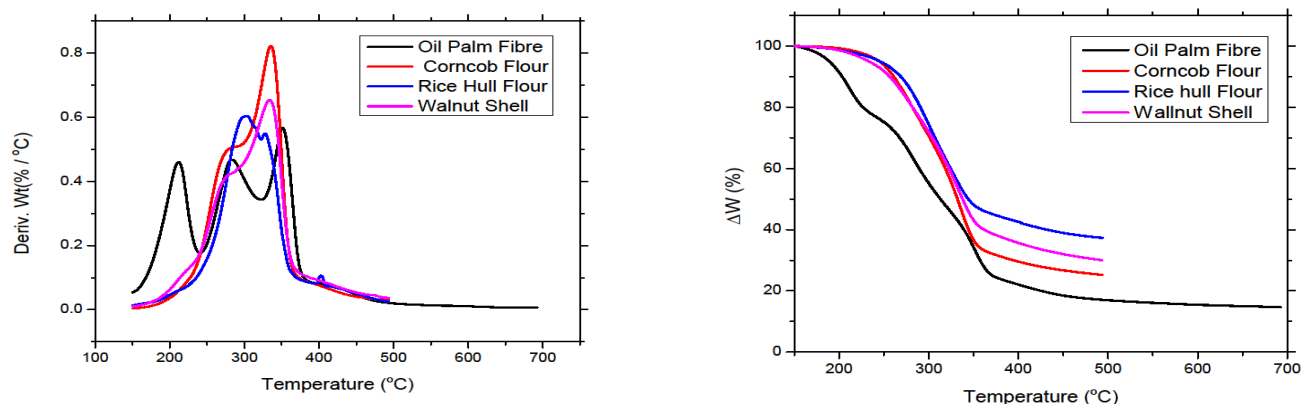


Fig.1: Thermograms showing (a) derivative of the weight loss curves and (b) weight loss curves

Compared with the other agro fibers, oil palm fiber shows larger changes in (E_a) and a higher overall (E_a) at 50 % conversion. The (E_a) of oil palm fiber shows a three-stage increase, which in turn suggests a complex multi-step degradation mechanism. It was found that the average (E_a) of oil palm fiber (141kJ/mol) is lower compared to the other three agro fibers. This indicates the lower thermal stability of the oil palm fiber compared to the other three agro fibers as shown by the Flynn-Wall-Ozawa and Coats Redfern models.

The differences in kinetic parameters can be attributable to complicated nature of agro residues constituted by a mixture of cellulose, hemicelluloses, lignin and extractives, with proportion reactivity and chemistry affected by variety. Based on the studied parameters it could be stated that the rice hull, corncob and walnut shell agro waste fibers qualify as good or potential composite materials. This agrees with the work of Yao *et al.* (2008) in which apparent activation energies of 160-170 kJ/mol was obtained for ten natural fibers throughout the polymer processing temperature range.

Table 1: Degradation kinetics and Activation Energy Parameters for Corn Cob Fiber at 1000K

(β)	log β	ln(β/T ²)	α									
			0.05	0.1	0.15	0.2	0.25	0.3	0.35	0.4	0.45	0.5
5	0.699	-11.212	1.932	1.872	1.835	1.802	1.771	1.741	1.714	1.691	1.670	1.653
10	1.000	-10.557	1.894	1.835	1.798	1.765	1.735	1.707	1.680	1.657	1.638	1.621
20	1.301	-9.904	1.858	1.768	1.768	1.730	1.701	1.674	1.648	1.625	1.589	1.589
40	1.602	-9.247	1.821	1.725	1.725	1.668	1.668	1.643	1.618	1.595	1.577	1.560

Table 2: Degradation kinetics and Activation Energy Parameters for Oil Palm Fiber at 1000K

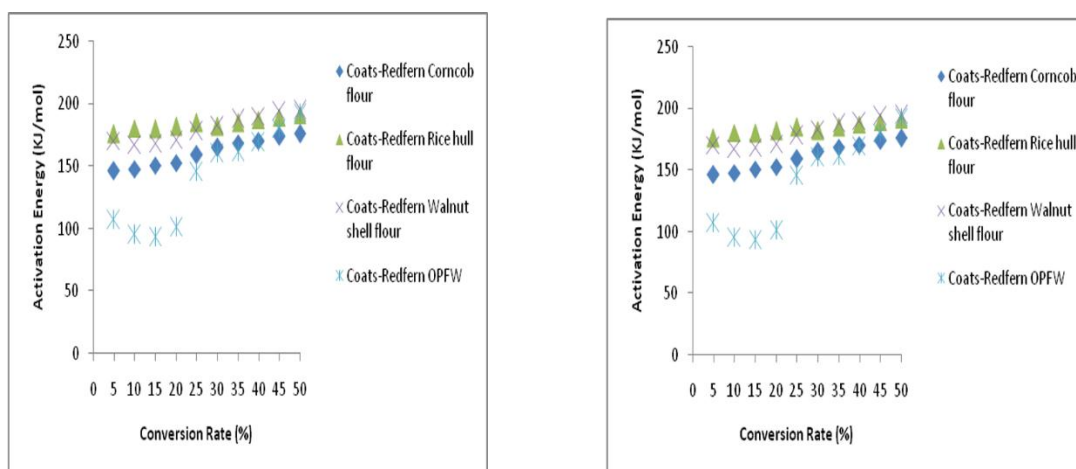
log β	ln(β/T ²)	α									
		0.05	0.1	0.15	0.20	0.25	0.30	0.35	0.40	0.45	0.50
0.699	-11.263	2.164	2.098	2.053	2.001	1.909	1.849	1.811	1.778	1.744	1.706
1.000	-10.608	2.114	2.044	1.997	1.953	1.878	1.818	1.779	1.747	1.713	1.677
1.301	-9.949	2.063	1.987	1.939	1.896	1.839	1.783	1.746	1.716	1.684	1.649
1.602	-9.302	2.011	1.927	1.878	1.840	1.798	1.748	1.710	1.681	1.653	1.621

Table 3: Degradation kinetics and Activation Energy Parameters for Walnut Shell Fiber at 1000K

Log β	$\ln(\beta/T^2)$	α									
		0.05	0.1	0.15	0.2	0.25	0.3	0.35	0.4	0.45	0.5
0.699	-11.199	1.975	1.888	1.840	1.801	1.765	1.733	1.704	1.679	1.657	1.637
1.000	-10.543	1.937	1.853	1.807	1.770	1.736	1.705	1.677	1.652	1.631	1.611
1.301	-9.898	1.900	1.816	1.772	1.735	1.702	1.672	1.644	1.621	1.601	1.581
1.602	-9.237	1.884	1.793	1.745	1.707	1.674	1.645	1.618	1.594	1.573	1.554

Table 4: Degradation kinetics and Activation Energy Parameters for Rice Hull Fiber at 1000K

Log β	$\ln(\beta/T^2)$	α									
		0.05	0.1	0.15	0.2	0.25	0.3	0.35	0.4	0.45	0.5
0.699	-11.104	1.928	1.846	1.804	1.774	1.748	1.724	1.670	1.674	1.649	1.620
1.000	-10.445	1.896	1.814	1.772	1.743	1.717	1.692	1.668	1.643	1.618	1.590
1.301	-9.782	1.868	1.785	1.743	1.714	1.688	1.663	1.638	1.613	1.588	1.560
1.602	-9.126	1.834	1.755	1.713	1.684	1.660	1.634	1.611	1.587	1.564	1.534

**Fig.2:** Comparison of activation energy of thermal decomposition of agro fibers by (a) F-W-O and (b) Coats Redfern

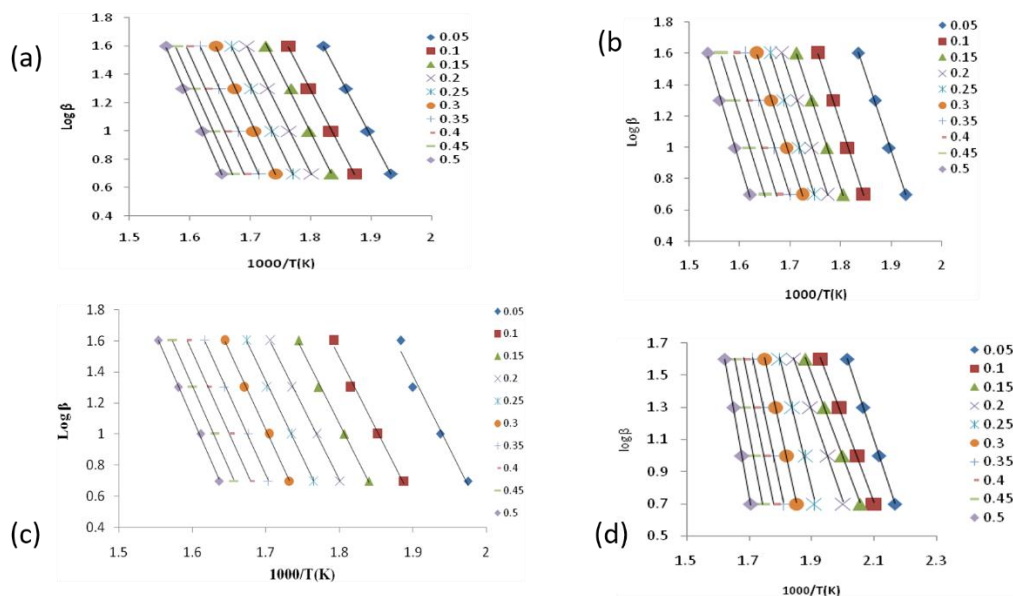


Fig. 3: Isoconversional curves of (a) corncob (b) rice hull (c) walnut shell and (d) oil palm fibers by Flynn-Wall-Ozawa expression.

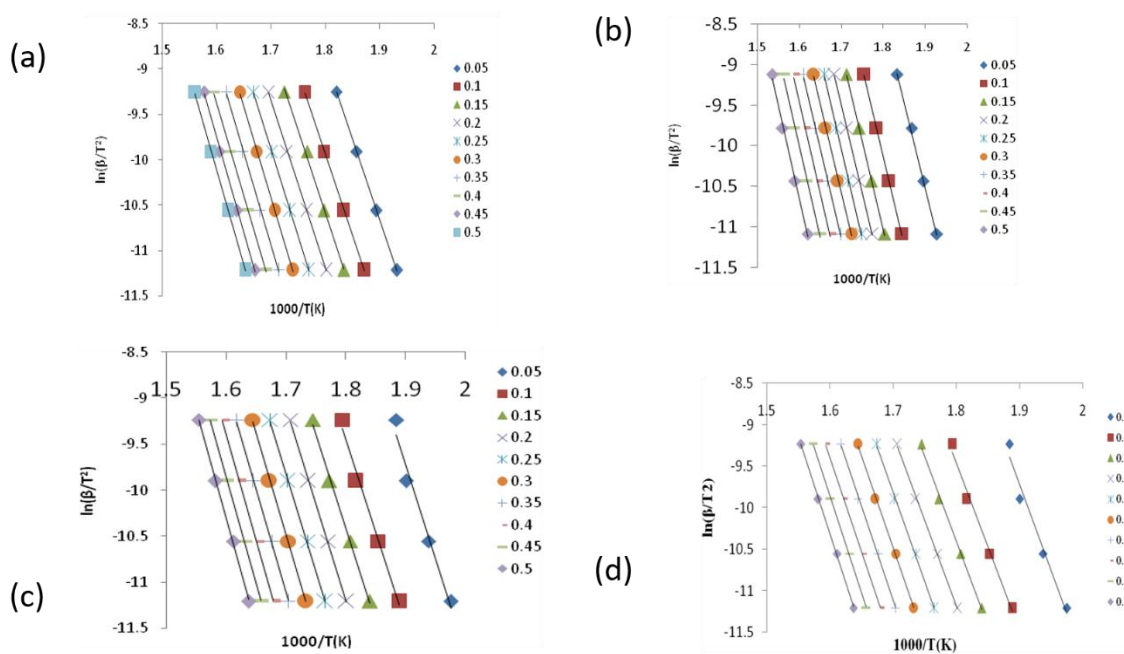


Fig. 4: Isoconversional curves of (a) corncob (b) rice hull (c) walnut shell and (d) oil palm fibers by Coats Redfern expression.

Conclusion

The thermal degradation (weight loss curves and derivative weight loss curves), thermal stability and apparent activation energies of four agro waste residues were characterized using TGA and model free approaches. The agro waste residues displayed different degradation profiles in their TGA/DTG curves respectively. The rice hull was the most thermally stable followed by walnut shell and corncob fibers, whereas the oil palm fiber showed the least thermal stability as confirmed by the average activation energies using the Flynn-Wall-Ozawa and Coats Redfern models. The study has confirmed that the evaluation of the thermal degradation and activation energies of the agro residues indicate their potential as composite materials.

Recommendations

The authors recommend that further work be done on the effect of coupling agents on the thermal stability and apparent activation energies of the studied agro residues.

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