

Kinetics of Pyrolysis of Olive Kernels

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Abstract : Olive kernels were crushed, ground and screened to be subsequently subjected to thermal analysis in nitrogen at four different rates ranging from 5 to 20 °C.min⁻¹. TGA and DTG traces revealed that the combustion process occurs on three steps, the last one ending at about 900 °C leaving 1.6% ash. The kinetics of the first two steps were elucidated using three non-isothermal methods of analysis, namely, Flynn – Wall – Ozawa iso-conversional method, Kissinger method and Coates – Redfern method. The activation energy of each step was calculated using the three methods and the controlling step determined through the third method.

Keywords: Analysis, Kernels, Kinetics, Olive, Pyrolysis, Thermal.

Date of Submission: 10-04-2019

Date of acceptance: 25-04-2019

I. Introduction

The use of biomass as a source of energy has seen a great leap in the past few decades owing to the continuous depletion of fossil fuels. In that connection, researches concerned with their kinetics of pyrolysis flourished along with studying the products of their pyrolysis that often proved out to be of nutritive or commercial importance.

One of the earlier attempts in that domain was the pyrolysis of cellulosic material. The early work of Shafizadeh et al [1] and Broido et al [2] indicated a series of transitions including at least one intermediate cellulose derivative. The kinetics of decomposition were later studied by Antal [3] who assumed a first order kinetic model and an activation energy for the whole process was determined by Varhegyi [4] to be 238 kJ.mol⁻¹. Later, other authors criticized that model and more elaborate studies were performed that took into consideration the kinetics of the different steps of decomposition [5 – 7].

On a more specific basis, some authors researched the kinetics of pyrolysis of fruit shells, kernels and leaves. De Moraes et al [8] studied the pyrolysis of orange peels from both thermodynamic and kinetic viewpoints. They concluded that this is a two – steps process although they eventually calculated the activation energy of the whole process as 92.6 kJ.mol⁻¹. A more detailed analysis was attempted by Cremiato et al [9] who also distinguished two different steps in degradation and determined their respective activation energies as 82.6 and 37.6 kJ.mol⁻¹. Other attempts were also tried on other vegetable residues such as mango peels [10], sunflower seeds [11], hazelnut shells [12] and date palm [13, 14]. In that respect, studies on the kinetics of pyrolysis of olive kernels are rather scarce. In an early work, Zabaniotou et al [15] considered the reaction to occur in one step and assumed a first order model. He obtained an overall activation energy of 47 kJ.mol⁻¹. The extremely elevated rate of heating (200 °C.min⁻¹) casts serious doubts on their results. In a study carried out by Vamvakia et al [16], two different types of olive kernels (along with other cellulosic residues) were subjected to thermal analysis. Three stages were obtained that were assumed to follow first order kinetics without solid justification. The last peak, corresponding to charring was not included in calculations. The activation energies of the two decomposition reactions were found not to depend on the type of kernel used. At a heating rate of 10 °C.min⁻¹, their values were determined as about 93 and 152 kJ.mol⁻¹ respectively. More recently, Al Farraji et al [17] investigated the pyrolysis of olive kernels in both fixed and fluidized bed conditions. They used a heating rate of 20 °C.min⁻¹ and obtained lower values for the activation energy of pyrolysis in case of the fluidized bed. They determined an overall activation energy the value of which in fixed bed was determined as 74.4 or 97 kJ.mol⁻¹ depending on the adopted kinetic model. In fluidized state the value dropped to 67.4 kJ.mol⁻¹.

In the present work, non – isothermal kinetics of olive kernels is investigated using three different methods, namely Kissinger method, the Flynn-Wall-Ozawa (FWO) iso-conversional method and the Coats – Redfern method.

II. Experimental Work

Raw olive kernels were purchased from the local market originating from Siwa oasis in the Western desert (Egypt). They were washed with ethyl alcohol then distilled water to be subsequently dried at 80°C overnight. These were then crushed using a laboratory disk mill and screened on a set of standard sieves. The portion used in this work was that retained between sieves of mesh 20 and 35, corresponding to opening sizes of

0.833 and 0.417 mm respectively. They were then subjected to thermal analysis in a thermal Analyzer type TGA 50-50H producing simultaneous TGA and DTG traces. The heating rates were adjusted at 5, 10, 15 and 20 °C.min⁻¹ in a flow of nitrogen at 20 ml.min⁻¹.

III. Results And Discussion

3.1. Results of thermal analysis

Fig 1 shows the thermograms obtained at a heating rate of 5°C.min⁻¹. Similar curves were obtained for the three other rates but were not displayed to avoid redundancy. The DTG curve clearly indicates the presence of two distinct peaks although the TGA trace failed to distinguish between them. After elimination of moisture, the first peak starts approximately at 150°C and ends at about 300°C, while the second peak ends at about 380°C. The remaining portion of the curve takes place at almost constant rate presumably due to volatilization of the formed char. The ash residue at the end of the run was found to equal to 1.6% of the original dry mass. Detailed data were available from the instrument printouts that recorded the time, temperature, weight and derivative of weight change. These enabled locating the required points with high precision.

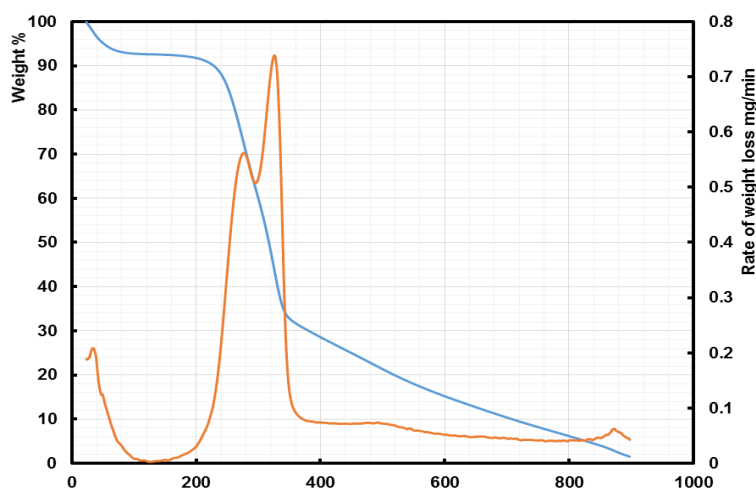


Figure 1: TGA – DTG curves at 5°C.min⁻¹

3.2. Results using the Kissinger method [18]

In this method, the value of the DTG peak temperatures (T_m K) are recorded at each heating rate (β °C.min⁻¹). Then a plot of $\ln \frac{\beta}{T_m^2}$ against $\frac{1}{T_m}$ is performed. Straight lines should be obtained the slope of which = $-\frac{E}{R}$ where E is the activation energy (J.mol⁻¹) and R , the general gas constant (J.mol⁻¹.K⁻¹). Table 1 illustrates the different values of temperatures corresponding to maximum peaks.

Table 1: Temperatures of DTG peaks (°C)

Heating rate °C.min ⁻¹	5	10	15	20
First peak	275.6	284	288.3	294.6
Second peak	327.4	340.36	348.5	353.6

The plots of $\ln \frac{\beta}{T_m^2}$ against $\frac{1}{T_m}$ for the two peaks are illustrated in Fig. 2 and Fig. 3 and show straight lines. Their slopes were calculated and the following values obtained for activation energies illustrated in Table 2.

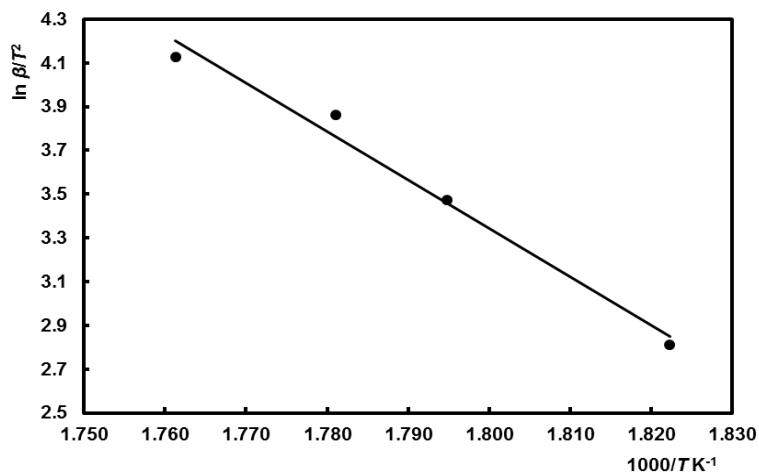


Fig 2: Kissinger plot for first step of pyrolysis

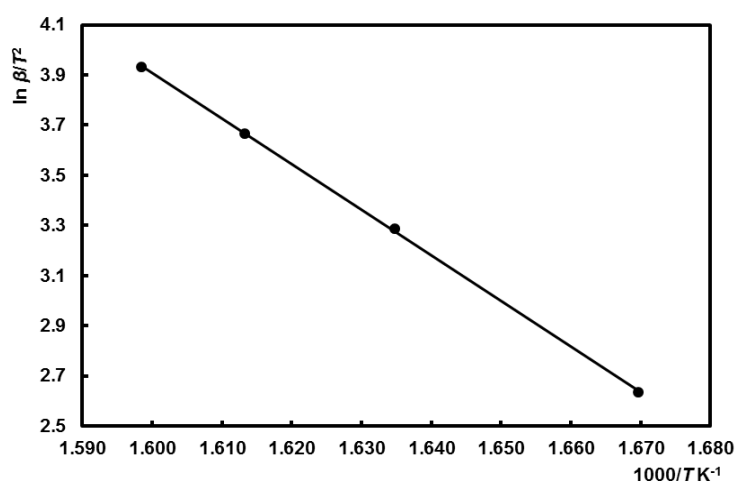


Fig 3: Kissinger plot for second step of pyrolysis

Table 2: Activation energies of the two pyrolysis steps (Kissinger method)

	$E \text{ kJ.mol}^{-1}$
First step	184
Second step	154

It is worth mentioning that on applying the Kissinger method, only the value of the activation energy can be determined. This method cannot be used to disclose the controlling step of the reaction.

3.3. Results using the FOW method [19]

This method relies on performing a set of experimental TGA runs at different heating rates (β °C.min⁻¹) and determining the temperatures (T K) corresponding to chosen conversion levels (α) at each rate. For each value of α , a plot of $\log \beta$ against $\frac{1}{T}$ is performed. These should yield straight lines of more or less equal slopes = $-\frac{0.4567 E}{R}$. In some instances, the value of activation energy varies with conversion so that the obtained lines are not parallel [20]. In any case, a mean value for activation energy is calculated.

Table 3 displays the values of temperatures obtained at four chosen conversion levels for the first step of pyrolysis while Fig. 4 shows the four straight lines obtained on plotting $\log \beta$ against $\frac{1}{T}$. As can be observed from that figure, the four lines are sensibly parallel. Table 4 shows the values of the four slopes and the corresponding value of activation energy each time. The calculated mean value of activation energy = 164.8 kJ.mol⁻¹.

Table 3: Temperatures at chosen conversion levels (°C) for first step (FWO)

β °C.min ⁻¹	5	10	15	20
$\alpha = 0.2$	248.2	260.45	264.54	267.88
$\alpha = 0.4$	263	273.3	278.24	281.24
$\alpha = 0.6$	274.3	283.6	289.24	294.64
$\alpha = 0.8$	282.4	294.5	300.99	303.64

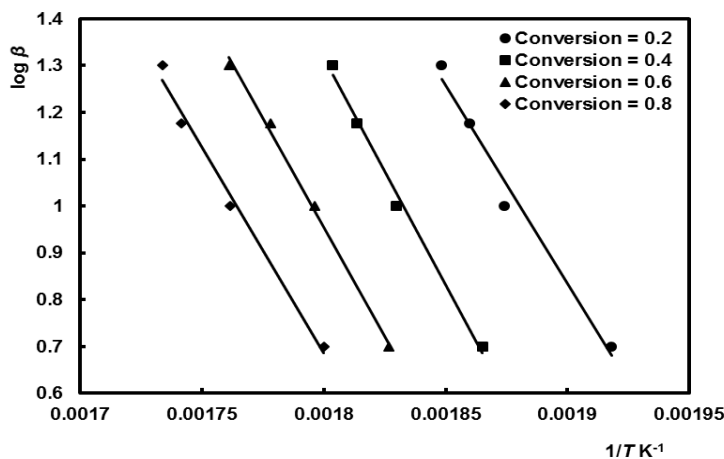


Fig 4: FWO plots for first step of pyrolysis

Table 4: Slopes of lines and activation energies for first step (FWO)

α	0.2	0.4	0.6	0.8
Slope	-8459.94	-9657.75	-9314.49	-8776.76
E kJ.mol ⁻¹	154.0	175.8	169.6	159.8

Similarly, the corresponding values for the second step of pyrolysis were established and shown in Tables 5 and 6.

Table 5: Temperatures at chosen conversion levels (°C) for second step (FWO)

β °C.min ⁻¹	5	10	15	20
$\alpha = 0.2$	309.15	318.6	329.6	335.15
$\alpha = 0.4$	318.8	328	339.5	345
$\alpha = 0.6$	327.6	336.6	347.3	353.1
$\alpha = 0.8$	337.74	344.3	355.6	361.4

Table 6: Slopes of lines and activation energies for second step (FWO)

α	0.2	0.4	0.6	0.8
Slope	-7900.79	-8040.89	-8567.97	-9199.64
E kJ.mol ⁻¹	143.83	146.3804	155.9758	167.4749

Here also, as can be revealed from Fig. 5, the straight lines obtained on plotting β against $\frac{1}{T}$ were practically parallel, of slopes displayed in Table 6. The mean activation energy was evaluated as 153.4 kJ.mol⁻¹.

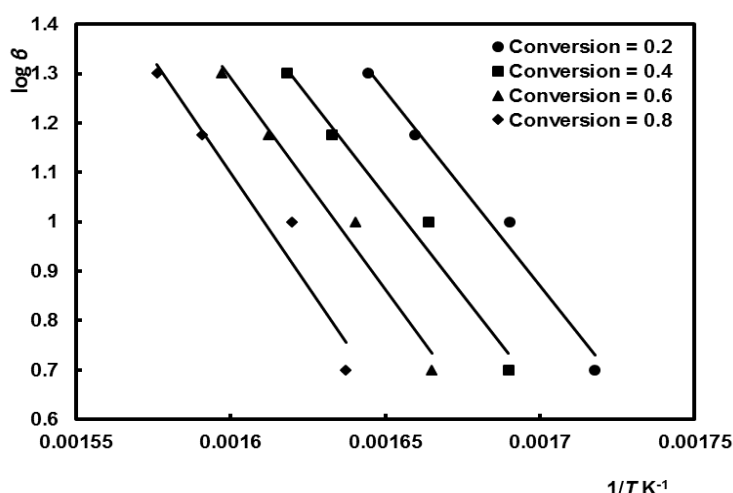


Fig 5: FWO plots for second step of pyrolysis

It is worth noticing that the FWO method, like the Kissinger method, does not indicate the controlling step of decomposition but serves only to evaluate the mean activation energy.

3.4. Results using the Coats – Redfern method (C-R) [21]

This method differs from the two previous ones in that it enables, not only to predict the value of activation energy, but also to determine the rate controlling step. For solid state reactions, a general relation can be written between reaction time (t) and conversion (α):

$$t = g(\alpha) \quad (1)$$

The expression of $g(\alpha)$ depends on the reaction controlling step. Khawam et al [22] have summarized all possible forms of that function for both spherical and cylindrical particle shapes.

In that technique, several models are assumed that decide about the form of the function $g(\alpha)$. Next, a plot is

performed for $\ln \frac{g(\alpha)}{T^2}$ against $\frac{1}{T}$. The model yielding the best linear fit is considered the most appropriate. The

slope of the straight line = $-\frac{E}{R}$ from which the value of activation energy can be deduced. A further merit of that method is that it requires only one TGA run at one heating rate, which makes it more advantageous than the two other methods.

For the first step of pyrolysis, values of conversion were obtained at different temperatures at all four heating rates. The best fit was obtained on assuming chemical reaction at interface between solid core and external ash to be the controlling mechanism. In that case, equation (1) $g(\alpha)$ takes the form:

$$t = \tau \cdot [1 - (1 - \alpha)^{1/3}] \quad (2)$$

Where: τ is the time required for complete reaction (min.).

As can be seen from Fig. 6, the relation between $\frac{1}{T}$ and $\ln \frac{g(\alpha)}{T^2}$ is linear with minimum value of $R^2 = 0.979$,

confirming the assumed reaction mechanism. From the slope of these lines, it was possible to calculate the activation energy each time. As can be followed from Table 7, the values of activation energy did not seem to depend on the heating rate as they were fairly close. The average value of $E = 118.3 \text{ kJ.mol}^{-1}$.

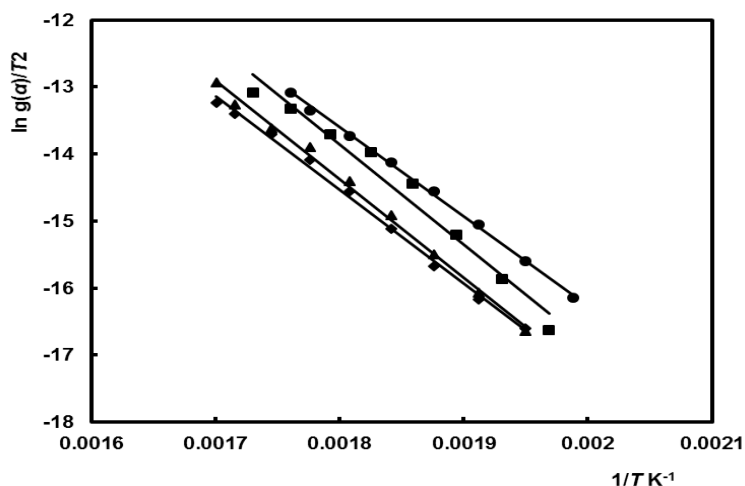


Fig 6: C-R plots for first step of pyrolysis

Table 7: Slopes of lines and activation energies for first step (C-R)

β °C.min ⁻¹	5	10	15	20
Slope	-13261	-14966	-14699	-14006
E kJ.mol ⁻¹	110.25	124.38	122.21	116.48

For the second step, the same procedure was adopted. Straight lines were obtained with best fits (Minimum $R^2 = 0.975$) when a first order reaction was assumed corresponding to:

$$kt = -\ln(1 - \alpha) \quad (3)$$

Where: k is the reaction rate constant (min⁻¹).

These lines are shown in Fig. 7 and corresponding slopes and activation energies displayed in Table 8.

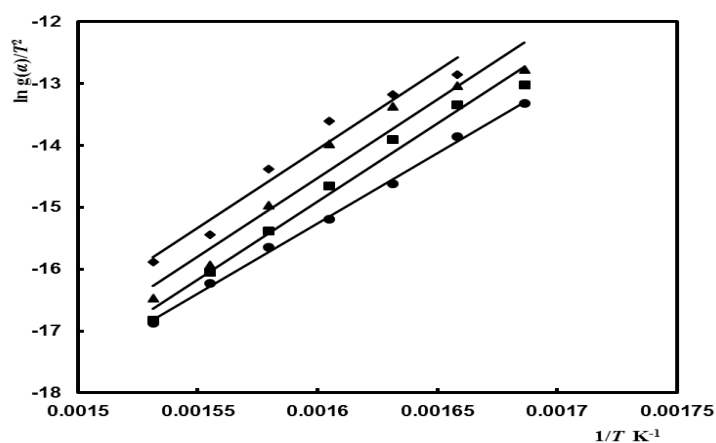


Fig 7: C-R plots for second step of pyrolysis.

Table 8: Slopes of lines and activation energies for second step (C-R)

β °C.min ⁻¹	5	10	15	20
Slope	22700	25254	25432	25422
E kJ.mol ⁻¹	188.73	209.96	211.44	211.35

Again, the values of activation energy do not depend on the heating rate with an average value $E = 205.3$ kJ.mol⁻¹.

IV. Conclusion

Three different techniques were applied to evaluate the activation energies of the two steps of pyrolysis of olive kernels. There were apparent differences with the results obtained on using each method as can be followed from Table 9, although the results of the Kissinger and FWO methods were comparable. This state of affairs have been reported by several authors who concluded that the use of different methods of thermal analysis could lead to different values of E . In their work, Conesa et al [23] compared the different methods and concluded that the value of the determined activation energy depends on a lot of factors including the particle size of powder, the nature of the containing crucible, the atmosphere used, etc. besides the rate of heating. The obtained values only serve as approximations whenever needed for designing the pyrolysis reactor. The value of 118.3 obtained by the C-R method for the first step fairly compares with the value reported by Vamvaki et al [16], while the value of about 154 obtained for the second step using the Kissinger or the FWP method is in full agreement with that observed by the same authors [16].

Table 9: Comparison of activation energy values

Method	Kissinger	FWO	C-R
First step	184	163.8	118.3
Second step	154	153.4	205.3

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M.F. Abadir. "Kinetics of Pyrolysis of Olive Kernels." *IOSR Journal of Applied Chemistry (IOSR-JAC)* 12.4 (2019): 50-56.