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Abstract

Pumpkin seeds are produced as agricultural waste worldwide in massive amounts as only a small fraction is used for cultivation. The pyrolysis of such waste can produce biochar, which is considered a valuable renewable energy source as well as a potential adsorbing material. In this work, pumpkin seeds were first dried and then ground to fine particle size. The waste was then subjected to thermal pyrolysis under a constant inert atmosphere flow rate, at four different heating rates 5, 10, 15, and 20 ^{o}C.min^{-1}. The TG-DTG curves indicated a significant weight loss followed by biochar formation. The kinetics of biochar formation were studied using three different iso-conversional methods: the Kissinger-Asahira-Sunoze (KAS), the Flynn-Wall-Ozawa (FWO), and the Friedman method. The values of activation energies obtained by the different methods were comparably ranging from about 104 to 116 kJ.mol^{-1}. Determination of the calorific values of the dry biowaste yielded a value of 16,080 kJ.kg^{-1}.

Keywords: Pumpkin seeds, pyrolysis, kinetics, biochar.

1. Introduction

Biomass is renowned worldwide as a major source of cheap energy. This includes municipal and agricultural wastes, and gas and liquid biofuels [1]. Biomass wastes can be transformed from useless residues into valuable renewable energy sources such as biogas, bio-oil, ethanol, biodiesel, and biochar through the pyrolysis conversion process [2-7]. Pyrolysis is the process of breaking chemical bonds solely using thermal energy, whereby when energy is added to the system, large molecules disintegrate into stable fragments providing pyrolysis process energy parameters; temperature, heating rate, and time are regulated conveniently.

Much research has been devoted to the theoretical and practical aspects of the pyrolysis process [8-12], in particular, to disclose the mechanism of thermal degradation of wood, silk, proteins, and cellulose [13-17]. In general, the pyrolysis of cellulosic materials takes place through the devolatilization of lignocellulosic components, namely, hemicellulose, cellulose, and lignin. As a result, char is formed that tends to undergo a cracking process as the temperature is raised, volatilizing off light organic components [18-25]. Several studies have been devoted to studying the kinetics of the degradation of cellulosic waste. In general, the complexity of this process prevented the proper use of the well-known Coats-Redfern method to disclose the nature of the kinetic mechanism involved, while the use of iso-conversional methods was found to produce many reliable results [18-25]. Lately, the study of

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materials produced through pyrolysis has expanded to encompass a wide range of applications [24] such as textile fibers [25], computer circuit boards [26], soil nutrients [27], forensic evidence [28, 29], bacteria, and fungi [30, 31].

Pumpkin seeds as an agricultural solid waste are produced in massive amounts worldwide and locally in Egypt [32] as a byproduct from numerous industries; pharmaceutical, cosmetic, and food oil industries. Furthermore, these solid wastes should be converted into valuable biomass sources for environmental and economic reasons [33, 34].

The industrial application of biochar obtained from pumpkin was investigated in various studies. Bal et al. in 2021 [35] employed pumpkin-derived biochar as an adsorbent to remove methylene blue dye from aqueous solutions. Also, the pumpkin biochar adsorption efficiency was measured by Özer et al. in 2022 [36] via ciprofloxacin removal from aqueous solutions. Ye et al. in 2019 [37] and in Cardarelli et al. in 2022 [38] studies the used the agriculture derived biochar including the pumpkin seed source to be used in ferrous metallurgy industry in side of coke and coal.

Due to that in the present work, the pyrolysis of pumpkin seeds industrial wastes as a potential source of cheap energy is studied, based on TG-DTG pyrolysis curves at several heating rates 5, 10, 15, and 20 ^{o}C.min^{-1}. The kinetics of biochar formation was investigated using three iso-conversional methods, namely the Kissinger-Asahira-Sunoze (KAS) method, the Flynn-Wall-Ozawa (FWO), and the Friedman method. The values of activation energy obtained by all three methods and their dependence on the extent of conversion were compared. Also, the calorific value of pumpkin seeds has been measured to assess the possibility of their use as biofuel.

2. Raw Material and Techniques

The raw material consists of pumpkin seeds which are first dried for an hour in a drying oven at 100°C, then ground in a laboratory ball mill to be screened following ASTM C136-01 standard [31]. The ground dried pumpkin seeds were then exposed to thermal analysis under an inert atmosphere with a constant flowrate of Nitrogen (N_2) of 20 ml.min^{-1}. The thermal analysis apparatus was of TGA-50H-Shimadzu type that can be operated at heating rates ranging from 2 to 50 ^{o}C.min^{-1}. The TGA and DTG data were saved as both spreadsheets and curves. In this study, the four heating rates selected for the thermal analysis process were 5, 10, 15, and 20 ^{o}C.min^{-1}.

A bomb calorimeter (PARR 6000 series model) was used to determine pumpkin seeds' calorific value. In this apparatus, one gram from the sample is placed in the water-jacketed stainless-steel container of the equipment, which is then electrically heated until the sample ignites. The container steel walls allow heat to pass through to the water in the jacket, where the increase in water temperature has been calibrated to give the heat of combustion.

The fraction conversion (α) due to degradation was determined from Equation (1).

$$\alpha = \frac{(m_0 - m)}{(m_f - m_0)} \tag{1}$$

The basic kinetic Equation (2) describing the degradation process takes the form:

$$\frac{d\alpha}{dt} = A.e^{-\frac{E}{RT}}.f(\alpha) \tag{2}$$

In this Equation, the kinetic function f(α) depends on the mechanism of reaction, and the integral kinetic function g(α) is defined by Equation (3), as summarized by Khawam et al. [39] in

Table (*1*:

$$g(\alpha) = k.t = Ae^{-\frac{E}{RT}}.t \tag{3}$$

Table (1): The kinetic functions f(α) and g(α) [39]

Code	Controlling step	$f(\alpha)$	$g(\alpha)$
A	Crystallization and grain growth	$m(1-\alpha).[\ln(1-\alpha)]^{\frac{m-1}{m}}$	$[-\ln(1-\alpha)]^{1/m}$
F_0	Zero order reaction	0	α
F_1	First order reaction	$1-\alpha$	$-\ln(1-\alpha)$
F_n	n^{th} order reaction ($n \neq 1$)	$(1-\alpha)^n$	$\frac{(1-\alpha)^{1-n}}{1-n}$
R_2	Contracting area	$2(1-\alpha)^{\frac{1}{2}}$	$1-(1-\alpha)^{\frac{1}{2}}$
R_3	Contracting volume	$3(1-\alpha)^{\frac{2}{3}}$	$1-(1-\alpha)^{\frac{1}{3}}$
D_1	One dimensional diffusion	$\frac{1}{2\alpha}$	α^2
D_2	Two-dimensional diffusion	$-[\ln(1-\alpha)]^{-1}$	$\alpha+(1-\alpha).\ln(1-\alpha)$
D_3	Three-dimensional diffusion (Thin ash layer)	$\frac{3(1-\alpha)^{\frac{2}{3}}}{2\left[1-(1-\alpha)^{\frac{1}{3}}\right]}$	$\left[1-(1-\alpha)^{\frac{1}{3}}\right]^2$
D_4	Spherical: diffusion through ash	$\frac{1}{2\left[(1-\alpha)^{-\frac{1}{3}}-1\right]}$	$1-\frac{2}{3}\alpha-(1-\alpha)^{\frac{2}{3}}$

Activation energy calculations were carried out using thermogravimetric data points applying Kissinger- Asahira-Sunoze (KAS) [40, 41], Flynn-Wall-Ozawa (FWO) [42, 43], and Friedman iso-conversional models [44, 45] using Equations (4), (5), and (7), respectively.

In the KAS model, β is the rate of rating (^{o}C.min^{-1}), T is the temperature at each conversion level (K), E is the activation energy (kJ.mol^{-1}), and $g(\alpha)$ is the kinetic function relating conversion to time defined by Equation (3). When plots of $\ln\frac{\beta}{T^2}$ against $\frac{1}{T}$ are carried out at each conversion level, the activation energy E can be calculated from the line slope $\left(\frac{-E}{R}\right)$.

$$\ln\frac{\beta}{T^2} = \frac{-E}{RT} + \ln - \left[\frac{R}{E}g(\alpha)\right] \tag{4}$$

On the other hand, in the FWO method, the activation energy is determined by plotting $\log\beta$ versus $\frac{1}{T}$ at each conversion value. Straight lines should show with a slope equal to $\frac{-0.4567E}{R}$, following Equation (5).

$$\log\beta = \log\frac{A.f(\alpha)}{\frac{d\alpha}{dT}} - \frac{0.4567E}{RT} \tag{5}$$

Finally, the Friedman method relies on applying the basic kinetic Equation (2) in a slightly modified form Equation (6):

$$\beta.\frac{d\alpha}{dT} = A.e^{-\frac{E}{RT}}.f(\alpha) \tag{6}$$

This can be modified to read:

$$\ln\beta.\frac{d\alpha}{dT} = \ln A.f(\alpha) - \frac{E}{RT} \tag{7}$$

Plots of $\ln\beta.\frac{d\alpha}{dT}$ against $\frac{1}{T}$ at various values of conversion (α) produce straight lines from which values of activation energies can be determined at each conversion level.

On the other hand, the intercepts of the aforementioned plots yield values of $\ln A.f(\alpha)$ for each conversion level. Once a certain mechanism is assumed, the values of $f(\alpha)$ can be evaluated at each conversion level. The logarithm of the pre-exponential term $(\ln A)$ can be then deduced for each value of α. If a correct mechanism is assumed, then, the kinetic compensation effect defines the interdependence of the various kinetic parameters in the Arrhenius equation. The activation energy of a reaction should possess a constant value throughout the reaction. However, since activation energy is conversion dependent, compensating this change occurs through a linear relation between $\ln A$ and E [46-48].

3. Results and Discussion

3.1. Particle Size Distribution

The cumulative particle size distribution of screened ground pumpkin seeds is illustrated in Figure 1, where the ground seeds have a median particle size (D_{50}) of about 1 mm.

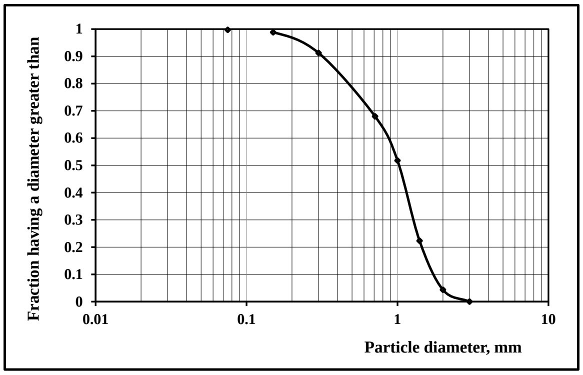

Figure 1: Cumulative particle size distribution of ground seeds

3.2. Determination of Calorific Value

The calorific value of ground dry pumpkin seeds, as determined using the bomb calorimeter was found to be 16,080 kJ.kg^{-1}. This value compares with the values obtained by Gravalos et al in 2016. for the calorific values of several types of seeds [3] who obtained values ranging from 14300 to 25400 kJ.kg^{-1}.

3.3.TG-DTG curves

TG-DTG for the pyrolysis of ground pumpkin seeds were obtained at the four rates. As an example, the TG-DTG curve for the pyrolysis reaction at a heating rate of 10 ^{o}C.min^{-1} is shown in Figure 2, where all the other curves showed a similar behavior except that devolatilization temperatures tended to have higher values. The main degradation reaction shows a distinct DTG peak at about 344.4^{o}C (617.6K). This step corresponds to the devolatilization of lignocellulosic components ends with biochar formation, as reported by several authors [49, 50].

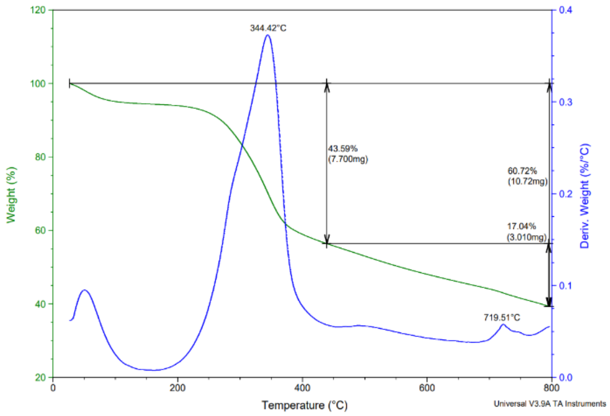

Figure 2: TG – DTG curves for the pyrolysis of pumpkin seeds at heating rate = 10 ^{o}C.min^{-1}

The beginning and end temperatures of that step as well as the peak DTG temperature could be determined at each heating rate. The results are summarized in Table (*2*.

The small peaks appearing short of 500 ^{o}C and 720 ^{o}C are probably associated with the cracking of the formed char and devolatilization of any remnant lignin [3, 51].

Table (2): Characteristic temperatures of devolatilization of lignocellulosic components

Heating rate (^{o}C.min^{-1})	5	10	15	20
Initial temperature (^{o}C)	200.1	220.5	228.0	258.5
Peak temperature (^{o}C)	329.5	344.4	360.8	369.5
Final temperature (^{o}C)	379.6	399.5	405.0	420.0

3.4. Fraction Conversion (α)

For all heating rates (5, 10, 15, and 20 ^{o}C.min^{-1}), Equation (1) was applied to calculate the conversion fraction (α) as a function of temperature. The results are displayed in Figure 3, where it appears that all four curves show a similar sigmoid trend.

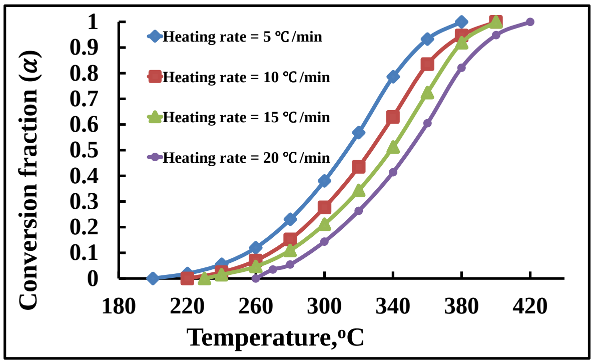

Figure 3: Conversion-temperature curves

3.5. Kinetics of Pyrolysis

Kinetic analysis of the pyrolysis process allows the determination of two parameters necessary to the design of a suitable bioreactor, namely, activation energy (E) and the pre-exponential term (A). The importance of calculating their values has been recently outlined by Vyazovkin [52].

3.5.1. Application of the Kissinger - Asahira -Sunoze (KAS method)

Following Equation (4), plots of $\ln\frac{\beta}{T^2}$ against $1/T$ were carried out for values of conversion α ranging from 0.1 to 0.8, the results being shown in

Figure *4*. The values of activation energy obtained are summarized in Table (*3*, where it appears that increased conversion causes a corresponding increase in the value of activation energy. The average activation energy was calculated and found to be equal to 104.00 kJ.mol^{-1}.

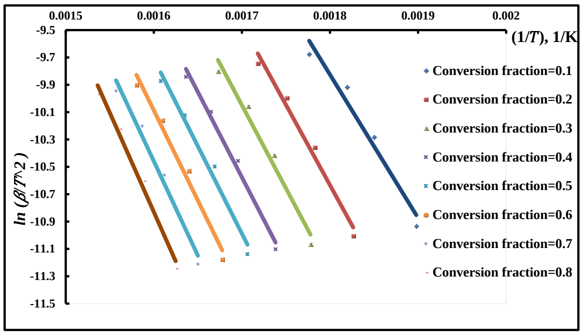

Figure 4: KAS plots for the main step in the pyrolysis of the pumpkin seeds

This value fairly checks with similar values obtained for the devolatilization of lignocellulosic materials from sunflower seeds (72.4 – 170.2 kJ.mol^{-1}) [53] but is higher than the activation energy of jatropha seeds (60 to 65 kJ/mol^{-1}) [54].

Table (3): Activation energy using the KAS method

Conversion	0.1	0.2	0.3	0.4
***E* kJ.mol^{-1}**	86.15	96.81	100.37	102.86
R^2	0.963	0.975	0.978	0.976
Conversion	0.5	0.6	0.7	0.8
***E* kJ.mol^{-1}**	105.46	108.90	112.95	118.38
R^2	0.983	0.980	0.984	0.989

3.5.2. Application of the Flynn-Wall-Ozawa Method

Figure 5 illustrates the FWO plots for pumpkin seeds for values of conversion ranging from 0.1 to 0.8. The slopes of the $\frac{1}{T} - \log\beta$ straight lines obtained were determined and values of activation energy were calculated (Table (*4*). The steady increase in activation energy following an increase in conversion is apparent. The average value of E = 108.28 kJ.mol^{-1}, a value very close to that obtained by the KAS method.

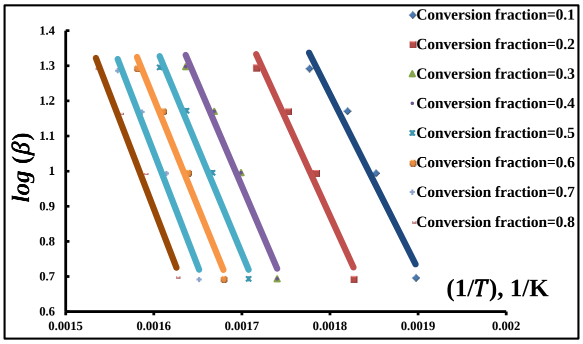

Figure 5: FWO plots for the main step in the pyrolysis of the pumpkin seeds

Table (4): Activation energy using the FWO method

Conversion	0.1	0.2	0.3	0.4
***E* kJ.mol^{-1}**	90.53	100.99	104.61	107.18
R^2	0.970	0.979	0.982	0.981
Conversion	0.5	0.6	0.7	0.8
***E* kJ.mol^{-1}**	109.83	113.26	117.25	122.57
R^2	0.986	0.984	0.986	0.991

3.5.3. Application of the Friedman method

Application of the Friedman technique required substituting $\frac{\Delta\alpha}{\Delta T}$ for $\frac{d\alpha}{dT}$ by using intervals of $\Delta\alpha = 0.025$ on the conversion span 0.2-0.8. The plots of $\ln \beta.\frac{d\alpha}{dT}$ against $\frac{1}{T}$ at the different values of α are illustrated in Figure 6 while Table (*5* shows the values of activation energy and the logarithm of the pre-exponential factor in each case. To calculate the values of $ln\,A$, it was necessary to assume a reaction mechanism to use a

Table (1) was thus assumed with a characteristic kinetic function $f(\alpha) = 1 - \alpha$ [55].

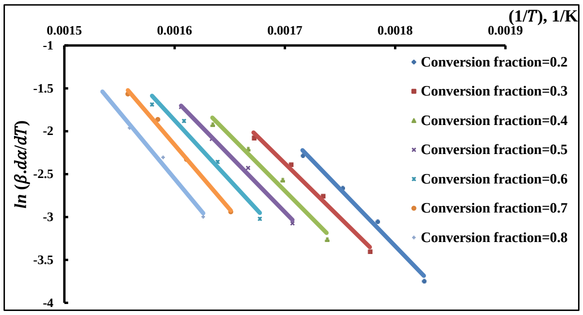

Figure 6: Friedman plots for the main step in the pyrolysis of the pumpkin seeds

In this expression the mean activation energy was found to be slightly higher than that calculated by the two previous methods $E = 116.08$ kJ.mol^{-1}.

Table (5): Activation energy and *ln A* using the Friedman method

Conversion	0.2	0.3	0.4	0.5
***E* kJ.mol^{-1}**	110.535	106.489	108.36	111.381
R^2	0.989	0.985	0.975	0.991
ln A	20.843	19.806	20.011	20.549
Conversion	0.6	0.7	0.8	
***E* kJ.mol^{-1}**	118.535	124.402	132.847	
R^2	0.971	0.991	0.995	
ln A	21.899	23.047	24.636	

On the other hand, the application of the kinetic compensation effect proved to yield a straight line when values of $ln\,A$ were plotted against E (Figure 7). The fact that the R^2 value is close to unity seems to

convenient form of the kinetic function $f(\alpha)$. A first-order reaction (Mechanism F1 in

validate the first-order assumption for the mechanism of the reaction.

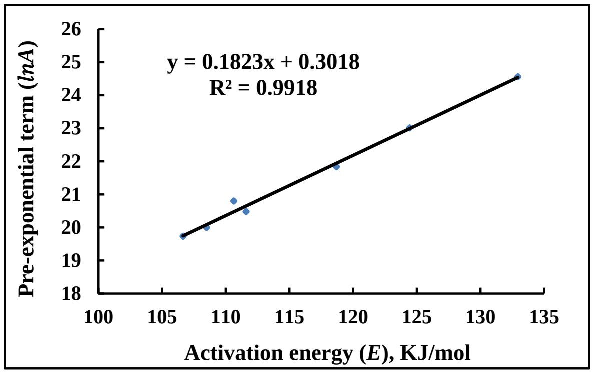

Figure 7: Linear plot of *ln A* against *E*

Finally, Figure 8 displays the variation of activation energy with conversion for all three methods used. It is clear that, except for a slight discrepancy regarding the Friedman plot at the early stages of conversion, all three models indicate an increase in activation energy following increasing conversion.

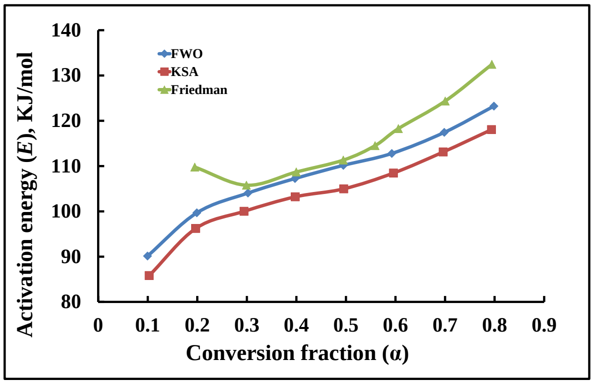

Figure 8: Variation of activation energy with conversion fraction

This phenomenon has been revealed by many authors in studying the pyrolysis of biowaste, although the values of activation energy tended to decrease as conversion levels approached unity [56, 57].

3.6. Conclusion

Pumpkin seeds were exposed to thermal analysis under inert gas flow (N_2). Thermogravimetric curves showed the presence of a significant DTG peak during the process ending with the formation of biochar at all examined heating rates (5, 10, 15, and 20 $^{o}C.min^{-1}$).

Three different iso-conversional kinetic models were used to determine the activation energy of the main degradation reaction. The mean values of activation energy determined by each method are summarized in Table (***6***. In all three models, the activation energy tended to increase with increased conversion.

Table (6): Activation energy values obtained using different kinetics models

Method	KAS	FWO	Friedman
Average E, kJ.mol^{-1}	104.00	108.28	116.08

Moreover, the calorific value of dry seeds and the resulting biochar were determined using a bomb calorimeter and found to equal 16080 kJ.kg^{-1}, respectively, qualifying this waste as a potential biofuel.

Since pumpkin seeds are mostly discarded as waste, it seems profitable to use them, either directly as biofuel or to obtain biochar through pyrolysis, the design of the pyrolysis reactor relies on the kinetic parameters determined in the present study.

Symbols

A	Pre-exponential factor
E	Reaction activation energy (J.mol^{-1})
m	Mass at any time during the reaction (mg)
m_0	Initial reaction mass (mg)
m_f	Remaining mass at the end of reaction (mg)
t	Time, s
T	Temperature (K)

Greek letters

α	Decomposition reaction fraction conversion
β	Heat of rating ($^{o}C.min^{-1}$)

Abbreviations

KAS	Kissinger-Asahira-Sunoze
FWO	Flynn-Wall-Ozawa

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Data availability All data generated or analyzed during this study are included in this published article.

Declarations

Ethics approval: Not applicable.

Competing interests: The authors declare no competing interests.

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