

Thermo-kinetic Combustion Performance of Date Palm Fronds: Isothermal TGA Study and Kinetic Modeling

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Abstract

This study investigates the characteristics of the Sudanese date palm frond (DPF) residues as potential fuel and available agricultural waste in arid regions. The effects of combustion temperatures (800, 900 and 1000 °C) on thermal behaviour, reactivity, thermo-kinetics, and combustion performance were examined via thermogravimetric analyzer (TGA). The shrinking core models (SCM) or phase boundary-controlled reactions (R2 and R3) and homogeneous model (HM), or the first-order chemical reaction (O1) through the Coats–Redfern method, were applied to estimate the kinetic parameters. As well as to find the optimum reaction model. The achieved results explored that, DPF showed high volatile matter content (69.84%), high calorific value (15.92 MJkg⁻¹), high oxygen content (54.31%) and low fixed carbon (12.93%) making it comparable to other common biomass fuels. The DPF combustion process occurred at two stages, the first one was primary devolatilization at temperature region of 146 - 364 °C, While the last stage was the char combustion occurred between 402 - 478 °C. The maximum weight loss rate and reactivity were found to be proportional to the temperature at stage 1 and inversely at stage 2. While, the thermodynamics, kinetics, combustion ignition and combustion performance parameters decreased as the combustion temperature increased for both reaction stages. The reactivity was improved by 2.4 - 17.99% at stage 1 and decreased by 6.36 - 9.64% at stage 2. Among the kinetic models, model R2 provided Lowest values of thermo-kinetics parameters for all investigation temperatures. However, model O1 showed the highest values. According to Lowest values of activation energies obtained, the model R2 was best one.

Key words-Date palm frond, combustion, reactivity, kinetics, thermodynamic parameters.

I. INTRODUCTION

The world's growing energy demand and environmental concerns are driving research into renewable energy sources[1]. Biomass, especially agricultural residues, offers a promising alternative to fossil fuels[2]. Interest in renewable energy resources has increased due to industrialization, population growth, environmental regulations, uncertain fossil fuel prices and supply. The utilization of biomass for energy production reduces dependency on oil, with the advantages of economic and environmental benefits[3]. Biomass is an organic material such as sugar cane, straw, wood waste, date palm fronds, and different varieties of agricultural and industrial waste products[4]. Globally, biomass production is estimated to be about 220 million tons per year, which could be used for energy generation[5]. Date palm frond is the branching part of date palm trees. According to the Food and Agriculture Organization, 1.14 million hectares were cultivated, and the tree sheds 14-20 kg annually. This could achieve up to 3.4 million tons of date palm fronds annually, depending on tree density per hectare. Sudan ranks in 8th place worldwide in date production. However, due to the lack of technologies, the fronds waste is burned traditionally for cooking and other uses[6]. The application of conversion process technologies (Pyrolysis, Gasification & combustion) of biomass for power generation requires a proper understanding of the thermal properties and reaction kinetics of

biomass. However, the knowledge of thermal characteristics and reaction kinetics may help to better understand pyrolysis, combustion and gasification processes at an industrial, and also necessary for the design and operation of conversion systems[7]. Recent researches were conducted the conversion processes of biomass such as Cardoso et al.[8] studied thermal decomposition of sorghum bagasse and tobacco waste at non-isothermal thermogravimetric conditions. The activation energy was -103.94 and 120.01 kJ/mol for tobacco waste and sorghum bagasse with Ozawa method, respectively. However, for the Starink method, these values were -135.95 and 148.91 kJ/mol for tobacco waste and sorghum bagasse, respectively. For the independent parallel reaction model, activation energy values were in the range of 39.7–272.0 and 35.7–220.0 kJ/mol for tobacco waste and sorghum bagasse respectively. Okoroigwe et al.[9] studied the devolatilization characteristics and kinetics of Gmelina, Mango, Neem, and Tropical Almond woods under synthetic air conditions at the heating rate of 30°C/min. Non-isothermal thermogravimetric analysis at a temperature of 30 and 750°C under synthetic air was used. The samples were found to follow two-stage reactions at a temperature range of 200–500°C, which indicated volatile oxidation and char combustion. The weight losses were 2.20, 1.50, 1.25 and 1.60 for Gmelina, Mango, Neem and Tropical almond woods, respectively, and occurred at peak temperatures of 310, 322, 320 and 320°C. At the volatile oxidation stage,

the activation energies with the Arrhenius model are 125,108, 142 and 113 KJ/mol, respectively, for Gmelina, Mango, Neem and Tropical almond woods, while at the char combustion stage, these values were 257, 210, 281 and 345 KJ/mol, respectively. However, few studies focus on the date palm frond thermal conversion process such as Jeguirim et al.[10] examined the behaviour of date palm leaflets, date palm rachis, date palm trunk, date stones, and fruitstalk prunings using thermogravimetric analyzer under non-isothermal conditions. Ultimate and proximate analyses showed that date stones have high energy density among the samples. The thermal degradation of the samples was found to be similar, except date stones. Date palm trunk was the most reactive at both oxidative atmosphere and pyrolysis, whereas a date stone was less reactive. The activation energy for the tested samples was in the range of 45.2– 89.1 and 49.6– 110.7 kJ mol^{-1} for pyrolysis and oxidation respectively. Moreover, in spite of significant on-going research of the thermal conversion technologies such as pyrolysis, gasification and combustion for production of energy and fuels, there is no information on the characteristics, reactivity, behaviour, kinetic, thermodynamics, combustion performance and ignition of the Sudanese date palm frond. From these points, this study conducts to investigate the characteristics and the effect of combustion temperature on the reactivity, behaviour, thermo-kinetic parameters and combustion performance and ignition of the Sudanese date palm frond during combustion processes using thermogravimetric analyzer (TGA). The shrinking core models (SCM) or phase boundary-controlled reactions (R2 and R3) and homogeneous model (HM), or the first-order chemical reaction (O1) through the Coats Redfern method, were applied to estimate the kinetic parameters. As well as to find the optimum reaction model.

II. MATERIAL AND METHODS

A. Materials and sample preparation

In this study, date palm fronds were used. Proximate and ultimate analyses were conducted to obtain the properties of the materials. TGA-2000 (Navas Instruments, Spain) and a Euro-CA 3000 (HEKAtech, Italy) elemental analyzer were used. Parr 6300 automatic isoperibol calorimeter was used to estimate the calorific values. While the ash was analyzed by X-ray fluorescence (XRF) technique.

B. Thermogravimetric analysis

The thermogravimetric analyser (TGA, NETZSCHSTA 449/F3) was used to investigate the combustion of date palm frond under isothermal conditions. A temperature of 800, 900 and 1000°C at a heating rate of 20 °C min^{-1} was studied. A 5 mg sample was used to avoid the mass transfer effect. The experiments were conducted three times, and the average values were used.

C. Reactivity and conversion estimation

The conversion degree (X) was estimated using Equation(1).

$$X = \frac{w_i - w_t}{w_i - w_f} \quad (1)$$

where w_i is the initial mass sample (mg), w_t is the mass sample at a specific time (min), and w_f is final mass sample at the end of the combustion process. The combustion reactivity was calculated based on the method proposed by Okoroigwe[11] and Edreis et al[12] using Equation(2).

$$R_m = 100 \sum \frac{DTG_{max}}{T_{DTG_{max}}} \quad (2)$$

where R_m is the mean reactivity (% $^{\circ}C^{-1}min^{-1}$), DTG_{max} is the maximum weight loss rate (% min^{-1}) and $T_{DTG_{max}}$ is the corresponding peak temperature ($^{\circ}C$). The reactivity indexes $R_{0.1}$, $R_{0.5}$, and $R_{0.9}$ were calculated using Equations(3,4 and 5) respectively, at different conversion degrees (10%,50%, and 90%)[13][14].

$$R_{0.1} = \frac{0.1}{t_{0.1}} \quad (3)$$

$$R_{0.5} = \frac{0.5}{t_{0.5}} \quad (4)$$

$$R_{0.9} = \frac{0.9}{t_{0.9}} \quad (5)$$

where $t_{0.1}$, $t_{0.5}$, and $t_{0.9}$ are the time (min) required to reach the carbon conversion of 10%, 50%, and 90% respectively.

D. Ignition and combustion analysis

The combustion performance, such as combustion index (S) and ignition index (D) was investigated using Equations(6 and 7), respectively[11][15][16][17].

$$S = \frac{R_{max} \cdot R_a}{T_i^2 \cdot T_b} \quad (6)$$

$$D_i = \frac{R_{max}}{t_i \cdot t_{max}} \quad (7)$$

where R_{max} is the maximum combustion rate (% s^{-1}), t_{max} is the time corresponding to the maximum combustion rate (s), t_i is the time corresponding to the ignition temperature (s), R_a is the average mass loss rate (% s^{-1}), T_i and T_b are the ignition and the burnout temperature ($^{\circ}C$), respectively.

E. Kinetic study

The TGA data were used to estimate the kinetic studies of the combustion process. Methods such as the shrinking core models (SCM) or phase boundary controlled reactions (R2 and R3), the homogeneous model (HM), or the first-order chemical reaction (O1) through the Coats–Redfern method, were applied to estimate the kinetic parameters such as activation energy (E) and pre-exponential factor (k_o). The overall

reaction rate (dX/dt) of a solid-gas reaction was calculated using Equation(8).

$$\frac{dX}{dt} = kf(X) \quad (8)$$

where k is the reaction rate constant, referred to the reasonable model of the reaction mechanism. Assuming that, the partial pressure of the combustion agent remains constant during the combustion process. Based on the temperature, the combustion rate can be described using the Arrhenius Equation(9).

$$k = k_o e^{\frac{-E}{RT}} \quad (9)$$

where k_o , E and R are the pre-exponential factor (min^{-1}), activation energy (kJmol^{-1}), and universal gas constant, respectively. The activation energy and pre-exponential factor were related to the reactivity and the material structure, respectively. Reactions with large activation energy require a long reaction time or a higher temperature[12][18]. The kinetic studies of the DPF combustion were conducted using SCM and HM through Coats–Redfern equation[19], using Equation(10)[20].

$$\ln\left[\frac{g(X)}{T^2}\right] = \ln\left[\frac{k_o R}{\beta E}\left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{RT} \quad (10)$$

where $g(X)$ is the reaction model mechanism used for the calculation of shrinking core models (SCM) and homogeneous model (HM)[21][22][23][24]. It is obvious that in Equation(10) the expression $\ln\left[\frac{k_o R}{\beta E}\left(1 - \frac{2RT}{E}\right)\right]$ is basically constant for the value of E in the combustion temperature range[25][26]. Therefore, the left side of Equation(10) is plotted versus $1/T$ and a straight line was found. Values of E and k_o were obtained through the slope of the straight line and the intercept of Equation(10), respectively. The HM assumes a homogeneous reaction throughout the particle[24]. The reaction mechanism of the first-order chemical reaction represents the process controlled by the chemical reactions, rather than the effect of intra-particle diffusion, and the reaction happens simultaneously in the whole particle. However, compared to diffusion, the chemical reaction is much faster, therefore, the model R2 and R3 assume the process is controlled by diffusion, rather than the chemical reaction. Moreover, in the SCM the reaction occurs initially at the external surface of the particle and moves gradually to the inside.

F. Thermodynamic parameters

Thermodynamic parameters such as enthalpies change ($\Delta H^\circ, \text{kJmol}^{-1}$), Gibbs free energies ($\Delta G^\circ, \text{kJmol}^{-1}$) and entropies change ($\Delta S^\circ, \text{mol}^{-1}\cdot\text{K}^{-1}$) were calculated using Equations(11,12 and 13) respectively[27][28].

$$\Delta H^\circ = E - RT \quad (11)$$

$$\Delta G^\circ = E + R.T_m.\ln\left(\frac{K_B.T_m}{h.k_o}\right) \quad (12)$$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T_m} \quad (13)$$

where, K_B is Boltzmann constant ($1.38 \times 10^{-23} \text{ JK}^{-1}$), h is Planck constant ($6.626 \times 10^{-34} \text{ Js}$), T is the peak temperature (K), The change of enthalpies (ΔH°) demonstrates the energy difference between the activated complex agrees with activation energies and the reagent[28]. However, the values of Gibbs free energies (ΔG°) showed the growth of overall energy[27]. Whereas, the ΔS° measures random energy and matter in the DPF combustion[27].

III. RESULTS AND DISCUSSION

A. Characterization of date palm frond

The proximate and ultimate analyses of date palm frond are shown in Table(I), while the ash analysis was presented in Table(II). Higher contents of hydrogen, carbon, oxygen, and volatiles were observed in the date palm frond; however, nitrogen and sulfur were lower. The higher heating value was found 15.92 MJkg^{-1} . Oxygen content was 54.31%; this is considerably higher than that of coal and most of biomasses, hence, a small amount of stoichiometric air could be required for the combustion. The higher value of volatiles (69.84%) indicated its suitability for gasification, pyrolysis, and combustion. However, the lower fixed carbon of 12.93% was due to low lignin content in the samples[29]. The ash content was found comparable with that of other biomass[30]. Therefore, DPF found appropriate fuel for continuous thermal processes because of the ash removal and handling problem.

B. Combustion behaviour and reactivity analysis

The DPF combustion process occurred at two stages, the first one was primary devolatilization at temperature region of 146 - 364 °C, while the last stage was the char combustion occurred between 402 - 478 °C. Combustion TG and DTG against the temperature are shown in Figures(1 and 2) respectively. However, the combustion characteristics of date palm frond are listed in Table(III). It was found that, the DPF combustion process occurred at two stages, the first one was primary devolatilization, at temperature ranges of (146.83 - 364.11), (152.75 - 360.23), and (152.75 - 360.23 °C), whereas the last stage was the char combustion occurred at temperature ranges of (402.87 - 472.86), (416.55- 464.69) and (408.80 - 478.56 °C) for the temperatures of 800, 900 and 1000 °C, respectively. The corresponding maximum weight losses rates were 5.76, 6.56 and 7.62% min⁻¹ for the first stage and 14.92, 14.33 and 12.58 % min⁻¹ for the second stage at temperatures of 800, 900 and 1000 °C, respectively. This indicated that the temperature is proportional to combustion mass loss at stage 1 and inversely at stage 2. However, Mejdí et al[10] found lower values of conversion and reaction rate with date palm residues. The shifting of TG and DTG curves to higher temperatures was due to heat and mass transfer delay that affected the decomposition rate. The reactivity index against temperature is shown in Figures(3 and 4) respectively. The reactivity found improved in the range of 2.4 - 17.99% at

stage 1 and decreased by 6.36 – 9.64% at stage 2 for the investigated temperature.

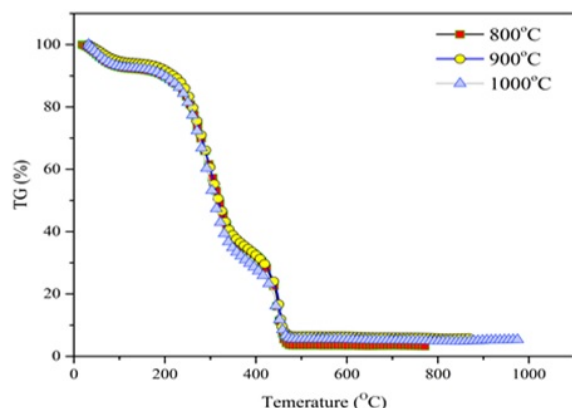


Fig. 1: TG of date palm frond against combustion temperature.

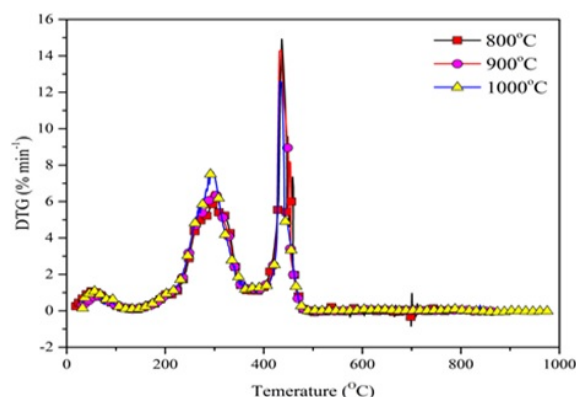


Fig. 2: DTG of date palm frond against combustion temperature.

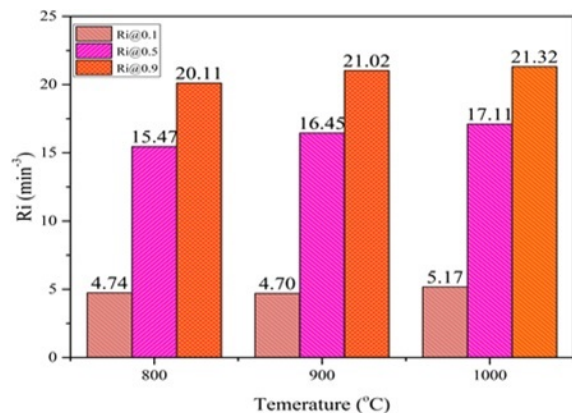


Fig. 3: Reactivity index against temperature.

C. Ignition and burnout temperature

Combustion characteristic of date palm frond against temperature is shown in Figure(5). Ignition and burnout temperatures are defined according to the Li et al.[31] method.

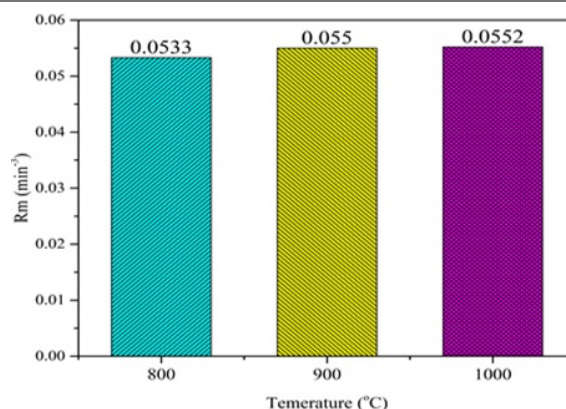


Fig. 4: Mean reactivity against temperature.

A vertical line was drawn from point (A) until reached the slope line at B see Figures(5,6 and 7). At point B a tangent line was drawn to meet point C. Another vertical line was drawn from point C and meets the cross-X axis at point D. The equivalent temperature at point D is the ignition temperature. The burnout temperature (T_b) was determined as the identical temperature of non-weight loss in the TG curve[31]. The ignition characteristics of date palm frond are listed in Table(IV). From the Figures(5,6 and 7), it's observed that the higher the combustion temperature, the lower the ignition temperature and the time see Table(IV). Vamvuka et al.[32] in their studies showed higher ignition and combustion time compared to our results. This was due to higher moisture content in sewage sludge. In contrast, Li et al.[31] obtained lower ignition and combustion times with waste tyres due to the hydrocarbon content. However, the burnout temperature change was found to be insignificant.

Tem.: combustion temperature ($^{\circ}\text{C}$); T_i : ignition temperature ($^{\circ}\text{C}$); t_i : time corresponding to ignition temperature (s); R_{max} : maximum combustion rate ($\% \text{ s}^{-1}$); T_{max} : temperature corresponding to maximum combustion rate ($^{\circ}\text{C}$); t_{max} : time corresponds to maximum combustion rate(s); R_a : average mass loss rate ($\% \text{ s}^{-1}$); T_b : burnout temperature ($^{\circ}\text{C}$); t_b : time corresponding to burnout temperature (s); D: ignition index; S: combustion index.

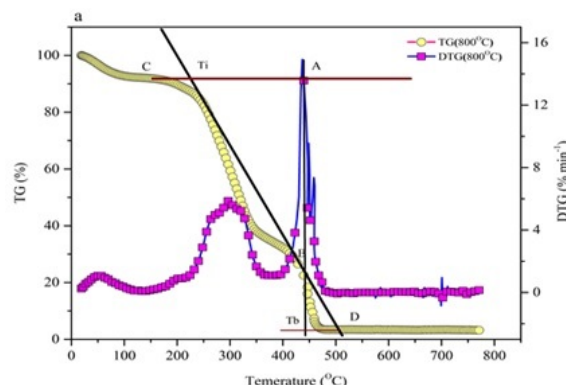


Fig. 5: Ignition and burnout temperatures of DPF at 800 °C.

TABLE I: Proximate and ultimate analyses and heating value of date palm frond.

Proximate analysis (w%) ^a				Ultimate analysis (w%) ^b					Heating Value
Ash	VM	FC	M	C	H	O ^c	N	S	HHV(MJ/kg) ^b
5.97	69.84	12.93	11.25	39.66	5.47	54.31	0.22	0.34	15.92

^aAs received basis.;^b as Dry ash basis.;^c Calculated by the difference

TABLE II: Ash analyses of date palm frond.

Mg	Si	P	S	CL	K	Ca	Fe	MgO	SiO ₂	P ₂ O ₅	SO ₃	Cl ₂ O	K ₂ O	CaO	Fe ₂ O ₃
8.61	4.22	4.26	3.94	21.78	42.42	14.55	0.23	12.35	7.33	7.67	7.51	19.31	33.38	12.26	0.19

TABLE III: Combustion characteristics of date palm frond.

Stage (1)					Stage (2)				
Combustion Temperature	Temperature Range	DTG _{max}	t _{max}	T _{max}	Temperature Range	DTG _{max}	t _{max}	T _{max}	R _m * 10 ²
°C	°C	%min ⁻¹	min	°C	°C	%min ⁻¹	min	°C	% min ⁻¹ °C ⁻¹
800	146.83-364.11	5.76	31.1	300.67	402.87-472.86	14.92	43.6	437.67	5.33
900	152.75-360.23	6.56	29.1	296.96	416.55-464.69	14.33	41.9	435.49	5.50
1000	142.95-360.23	7.62	28.7	290.84	408.80-478.56	12.58	41.9	431.82	5.52

DTG_{max}: maximum weight loss rate (% min⁻¹); Tmax (°C) and tmax(min): temperature and time corresponding to maximum weight loss rate; R_m: mean reactivity (% min⁻¹ °C⁻¹).

TABLE IV: Ignition characteristics of date palm frond.

Temperature	T _i	t _i	R _{max}	T _{max}	t _{max}	Ra	T _b	t _b	D * 10 ⁷	S * 10 ¹⁰
800	223	1440	0.248	436	2616	0.0208	444	2640	0.75	2.34
900	220	1320	0.238	435	2514	0.0182	441	2520	0.71	2.03
1000	217	1320	0.209	431	2514	0.0163	436	2520	0.63	1.67

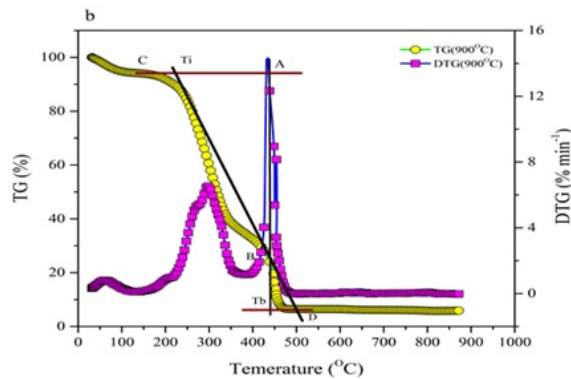


Fig. 6: Ignition and burnout temperatures of DPF at 900°C.

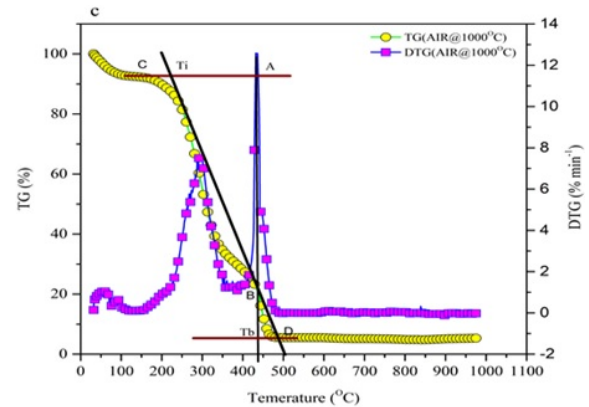


Fig. 7: Ignition and burnout temperatures of DPF at 1000°C.

D. Kinetic analysis of date palm frond

The kinetic parameters and correlation coefficients obtained by the phase boundary-controlled reaction (R2 and R3) and first order chemical reaction models (O1) are presented in Table(V). while the plots of $\ln[g(x)/T^2]$ versus $1/T$ with correlation coefficients values obtained by models O1, R 2 and R 3 were showed in Figures(8,9 and 10), respectively. From Table(V) it was found that, the phase boundary-controlled reaction showed the lowest values of activation energy and pre-exponential factor; however opposite trend was observed with first order chemical reaction model. The higher activation energy value achieved was 72.54 and 222.24 kJ/mol obtained by O1 model at 800 °C for stage 1 and 2, respectively, whereas the lowest value of 51.80 and 181.98 kJ/mol was obtained by

R2 model at 1000 °C. The reaction mechanism of the model O1 (HM), can be explained as follows: the reaction controlled by the chemical, the effect of intra-particle diffusion can be ignored, and the reaction happened simultaneously in the whole particle. However, in models R2 and R3 (SCM), the reaction is controlled by the diffusion because the reaction happened very fast, and the resistance of diffusion is much higher than the chemical reaction[33]. The higher pre-exponential factor values achieved were $1.76E+06\text{min}^{-1}$ and $2.14E+16\text{min}^{-1}$ obtained by O1 model at 800 °C, whereas the lowest values were $5.38E+03\text{min}^{-1}$ and $5.72E+13\text{min}^{-1}$ obtained by R2 model at 1000 °C for stage 1 and stage 2 respectively. The correlation coefficients obtained by O1 model were in the range of (0.996 - 0.998) and (0.981- 0.998) for stage 1 and

stage 2 respectively. The correlation coefficient range values were (0.973- 0.995) for stage 1 and (0.991- 0.996) for stage 2 obtained by model R2, while model R3 provided (0.991- 0.997) and (0.913- 0.994) for stage1 and stage2 respectively. Among the investigated models, O1 model best fitted the experimental data. Furthermore, it is found that increasing the combustion temperature reduces the activation energy and pre-exponential factor. It's concluded that high combustion temperature was more reactive for date palm frond compared to those of low combustion temperature; R2 was the most reactive model. Similar results were reported by[34][35][36][37].

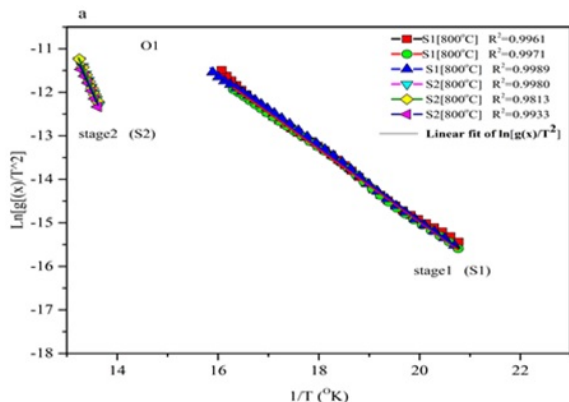


Fig. 8: Plots of $\ln[g(X)/T^2]$ versus $1/T$ with correlation coefficients values obtained by O1 model.

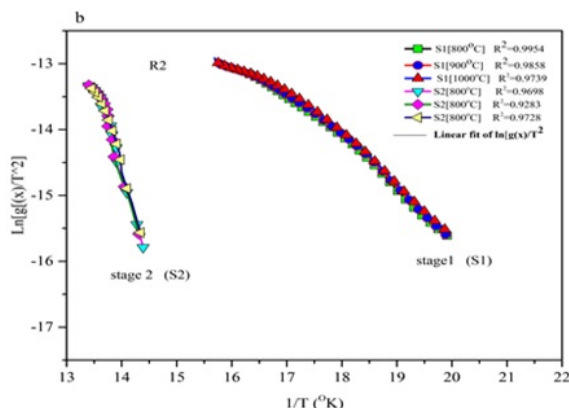


Fig. 9: Plots of $\ln[g(X)/T^2]$ versus $1/T$ with correlation coefficients values obtained by R 2 model.

E. Thermodynamic parameters analysis

Thermodynamic parameters such as enthalpy, Gibbs's free energy and entropy are presented in Table(6). Enthalpy is defined as energy absorbed or released from the reaction at constant pressure. Date palm frond decompose in two stages. From Table 6, the higher enthalpy change values at stage 1 were 67.77, 66.39 and 65.39kJ/mol for 800, 900 and 1000, obtained by O1 model respectively. Whereas the lowest values were 54.63, 51.09 and 47.06 kJ/mol for 800, 900 and 1000, obtained by R2 model, respectively. At stage 2 the higher enthalpy change values were 216.34, 213.15 and

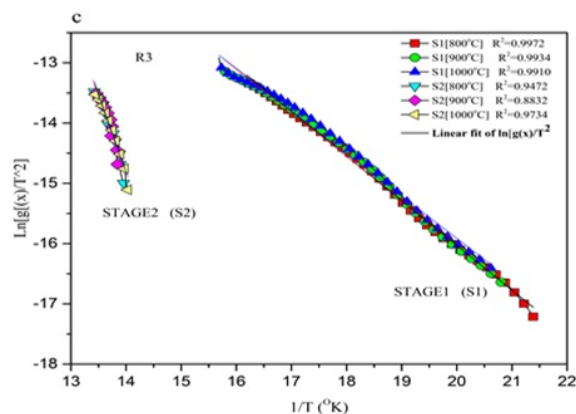


Fig. 10: Plots of $\ln[g(X)/T^2]$ versus $1/T$ with correlation coefficients values obtained by R 3 model.

205.26 kJ/mol for 800, 900 and 1000, obtained by O1 model, respectively. However, the lowest values were 213.26 ,210.93 and 200.47 kJ/mol for 800, 900 and 1000, obtained by R2 model respectively. Gibbs free energy values were similar among the combustion temperatures. The high Gibbs free energy values were 154.96 and 194.80 obtained by R3 model for stage 1 and stage 2, respectively. Whereas the low Gibbs free energy values were 147.31 and 184.15 obtained by model O1 and model for stage 1 and stage 2, respectively. Among the models investigated, R2 showed the lowest enthalpy change values, but the lowest Gibbs free energy value was obtained by O1 model for the entire combustion temperature studied. However, an insignificant entropy change was observed for the tested models. Comparison with different biomass studies from the literature is presented in Table(7).

The thermal behaviour of DPF was similar to other biomasses studied by some researcher such as[38][39][40], but the DPF was occurred at lower temperature ranges, this issue is most important for kinetics, combustion ignition and performance. In addition, the activation energies obtained at the both stages devolatilization and char combustion were lower compared to previous studies of [38][39][40]. Hence, it concluded that Sudanese DPF is the most reactive biomass waste.

IV. CONCLUSION

This study systematically evaluates the thermo-kinetics and combustion behaviour and performance of the Sudanese date palm fronds (DPF) using thermogravimetric analyzer (TGA) at different temperatures. The results confirm that, DPF with high volatile matter (69.84%), high calorific value (15.92 MJ kg^{-1}), high oxygen (54.31%) and low fixed carbon (12.93%) comparable to other biomass sources, and favorable kinetic parameters, is a technically viable feedstock for energy generation. The DPF combustion occurred at two stages, devolatilization stage at temperature region of (146 - 364 °C), due to the decomposition of hemicellulose and cellulose. and char combustion stage at temperature region of (402 - 478 °C) due to the oxidation of remaining fixed carbon and lignin. The reactivity was improved by 2.4 -

TABLE V: Kinetic parameters of date palm frond.

		Stage 1			Stage 2		
		Parameters					
Samples	Models	E	K_0	R^2	E	K_0	R^2
800°C	O1	72.54	1.76E+06	0.996	222.24	2.14E+16	0.998
	R2	59.40	3.17E+04	0.995	219.16	2.26E+15	0.996
	R3	61.66	3.82E+04	0.997	221.60	1.50E+16	0.994
900°C	O1	71.12	1.20E+06	0.997	219.04	1.57E+16	0.981
	R2	55.82	1.31E+04	0.985	213.15	8.20E+14	0.911
	R3	60.05	2.60E+04	0.993	216.82	9.01E+15	0.913
1000°C	O1	70.13	1.00E+06	0.998	211.16	3.23E+14	0.993
	R2	51.80	5.38E+03	0.973	181.98	5.72E+13	0.994
	R3	58.57	1.91E+04	0.991	210.09	2.22E+15	0.993

E : Activation Energy (kJ mol^{-1}), K_0 : Pre-exponential factor (min^{-1})

TABLE VI: The thermodynamic parameters of date palm frond.

Temperature	Model	Stage 1			Stage 2		
		ΔH°	ΔG°	ΔS°	ΔH°	ΔG°	ΔS°
800	O1	67.77	147.57	-0.13909	216.34	192.79	0.03318
	R2	54.63	153.59	-0.17249	213.26	194.66	0.02620
	R3	56.89	154.96	-0.17094	215.70	194.80	0.02945
900	O1	66.39	147.31	-0.14221	213.15	184.15	0.04093
	R2	51.09	153.38	-0.17977	207.26	189.25	0.02541
	R3	55.32	154.37	-0.17407	210.93	192.13	0.02653
1000	O1	65.39	147.43	-0.14370	205.26	191.90	0.03444
	R2	47.06	153.89	-0.18719	200.47	192.61	0.02067
	R3	53.83	154.65	-0.17666	204.19	194.16	0.02461

ΔH° : Enthalpy change, ΔG° : Gibbs free energy, ΔS° : Entropy change

TABLE VII: Comparison of different biomass activation energy and thermodynamic properties.

Material	E (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔG° (kJ mol^{-1})	ΔS° ($\text{kJ mol}^{-1} \text{K}^{-1}$)	Ref
Date palm front	51- 222	47-216	147-194	-0.179 - +0.0409	This study
Date palm surface fibers	96-113	93-108	205-280	-0.30 -0.32	[38]
Raw rice husk	218-220	145 - 214	156 - 226	-0.021 - +0.041	[39]
Ficus nitida wood	171-248	170 - 235	170 - 220	-0.0053 - +2.28	[40]

17.99% at stage 1 and decreased by 6.36 - 9.64% at stage 2. While the ignition and burnout temperatures decreased by Model R2 provided the lowest E , ΔH° , ΔG° , and ΔS° with values of $51.80 \text{ kJ mol}^{-1}$, $47.06 \text{ kJ mol}^{-1}$, $153.89 \text{ kJ mol}^{-1}$, and $-0.1872 \text{ kJ mol}^{-1} \text{K}^{-1}$ for stage 1 and $181.98 \text{ kJ mol}^{-1}$, $200.47 \text{ kJ mol}^{-1}$, $192.61 \text{ kJ mol}^{-1}$, and $0.02067 \text{ kJ mol}^{-1} \text{K}^{-1}$ for stage 2, which were achieved at 1000°C . these values were lower than that obtained by previous studies,[38][39][40] as mentioned in Table(VI). Model R2 was the best one since provided lowest activation energy values. According to higher correlation coefficient of fitting (R2) all models were successfully utilized to predict the experimental data since provided highest R2 values ($> 99\%$). The kinetics provides crucial insights for designing efficient thermochemical conversion systems. The Future research should focus on combustion emissions, such as CO_2 , CO , NO_x , and SO_2 .

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