

THERMAL STUDY OF DATE KERNELS VIA TG AND DTA

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Thermal analyses was performed on Egyptian date kernels to assess the value of the products as possible sources of valuable compounds. It also furnished technical data necessary for determination of the optimum degree of temperature for the design and operation of units for the pyrolytic processing of date kernels.

Two different sets of experiments were carried out, involving thermogravimetry (TG) and differential thermal analysis (DTA).

The TG results revealed a purely kinetically controlled, first-order reaction. The activation energy and the Arrhenius constant were 8.17 kJ/mol and 0.0115 min^{-1} , respectively.

The DTA results indicated the nature of the reactions involved in the pyrolysis and the corresponding products.

Numerous methods have been found for the utilisation of agricultural wastes, i.e. via acid and enzymatic hydrolysis, alkaline degradation, fermentation, and low-temperature pyrolysis, or as thermal energy sources [1–10].

Date kernels have not been studied thoroughly previously. The useful products in the kernels may be released by pyrolysis and a knowledge of the reaction kinetics involved is imperative.

Again, it would be highly desirable to obtain both a quantitative and qualitative picture of the various products which could be obtained from the kernels. Such information would help in the assess of their value as a source of fuel and of other chemicals.

This work was carried out by using pyrolysis procedures. These procedures are classified according to the type and operating mode of the reactor, the method of heat supply and the operating temperature range [11].

During pyrolysis, the feed material is gradually decomposed into volatile products (moisture, gas, oil and tar) and a charred residue.

The relative quantities and compositions of the various fractions depend on the nature of the feed stock (composition, particle size and moisture) and operating conditions (temperature, heating rate, reaction time of volatile products and charred residue).

Recent theory was developed by Pyle and Zaror [12] to define the parameters controlling the pyrolysis rate of single particles. It was shown that the relative importance of internal and external heat transfer and of the intrinsic pyrolysis kinetics could be determined.

Experimental

Materials

Kernels of Iglani dates were used. This type of date was selected for study as it was readily available from the Agwa factories. The kernel comprises 15–18% of the date by weight. The particle size used was 400 mesh.

Chemical structure of the kernels

Standard elementary analysis methods gave (wt%): C 47.2, H 6.8, N 2.9, S 0, ash 5.2, and O 37.9.

Infrared spectroscopy was used to investigate the chemical structure of the date kernels. Perkin–Elmer model 598 double beam IR instrument was applied over the wavenumber range 4000–200 cm^{-1} . Table 1 lists the chemical groups present in the kernels.

Experimental techniques

A Stanton Redcroft model 674/4 differential thermal analyser was used. Forty mg of sample and reference material was taken, with a heating rate of 5 deg/min.

DTA run was carried out to determine the temperatures at which the physical and chemical changes take place.

A Stanton Redcroft model 770 thermal balance was used, with 10 mg of sample and a heating rate of 5 deg/min. The weight change was recorded as a function of furnace temperature.

A single TG run was carried out at linear heating rate, and the loss in weight of the sample was recorded as a function of time and temperature, to yield a complete survey of the thermal behaviour of the sample. The temperature was raised from ambient to 700° in both DTA and TG experiments.

Alternatively, either the required operating temperature was rapidly raised to the required level, and then maintained constant. Five runs were carried out with the

Table 1 Chemical groups present in kernels

Wavenumber of bands, cm^{-1}	Characteristic chemical groups	Compound in which group occurs
3600–3200	OH	phenolic or alcoholic compounds
3000–2900	C—H	aliphatic compounds
1800–1700	C=O	organic acids and esters
1610	aromatic ring	aromatic compounds
1550–1500	N	amines and amides
1485–1440	CH_2 and CH_3	aliphatic compounds
1390–1360	CH_3	hydrocarbon compounds
1300–1200	C—O—C	oxygenated compounds (esters, resins, peroxides)
1200–1000	OH	alcoholic compounds
900–860	cyclic compounds or substitution in aromatic ring	naphthenes or substitution in aromatic ring
850–800	C=C substitution in benzene ring	conjugated compounds and saturated compounds or substitution in benzene ring
800–700	alkyl groups above C_4	aliphatic chains
700–400	substitution in benzene ring	substitution in benzene ring

former procedure, and five with the latter. The temperature was maintained at 260, 315, 400, 470 and 540°, these values being selected because the DTA indicated sharp peaks at these temperatures. Also, in some TG experiments, the samples were preheated at a rate of 5 deg/min to the required temperature levels, at which the furnace was maintained, as mentioned above.

Results and discussion

Thermal analysis of date kernels

Figure 1 shows the DTA curve for a date kernel sample. Both endo- and exothermic reactions take place during the pyrolysis from 25 to 700°.

The endothermic reactions are due to physical processes inside the kernels (e.g. evaporation), and the exothermic reactions to chemical processes (e.g. cracking). These reactions are indicated in Table 2.

The data in Table 2 indicate that the pyrolysis involves various stages. During the first stage, which extends up to 200°, gases and moisture are evolved. The first exothermic reaction begins at 200°, with cracking of light products in the range 200–315°. This is accompanied by slight evaporation and the light products are evolved between 315 and 400°.

The second stage, corresponding to the cracking of heavy molecular weight compounds, begins at 360°, and the heavy cracking products are evolved at

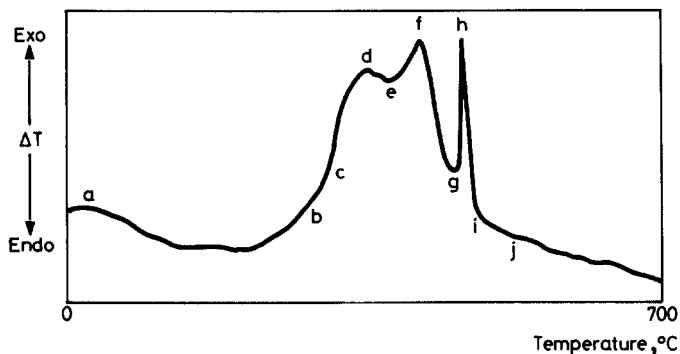


Fig. 1 DTA curve of date kernel sample

Table 2 DTA of date kernel sample

Stage	Temperature range, °C	Exothermic process	Endothermic process
a-b	25-200	—	Evolution of gases and moisture
b	200 onset peak temp.	Beginning of first exothermic reaction	—
bcd	200-315	Cracking of light products	Light product evaporation in platinum cell
d	Max. peak temp.	Max. exothermic reaction	—
def	315-400	—	Evolution of light products
efg	360-460	Second cracking stage for heavy molecular weight compounds	—
fgh	400-470	—	Evolution of heavy cracking products
ghi	460-510	Change to carbonized materials	—
i-j	510-540	Stability of final residue. End of exothermic reaction	—

400-460°. At 460-510° carbonization sets in, and the exothermic reaction finally ends at 540°, leaving behind a stable carbonaceous residue.

Figure 2 shows the TG curve of a date kernel sample, data obtained from this curve are listed in Table 3. These are three sharp deviations in the curve, at points *c*, *d*, and *e*. These correspond to the temperatures 260, 315 and 540° at which physical or chemical change (weight loss) take place. These temperatures were therefore selected for this study.

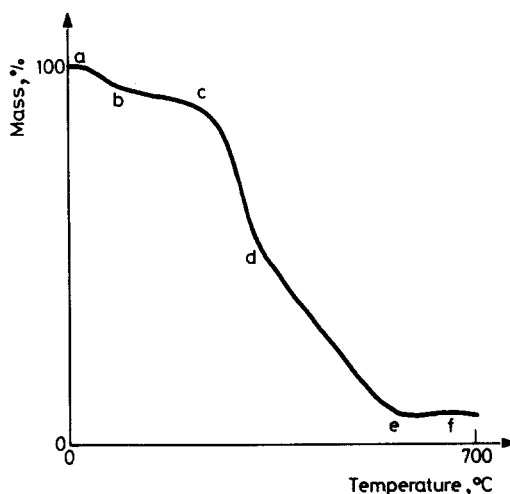


Fig. 2 TG curve of date kernel sample

Table 3 TG of date kernel sample

Stage	Temperature range, °C	Weight loss, %	Reaction
a-b	25-105	6.13	Evolution of moisture content
b-c	105-260	9.18	Evolution of gases
c-d	260-315	31.63	Evolution of light liquids and gases
d-e	315-540	45.92	Evolution of heavy liquids and gases
e-f	540	7.14	Residue

TG study of pyrolysis of date kernels

Effect of preheating on pyrolysis

To study the effect of preheating on the pyrolysis, two sets of experiments were carried out. The first set (five runs) involved the preheating of samples at 5 deg/min to the required isothermal temperatures (260, 315, 400, 470 and 540°), with recording of weight *vs.* time. The temperatures of the samples were then maintained at these levels.

The second set (five runs) involved pyrolyzing 10 samples directly at the required temperatures, again with recording of weight *vs.* time. Figures 3 and 4 show the TG curves for these ten runs.

The fractional conversion was calculated as the ratio of the weight loss at time *t* and the maximum weight loss.

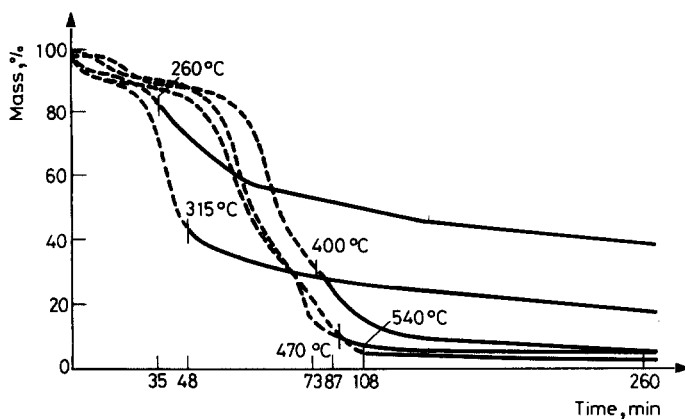


Fig. 3 TG curves of preheated date kernels

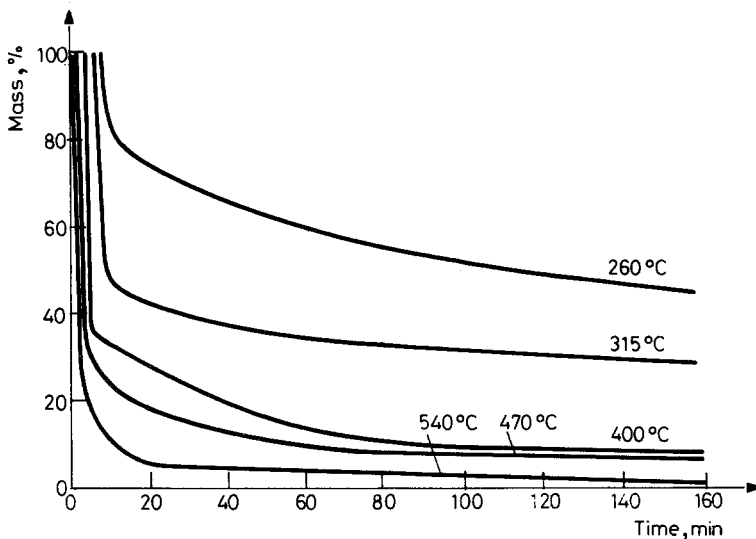


Fig. 4 Isothermal mass loss curves of non-preheated date kernels

The results are presented in Fig. 5.

It is obvious that the same trend is followed at each temperature level, but the preheated samples undergo a slightly higher conversion than those suddenly introduced into the hot chamber. For illustration, let us consider the curve corresponding to 540°. It may be seen that 95% conversion is reached after 1 minute of pyrolysis in the case of the preheated run, whereas in the absence of preheating it is reached after 15 minutes. These figures appear at first sight to indicate that the conversion is much more rapid when preheating is applied.

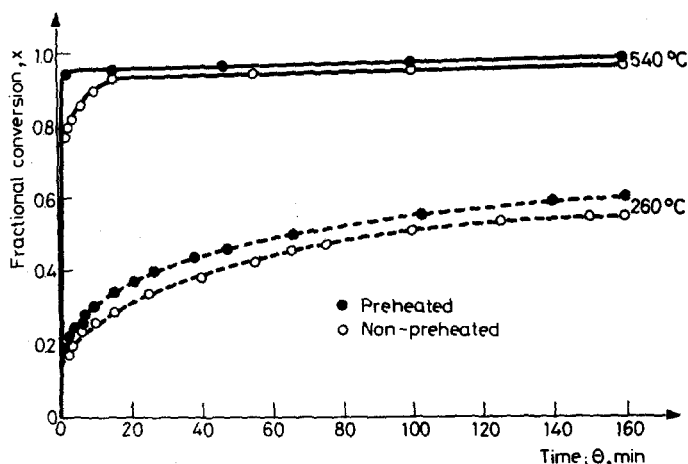


Fig. 5 Effect of preheating on pyrolysis of fine particles

This is misleading, however, for the actual preheating time was 108 minutes, during which some conversion already occurred; thus the total time between the beginning of heating and the attainment of 95% conversion was 109 minutes, compared to 15 minutes only when preheating was not used.

Furthermore, the maximum conversion attained with preheating was only slightly higher than without, especially at the high temperature levels used (400, 470 and 540°), the differences being 1–2% only. It seems therefore, that preheating is quite unnecessary from the aspect of maximum conversion.

In the remaining part of this work the experiments were carried out without preheating.

Effect of temperature on pyrolysis

An investigation of the effect of temperature on the rate of pyrolysis of kernels was carried out in isothermal runs at 260, 315, 400, 470 and 540°. In these experiments, the temperature of the sample can be taken as equal to the furnace wall temperature if the rate of heat transfer to and within the particles is very rapid. Under such conditions, if the reaction rate is comparatively low, the pyrolysis will be kinetically controlled. According to Pyle and Zaror [12], this is more likely to happen with small particles (400 mesh).

The weight was recorded vs. time and the fractional conversion was calculated. The experimental results are given in Fig. 6.

The initial conversion rate is high, and then decreases continuously. The very high conversion reached within the first few minutes may be attributed to the fact that the sample has a very small particle size (i.e. 400 mesh). The surface area

exposed to the heat is therefore very large, and the fine particles possess practically no resistance; thus the sample interior reaches the furnace temperature virtually as soon as it is introduced into the pan, resulting in rapid conversion associated with the high temperature (the conversion increases with increasing operating temperature). The decrease in rate with time could be explained as being a result of the decrease in the proportion of the reactants.

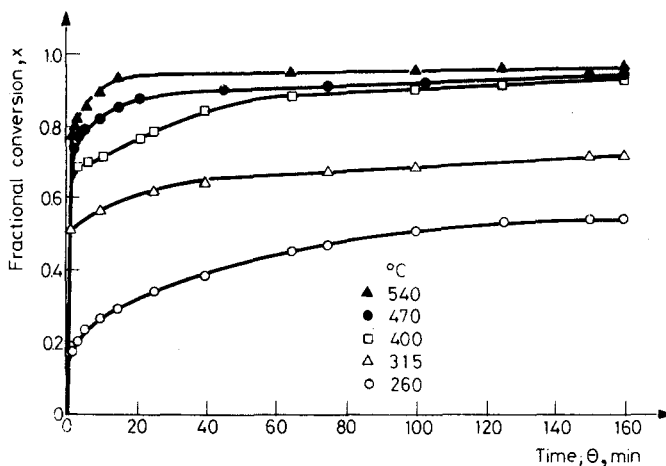


Fig. 6 Effect of temperature on pyrolysis of fine particles

The maximum conversion attained is the higher, the higher the operating temperature. Thus possibly, follow from the fact, that, at the lower temperatures, some of the reactions indicated in Fig. 1 have not yet occurred.

Analysis and experimental data of TG runs

It is reasonable to suppose that, in view of the small radius of the pan used, the pyrolysis process is kinetically controlled. If this is the case, according to Pyle and Zaror [12], the reaction rate should obey the first-order reaction relation

$$\frac{dw}{d\theta} = kw \quad (1)$$

where $\frac{dw}{d\theta}$ = rate of weight loss, θ = time, and k = specific rate constant, equal to

$$k = Ae^{-E/RT} \quad (2)$$

where A = Arrhenius constant, E = activation energy, T = temperature and R = universal gas constant.

On integration Eq. (1) yields

$$\ln \frac{w_{\theta} - w_{\infty}}{w_0 - w_{\infty}} = K\theta$$

where w_{θ} = weight at any time θ , w_0 = initial weight, at $\theta = 0$, w_{∞} = final weight, at $\theta = \infty$

$\frac{w_0 - w_{\theta}}{w_0 - w_{\infty}}$ relates to the unreacted fraction of the kernels ($1 - x$).

If the process is indeed both first-order and kinetically controlled, the a plot of $\ln(w_{\theta} - w_{\infty})/(w_0 - w_{\infty})$ vs. θ for each temperature should yield a straight line relation.

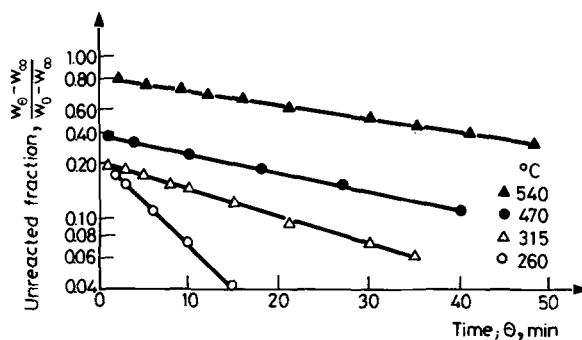


Fig. 7 Unreacted fraction of fine particles vs. time

The experimental data were analysed by plotting the unreacted fraction vs. time. It is observed that straight lines fit the data well. This would tend to indicate that the pyrolysis is in fact controlled by the kinetics and furthermore, that a first-order reaction is involved, the reaction rate constant (k) of which at given temperature may be determined from the slope of the corresponding relation $\ln \frac{w_{\theta} - w_{\infty}}{w_0 - w_{\infty}}$ vs. θ .

The values of k as a function of absolute temperature are reported in Table 4 and plotted in Fig. 8.

Equation (2) could be written as $\ln k = \ln A - E/RT$. The plot of $\ln k$ vs. $1/T$ should yield a straight line of slope $-E/R$ and intercept $\ln A$.

Table 4 Specific reaction rate constant at different temperatures

$T, ^\circ\text{C}$	260	315	470	540
$1/T \times 10^{-3} \text{ K}$	1.876	1.70	1.345	1.23
k, min^{-1}	0.0053	0.006	0.0086	0.01

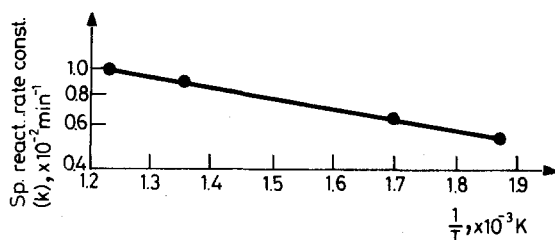


Fig. 8 Specific reaction rate constant vs. reciprocal temperature

The values of the Arrhenius constant and activation energy obtained from Fig. 8 are 0.0115 min^{-1} and 8.17 kJ/mol , respectively.

It would be desirable to compare the values of Bi and Py' relevant to this work with those reported by Pyle and Zaror [12]. A rough estimation of the values of these dimensionless groups may be obtained as follows:

In the absence of reliable values of the thermal conductivity and specific heat for date kernels, the corresponding values for wood ($K = 12.56 \times 10^{-4} \text{ w/cm deg}$, $c_p = 1.67 \text{ J/g deg}$ [12]), will be used together with the corresponding reported values for charcoal ($K = 8.37 \times 10^{-4} \text{ w/cm deg}$, $c_p = 1.0 \text{ J/g deg}$). The densities of the kernels and the residue were found to be 1.2 and 0.8 g/cm^3 respectively. The above values will be used to calculate average values representative of the overall pyrolysis process. Again, the coefficient of heat transfer reported in [12] ($8.4 \times 10^{-4} \text{ w/cm deg}$) will be used here. With a sample tube radius of 2.25 cm , and a reaction rate constant of $1.66 \times 10^{-4} \text{ s}^{-1}$, corresponding to a temperature of 540° , we obtain:

$$Bi = \frac{hR'}{k} = \frac{8.4 \times 10^{-4} \times 0.25}{10.465 \times 10^{-4}} = 0.2$$

$$Py' = \frac{h}{KSc_pR'} = \frac{8.4 \times 10^{-4}}{1.66 \times 10^{-4} \times 1.0 \times 1.335 \times (0.25)} = 15.0$$

Table 5 Regions of validity of models I-IV

Model	Approximate range of validity			Controlling processes
	Bi	BY	PY'	
I		all values		Internal + external heat transfer and kinetics
II	< 1	> 1	> 1	External heat transfer
III	< 1	0(10)	> 10	Kinetics
IV	> 50	> 10	≤ 1	Internal heat transfer

According to Pyle and Zaror [12], pure kinetic control and a first-order reaction should hold for values of $Bi = 1$ and $Py' = 10$, as illustrated in Table 5.

The values of Bi and Py' calculated for the present work are consistent with values suggested by the above authors. The small value of Bi obtained here would confirm, that, for the small cylinder used, the sample temperature is essentially uniform as far as position is concerned. As discussed above, the fractional conversion obtained seems to indicate that the sample temperature is also uniform in time, and that the reaction involved is of first order.

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Zusammenfassung — Ägyptische Dattelkerne wurden thermisch untersucht, um die Möglichkeit einer Verwendung als Quellen für wertvolle Verbindungen zu ergründen. Außerdem wurden technische Daten ermittelt, die zur Festlegung der Optimumtemperatur für die Gestaltung und den Betrieb der Geräte zur pyrolytischen Behandlung von Dattelkernen benötigt werden. Es wurden zwei Versuchsreihen durchgeführt, bei denen einerseits Thermogravimetrie (TG) und andererseits Differentialthermoanalyse (DTA) Anwendung fand. Die TG Ergebnisse eröffnen eine rein kinetisch kontrollierte Reaktion erster Ordnung. Die Aktivierungsenergie und die Arrheniuskonstante betragen 8,17 kJ/mol bzw. 0,0115 min⁻¹. DTA Resultate gaben Auskunft über den Charakter und Reaktionsprodukte der Reaktionen bei der Pyrolyse.

Резюме — С целью оценки продуктов, как возможных источников получения различных соединений, проведен термический анализ египетских финиковых косточек. Приведены также технические данные, необходимые для определения оптимальной температуры созданной пиролитической установки для обработки финиковых косточек. Проведено две различные серии экспериментов, включающих ТГ и ДТА. Результаты ТГ показали чисто кинетические контролируемую реакцию первого порядка. Энергия активации и аррениусовская константа равнялись, соответственно, $8,17 \text{ кдж} \cdot \text{моль}^{-1}$ и $0,0115 \text{ мин}^{-1}$. Результаты ДТА показали характер реакций, протекающих в процессе пиролиза и соответствующие продукты реакций.