

Isothermal Kinetics of Thermal Decomposition of Corncobs

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Abstract: *The kinetics of corncobs thermal decomposition in air was studied to elucidate the reactions occurring and their mechanisms as this material is widely used as biofuel particularly in rural areas. First, powdered material was thermally decomposed at fixed heating rates to assess the different steps of decomposition. The mechanism of each step and corresponding activation energy was revealed by applying Coates – Redfernand Flint – Wall – Ozawa isoconversional method. Next, isothermal decomposition was performed in a thermo balance on corncobs in their natural state to better simulate the conditions experienced on using corncobs as biofuel. A simple model was elaborated to relate the thickness of ash layer formed to the percent conversion in the second step of decomposition. On the other hand, the first step of decomposition on using sliced cobs was controlled by diffusion through the reacted layer rather than chemical reaction at interface as obtained when powdered material was tested.*

Key words: *Corncobs – Isothermal – Kinetics – Activation energy*

I. INTRODUCTION

The use of waste derived fuels has attracted much interest in the past decade owing to the depletion of fossil fuel reserves. Among these, agricultural waste played a key role due to their practically non – existent cost, moderate calorific value besides offering an alternative to the non-environmental friendly dumping or in situ burning process that are sometimes used to dispose of the waste [1-2]. In this respect, corncobs have been the object of much attention, being used as cheap fuel in rural areas [3], as an alternative cheap source for power generation [4] or a waste derived fuel in cement kilns [5]. According to Bruner et al [6], the high calorific value of corncobs can reach 18900 kJ.kg⁻¹, the low value depending on the amount of moisture which can reach up to 18%. In this respect, Kindler [7] has calculated that fully using corncobs as alternative for fossil fuels will reduce CO₂ emissions worldwide by 7.7×10⁷ tons per year.

The thermal decomposition of corncobs has been studied by many authors. Cao et al [8] performed pyrolysis under nitrogen atmosphere and a heating rate of 30 K.min⁻¹. They analyzed the gases and liquid produced and indicated that the decomposition temperatures increased with increasing heating rate. On the other hand, Danje [9] disclosed the lignocellulosic analysis of corn cobs. He found it to consist of 15% lignin, 48% cellulose and 33% hemicelluloses

which were converted to volatile matter on raising temperature. He presented a TGA trace for pyrolysis in nitrogen which consisted of three main portions: The first stage extending to about 100°C corresponded to loss of moisture (about 7%). The next stage was associated with devolatilization of cellulose, hemicellulose and lignin. A similar mechanism of devolatilization was observed by Poskrobko and Crol [10] during the pyrolysis of grains, oat and straw.

Calculation of activation energy of pyrolysis was effected by Yu et al [11], who suggested a two step and a global mechanism to interpret experimental data. They concluded that investigating the global kinetics of the two steps offered a clue to the mechanism of degradation. Danje [9] also calculated the activation energy of global degradation in the temperature range 175 – 325°C using an iso-conversional method to range from 175 – 270 kJ/mol according to the degree of degradation, a range of values comparable to that obtained by Yu et al [11]. He introduced oxygen to oxidize the carbon residue left. Final combustion started at about 330°C and ended at 650°C after which ash was left. The activation energy of the devolatilization step was also determined by Trninić et al [12] in inert atmosphere and found to range from 177 – 261 kJ/mol. Subjecting corncobs powder to oxidizing atmosphere by heating in air was researched by Kaloustian et al [13] who performed their experiments in an air flow, thus subjecting the cobs to oxidizing conditions. They obtained an activation energy of 185 kJ/mol for the volatilization step.

It is to be noted that most of the previous research work considered only global kinetic mechanism of decomposition. On the other hand, no study was available on the use of corncobs in their natural state to study the decomposition kinetics.

II. RAW MATERIALS AND EXPERIMENTAL TECHNIQUES

Corncobs were obtained from agricultural residues from a plantation in the Nile Delta region, Egypt. They were dried and their moisture content evaluated. The dry sample was then ground to pass 200 mesh screen (75 µm). This powder was used for preliminary analysis using a Universal V3.9A Thermal Analyzer after being left under ambient

conditions of temperature and humidity to allow absorption of humidity.

On the other hand, dried cobs were cut into cylindrical shapes of approximately 25 mm diameter and 30 mm height. These were used for isothermal runs by placing the specimen in the hottest zone of a thermobalance consisting of a vertical tube furnace in which is suspended a platinum crucible the upper end of which is fixed to a digital balance with ± 0.1 mg accuracy. The furnace tube was made of alumina and wound with nickel chrome wire. Its maximum operating temperature was 1200°C. The diameters of thermally treated compacts as function of time were determined using an electronic digital caliper by heating a cob in a horizontal tube furnace at 250°C and periodically extracting the specimen from the furnace to perform the required measurements.

III. RESULTS AND DISCUSSION

TG – DTG results

Samples of finely ground corncobs were subjected to TG and DTG analyses in air at heating rates of 2, 5, 10 and 15°C.min⁻¹. Fig 1 shows the results obtained at a heating rate of 10°C.min⁻¹. The thermograms obtained at other heating rates were similar except for the decomposition temperatures being shifted to higher values at higher rates. This figure shows four stages; the first step of decomposition relates to loss of moisture amounting to about 8%. Next there come two consecutive steps, presumably corresponding to devolatilization of cellulose, hemicellulose and lignin [9]. The DTG curve shows the first step to end at about 300°C, while the second step extends to 370°C. By the end of that step, the percent loss in weight reached about 65%. The combustion of the remaining char portion ended at about 800°C leaving 5% ash.

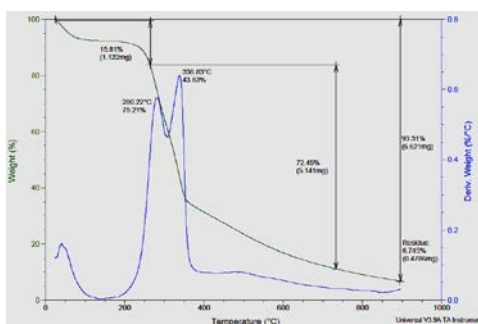


Fig. 1 TG – DTG curve for decomposition of corncob powder at 15°C.min⁻¹

In all subsequent discussions the first and second steps of decomposition will refer to the two devolatilization steps. The Coates – Redfern method was used to identify the controlling step in the first and second stages of decomposition.

First decomposition step: The best fit of experimental results for $\ln \frac{g(\alpha)}{T^2}$ against $\frac{1}{T}$ was obtained by assuming that reaction at interface is the controlling step [14]:

$$g(\alpha) = 1 - (1 - \alpha)^{1/3} \tag{1}$$

The plots at the four heating rates are illustrated in Fig 2. The minimum determination coefficient obtained was $R^2 = 0.986$. When a diffusion mechanism was assumed, the plots were of much poorer linear nature, achieving a maximum R^2 of 0.845.

The values of activation energy were calculated each time from the slopes of the curves. They are shown in Table 1. The values range from about 87 to 123 kJ.mol⁻¹ with an average of 102.7 kJ.mol⁻¹. These values are lower than those obtained by previous authors [11- 13]. One reason for that discrepancy is that all three works considered the devolatilization step as one single step.

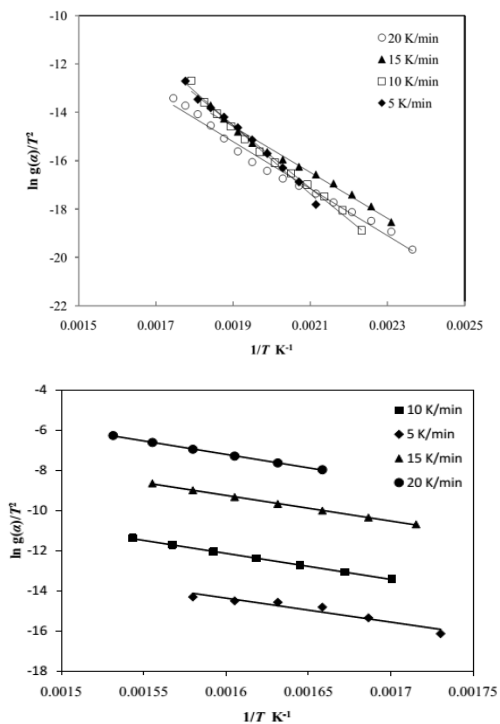


Fig. 2 Coates – Redfern plot for first decomposition step

Table 1 Activation energy of firststep /Coates – Redfern

Rate °C.min ⁻¹	5	10	15	20
E kJ.mol ⁻¹	122.3	112.8	86.7	89

To further assess the correctness of these values, the iso – conversational method of Flynn – Wall – Ozawa was applied by plotting $\log \beta$ against $1/T$ for four values of conversion, where β is the heating rate°C.min⁻¹. The results displayed in Fig 3 and table 2. The values of activation energy obtained are fairly close to those obtained by the first method as they range from about 87 to 102 kJ.mol⁻¹ with an average of 95.4 kJ.mol⁻¹.

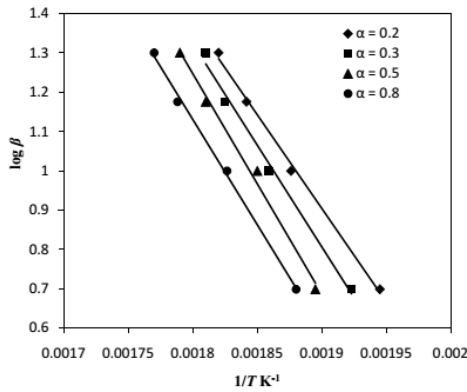


Fig. 3 Flynn – Wall – Ozawa plot for first decomposition step

Table 2 Activation energy of first step / Flynn – Wall – Ozawa

Conversion	0.2	0.3	0.5	0.8
E kJ.mol ⁻¹	86.8	94.2	102	97.6

Second decomposition step: On applying the Coates – Redfern method on that step, it yielded practically the same values of activation energy for all heating rates on assuming chemical reaction controlling at core – ash interface (Fig. 4). The results are presented in Table 3 of average value = 106.2 kJ.mol⁻¹.

Fig. 4 Coates – Redfern plot for second decomposition step

Table 3 Activation energy of second step / Coates – Redfern

Rate oC.min ⁻¹	5	10	15	20
E kJ.mol ⁻¹	94.5	107.8	106.1	111.4

When the iso-conversional method was used, different values of activation energies were obtained at the chosen conversions. It was thought sufficient to present the results in Table 4 without the log β – 1/T plots. The average value obtained by this method was 166.3 kJ.mol⁻¹, higher a figure than that obtained by the Coates – Redfern method. This discrepancy has been observed in case of using different techniques in calculating the activation energies of solid state reactions, possible reasons being difference in heating rates, mass of specimen and its packing state [15].

Table 4 Activation energy for different conversion values

α	0.2	0.3	0.5	0.8
E kJ.mol ⁻¹	169.3	157.9	175.1	168.1

Isothermal results

Each corncob cylinders of approximate dimensions 25 mm diameter and 30 mm height was placed into an alumina crucible and hanged into the thermobalance in its hottest zone. The specimen was introduced at a specified temperature and weight loss recorded with time.

First decomposition step: This was followed by fixing the temperature values ranging from 250 to 290°C. Fig. 5 shows the dependence of conversion at different temperatures on time.

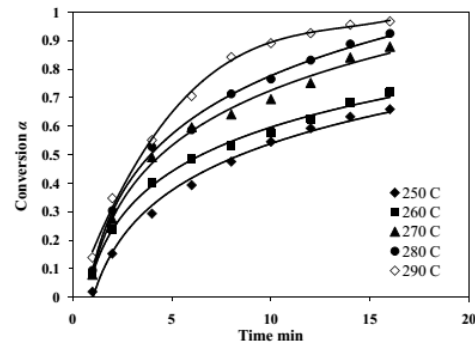


Fig 5 Conversion – time isotherms for second decomposition step

First, the reaction at interface was assumed to be the controlling step. For cylindrical bodies, this corresponds to the following equation [14]:

$$kt = g(\alpha) = 1 - (1 - \alpha)^{1/2} \tag{2}$$

Consequently, a plot of g(α) against time was performed at the different temperatures. This did not yield straight lines passing through origin as the maximum value of R² obtained was 0.852.

On the other hand, when diffusion through the reacted layer was assumed to control the decomposition reaction, the following the equation was used [14]:

$$kt = g(\alpha) = \alpha + (1 - \alpha). \ln(1 - \alpha) \tag{3}$$

Plots of g(α) were performed against time whereby straight lines passing through origin were obtained illustrated in Fig. 6 with a minimum value of R² of 0.982.

From the slopes of these lines, reaction rate constants (k) were calculated and an Arrhenius plot of ln k against 1/T performed. The result is plotted in Fig.7 with a slope E/R = 8909 corresponding to an activation energy of 74.1 kJ/mol.

Comparison of the results of non – isothermal and isothermal decomposition for the first step shows two major differences; First, while the controlling step on heating at constant rate of corncob powder was found to be reaction at ash – core interface, it turned out to be a diffusion controlled process when plain corncob cylinders were tested under isothermal conditions. Second, the value of activation energy obtained in the isothermal case was less than that obtained on heating at constant rate, a behavior that has been reported before [15].

On the other hand, it was possible to follow the thickness of the ash layer produced with time at one chosen temperature (250°C). The initial diameter of the cob was 25.6 mm and the thickness of ash layer (x) increased with time as evidenced from Table 5.

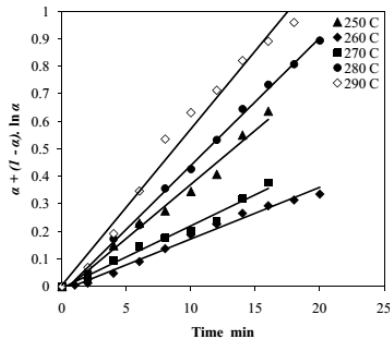


Fig 6 Plots of diffusion controlled kinetics of second decomposition step

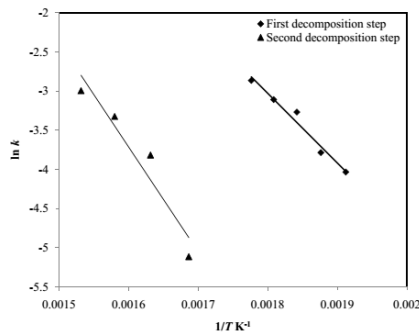


Fig 7 Arrhenius plot for the first and second decomposition steps

Table 5 Variation of ash thickness with time at 250°C

t min	0	2	4	6	8	10	12	14	16
x mm	0	1.4	1.8	2	2.5	2.6	3	3.2	3.7

A simple mathematical model is suggested to interpret these results:

In case of a cylindrical body, assuming the densities of ash layer and undecomposed core to be equal we get [16]:

$$\alpha = 1 - \left(\frac{r}{R_0}\right)^2 \quad (4)$$

Where, r is the radius of unreacted core and R₀ the initial particle radius assumed to remain constant throughout the process.

The thickness of ash layer:

$$x = R_0 - r$$

$$\text{Hence } \alpha = 1 - \left(\frac{R_0 - x}{R_0}\right)^2 = \frac{2xR_0 - x^2}{R_0^2}$$

Neglecting x² term with respect to R₀², we get:

$$\alpha \approx \frac{2x}{R_0} \quad (5)$$

Combining equations (2) and (5), we get:

$$kt = \frac{2x}{R_0} + \left(1 - \frac{2x}{R_0}\right) \cdot \ln\left(1 - \frac{2x}{R_0}\right) \quad (6)$$

Expanding $\ln\left(1 - \frac{2x}{R_0}\right)$ in Mc – Laurin series:

$$\ln\left(1 - \frac{2x}{R_0}\right) = -\frac{2x}{R_0} - \frac{1}{2}\left(\frac{2x}{R_0}\right)^2 \dots \approx -\frac{2x}{R_0}$$

Equation (6) simplifies to:

$$kt \approx \frac{2x}{R_0} - \left(1 - \frac{2x}{R_0}\right) \cdot \frac{2x}{R_0} \quad (7)$$

The above equation yields:

$$kt \approx \frac{4x^2}{R_0^2} \quad (8)$$

Substituting with the reaction rate constant obtained at 250°C:

k = 0.0177 min⁻¹ and R₀ = 12.8 mm, we get:

$$x \approx 0.871 \sqrt{t}$$

A plot of x against \sqrt{t} is shown in Fig.8 comparing experimental values of thickness obtained at different times with predicted values from equation (8). This supports the validity of the model as long as the thickness of ash layer can be neglected compared to the corncob base radius.

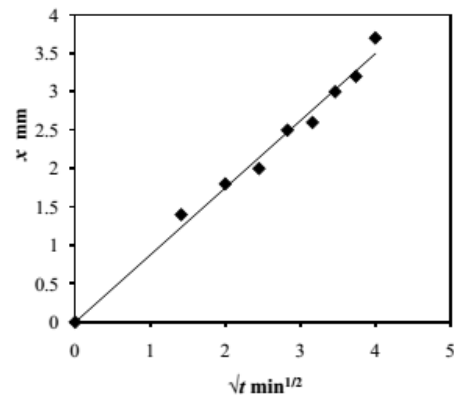


Fig 8 Thickness of reacted shell as function of time at 250°C

Second decomposition step: To ensure that the second step has come to end, all cob specimens intended for use in the study of that step were heated to 300°C for 20 minutes in a muffle kiln. According to Fig. 5, these conditions are sufficient to totally perform the first step of decomposition. Next, the specimen was introduced in the thermobalance at its hottest zone at temperatures ranging from 320 to 380°C, and loss in weight followed with time. The extent of decomposition following the second step (α) was then calculated.

When diffusion through ash layer was assumed to be controlling, the curves drawn between

$\alpha + (1 - \alpha). \ln(1 - \alpha)$ and t did not yield any straight lines. The values of determination coefficient R^2 varied from 0.702 to 0.903. On the other hand, when reaction at ash – core interface was assumed, plots of $1 - (1 - \alpha)^{1/2}$ against time did yield straight lines with determination coefficients R^2 ranging from 0.955 to 0.99. These plots are illustrated in Fig 9. From the slope of these lines, an Arrhenius plot was prepared that is shown in Fig. 7. The activation energy for the second step of decomposition was calculated from its slope and found to be $E = 111 \text{ kJ.mol}^{-1}$ a figure comparable to that obtained from non – isothermal methods.

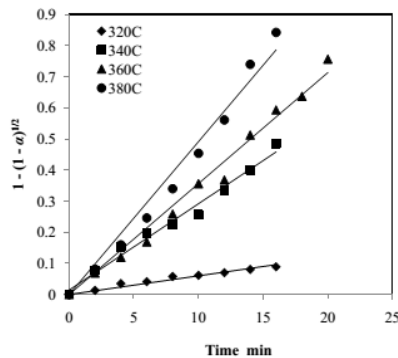


Fig 9 Plots of reaction controlled kinetics of third decomposition step

Actually, the fact that this reaction has been found to be controlled by chemical reaction rather than diffusion is explained by the porous character of the ash layer above 300°C where most of its organic content has devolatilized leaving a lot of voids. This is clarified by the SEM micrograph taken for the core – ash boundary shown in Fig. 10 of a specimen fired at 320°C for 20 minutes, where large pores are evident in the ash portion.

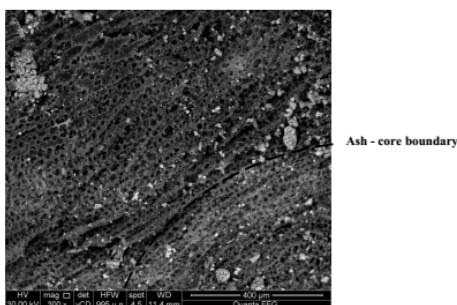


Fig 10 SEM micrograph of core – ash interface for a specimen fired at 320°C for 20 minutes

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