دراسة مقارنة لحساب تنشيط طاقة التحلل الحراري
لمادة الكافيين باستخدام طرق مختلفة

ليلى كامل

تمت دراسة التحلل الحراري لمادة الكافيين في جو نتروجيني لبداء من درجة حرارة الغرفة حتى 500 درجة منوية، وذلك من خلال ثلاثة معدلات حرارية مختلفة 5 و 10 و 20 درجة منوية في الدقيقة الواحدة.

لواحظ اكتمال التحلل الحراري لمادة الكافيين في خطوطتين رئيسيتين. تم حساب طاقات التنشيط (E_a) باستخدام طرق Isoconverional Methods لهما عن طريق استخدام Isoconverional Methods (AB)، و (KAS) على أوزارى (FR) وكيسنجر- أكاهيرا- سانوز (FWO) المستخدمة.

تم أيضاً مقارنة نتائج تنشيط الطاقة (E_a) باستخدام طريقة كيسنجر وأوجس- بينيت (AB). أوضحت النتائج أن طاقات التنشيط (E_a) المحوسية عن طريق استخدام طريقة كيسنجر وطريقة أوجس- بينيت (AB) أظهرت أücü من النتائج المحوسية باستخدام Isoconverional Methods (E_a) للخطوة الأولى أكبر من الخطوة الثانية.

تغذى هذه الدراسة في تحديد درجات الحرارة المناسبة لصناعة المقاور الصيدلانية حتى لا يحدث تكميم حراري للمركبات أثناء التصنيع.
19- Kissing, H. E., op. cit.


22- Dong, J-X. et al., op. cit.

23- Zhang, J. et al., op. cit.


26-Ibid.


And Also:


And Also:


References


Fig(13) Kissinger Plots for CF (First and Second Step)

Fig(14) Augis and Bennett Plots for CF (First and Second Step)

21
Fig (11) The Dependence of the Apparent Activation Energy ($E_a$) on the Degree of Conversion ($\alpha$) for Nonisothermal Decomposition Process of CF (First Step)

- FWO
- KAS
- Tang
- FR

Fig (12) The Dependence of the Apparent Activation Energy ($E_a$) on the Degree of Conversion ($\alpha$) for Nonisothermal Decomposition Process of CF (Second Step)

- FWO
- KAS
- Tang
- FR

20
Fig. (9) FR Plots of CF for Different Degrees of Conversion (α) (First Step)

Fig. (10) FR Plots of CF for Different Degrees of Conversion (α) (Second Step)
Fig (7) Tang Plots of CF for Different Degrees of Conversion ($\omega$) (First Step)

Fig (8) Tang Plots of CF for Different Degrees of Conversion ($\omega$) (Second Step)
Fig(5) KAS plots of CF for Different Degrees of Conversion ($\alpha$) (First Step)

Fig(6) KAS Plots of CF for Different Degrees of Conversion ($\alpha$) (Second Step)
Fig (3) FWO Plots of CF For Different Degrees of Conversion ($\alpha$) (First Step)

Fig (4) FWO Plots of CF For Different degrees of Conversion ($\alpha$) (Second Step)
Fig (1) The TGA Curve of CF at Different Heating Rates

Fig (2) DTG Curves of CF at Different Heating Rates
Table (2)
The Apparent Activation Energies of Thermal Decomposition and Correlation Coefficient of CF Obtained by FR, FWO, KAS and Tang (Second Step)

<table>
<thead>
<tr>
<th>Conversion</th>
<th>FR method</th>
<th>FWO method</th>
<th>KAS method</th>
<th>Tang method</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_a$</td>
<td>$R^2$</td>
<td>$E_a$</td>
<td>$R^2$</td>
</tr>
<tr>
<td></td>
<td>kJ/mol</td>
<td></td>
<td>kJ/mol</td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>43</td>
<td>0.999</td>
<td>47</td>
<td>0.987</td>
</tr>
<tr>
<td>0.3</td>
<td>44</td>
<td>0.997</td>
<td>46</td>
<td>0.994</td>
</tr>
<tr>
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<td>45</td>
<td>0.997</td>
<td>46</td>
<td>0.994</td>
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<td>45</td>
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<td>49</td>
<td>0.999</td>
</tr>
<tr>
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<td>51</td>
<td>0.993</td>
<td>49</td>
<td>0.999</td>
</tr>
<tr>
<td>0.8</td>
<td>57*</td>
<td></td>
<td>51*</td>
<td>0.999</td>
</tr>
</tbody>
</table>

*excluded

Table (3)
The Apparent Activation Energies of Thermal Decomposition and Correlation Coefficient of CF obtained by Kissinger Method and AB Method

<table>
<thead>
<tr>
<th>Step</th>
<th>Kissinger method</th>
<th>Augis and Bennett’s method</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_a$</td>
<td>$R^2$</td>
</tr>
<tr>
<td></td>
<td>kJ/mol</td>
<td></td>
</tr>
<tr>
<td>First</td>
<td>80</td>
<td>0.998</td>
</tr>
<tr>
<td>Second</td>
<td>60</td>
<td>0.999</td>
</tr>
</tbody>
</table>

14

\&^\text{\textsuperscript{\textdegree}}
Activation energy calculated using AB method was 78 kJ/mol for the first step and 61 kJ/mol for the second step. Where that using Kissinger method were 80 kJ/mol and 60 kJ/mol for the first and second step respectively.

The results obtained using Kissinger and AB methods showed higher activation energy values in both steps than the activation energy calculated from the isoconversional methods this may be attributed to the rely solely on the relative positions of $T_p$ rather than considering the whole heat flow profile.

<table>
<thead>
<tr>
<th>Conversion</th>
<th>FR method</th>
<th>FWO method</th>
<th>KAS method</th>
<th>Tang method</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_a$ kJ/mol</td>
<td>$R^2$</td>
<td>$E_a$ kJ/mol</td>
<td>$R^2$</td>
</tr>
<tr>
<td>0.2</td>
<td>87</td>
<td>0.991</td>
<td>73</td>
<td>0.997</td>
</tr>
<tr>
<td>0.3</td>
<td>85</td>
<td>0.994</td>
<td>78</td>
<td>1.00</td>
</tr>
<tr>
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<td>81</td>
<td>0.992</td>
<td>78</td>
<td>0.996</td>
</tr>
<tr>
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</tr>
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<tr>
<td>0.8</td>
<td>69*</td>
<td></td>
<td>76</td>
<td>0.985</td>
</tr>
</tbody>
</table>

*excluded
\(\ln(\beta/(T_p-T_0))\) vs. \(1/T_p\), were plotted as shown in Fig (14), where the \(E_a\) was 78 kJ/mol for the first step and 61 kJ/mol for the second step.

The calculated values of activation energy, \(E_a\), using AB and Kissinger's methods and the correlation coefficients are listed in Table(3).

It can be observed that the calculated apparent activation energy for Kissinger and AB methods which correspond to the peak temperature of the DTG curve are very similar.

The results obtained from Kissinger and AB methods show higher activation energy values in both steps than the activation energy calculated from the isoconversional methods. The reason could be because Kissinger and AB methods rely solely on the relative positions of \(T_p\) rather than considering the whole heat flow profile\(^{(26)}\).

**Conclusion**

The thermal decomposition of CF in nitrogen atmosphere occurs in two steps. The apparent activation energies, \(E_a\), for the two steps were calculated by four different isoconversional methods, one differential (FR), three linear integral (KAS, FWO and Tang). A comparison has been made between \(E_a\) calculated from the isoconversional methods and the \(E_a\) values calculated using the Kissinger and AB methods.

Calculated \(E_a\) mean values were 77 kJ/mol for the first step and 47 kJ/mol for the second step using FWO method, while \(E_a\) was 74 kJ/mol for the first step and 45 kJ/mol for the second step using Tang method. Using KAS method the \(E_a\) was 65 kJ/mol and 37 kJ/mol for the first and second step respectively. As shown the activation energy calculated by KAS is lower than that calculated from FWO and Tang methods. \(E_a\) calculated using FR method was 77 kJ/mol for the first step and 46 kJ/mol for the second step.
using Tang, KAS, FWO and FR methods are listed in Tables (1, 2) for the first and second step respectively.

Fig. (11) shows that the curves of $E_a$ versus $\alpha$ have the same shapes, corresponding to Tang, KAS, and FWO methods. Same behavior have been observed in the second step, Fig.(12), where the curves of $E_a$ versus $\alpha$ have the same shapes of the corresponding to Tang, KAS, and FWO methods also. This means that the thermal decomposition of CF in N$_2$ atmosphere presented a same behavior for Tang, KAS and FWO method. The average values of $E_a$ for Tang, KAS and FWO methods obtained in the range $0.2 \leq \alpha \leq 0.8$ are lower than the average values of $E_a$ obtained for FR (for both steps). That may be due to the well known that FR method is very sensitive to experimental noise$^{(24)}$ and tends to be numerically unstable because of employing instantaneous rate value. Some of the differences observed between the values of $E_a$ obtained using linear integral methods (Tang, KAS and FWO) can be assigned to the different approximations of the temperature integral which ground them$^{(25)}$.

The calculation of the activation energy using more than one isoconversional method can give an area of values for every particular value of $\alpha$, where the true values of $E$ can be found. As observed the larger activation energy of the first step of decomposition may be due to the additional destroy of crystal lattice.

Using Kissinger equation (8) the plots line $\ln \left( \frac{\beta}{T_p^2} \right)$ versus $1/T_p$, for each step of thermal decomposition of CF were plotted as shown in Fig (13). The activation energy of decomposition was 80 kJ/mol for the first step and 60 kJ/mol for the second step.

Augis - Bennett’s equation (9) was also used to calculate, activation energy $E_\alpha$ can be obtained from the slope of the straight line
slope of such a line given by -0.456E/RT. Figs (3,4) illustrates the plots of lnβ versus 1/T at varying conversion for the first and second step respectively. The apparent activation energies calculated from the slopes were tabulated in Tables (1 and 2) and the mean values are 77 kJ/mol for the first step and 47 kJ/mol for the second step.

Another isoconversional method used in this paper was KAS where the activation energy can be calculated from the slopes of the straight lines obtained from the plots of ln(β/T²) against 1/T as shown in Figs (5,6) for the two steps and the mean apparent activation energies were 65 kJ/mol for the first step and 37 kJ/mol for the second step.

Using Tang equation (5) the plots of ln(β/T¹.894661) versus 1/T for each step of thermal decomposition of CF were plotted as shown in Figs (7,8). The calculated decomposition activation energies were 74 kJ/mol for the first step and 45 kJ/mol for the second step.

Friedman method is also used to determine the apparent activation energy from the slope of the plot of ln(da/dt) versus 1/T gives a straight line with a slope of -Ea/R. as shown in Figs (9,10) for the two steps. The mean apparent activation energies were 77 kJ/mol for the first step and 46 kJ/mol for the second step.

For all the sets of α values, the linear isoconversional plots of FR, KAS, FWO and Tang methods result in a correlation coefficient (r²) higher than 0.9950. The straight lines fitting the data are nearly parallel, which is an indication that the activation energies at different degrees of conversion are almost similar. The dependence of the apparent activation energy (Ea) on the degree of conversion (α) (Ea-α curve) for the nonisothermal decomposition process of CF obtained by isoconversional methods for the first and second step are presented in Figs (11,12) respectively. The calculated apparent activation energies
The DTG curves for CF for the three rates are shown in Fig. (2). The main weight loss about 88% for the three rates occurs in one step in the temperature range 155-230, 170-280 and 200-270°C for the rates 5, 15 and 20°C/min respectively with a temperature peak 220.11°C, 247.59°C and 253.54°C respectively. A second step with a smaller weight loss 12% in the temperature range 230.23-315.45, 271.72-360.75 and 272.15-379.25°C with peak temperature 307.97, 361.64 and 369.05°C for the rates 5, 15 and 20°C/min respectively.

Several techniques using different approaches have been developed for solving the integral equation (2). The nonisothermal decomposition process of CF was analyzed by Friedman (FR), Kissinger-Akahira-Sunose (KAS), Flynn-Wall-Ozawa (FWO) and Tang isoconversional methods. All mentioned methods are based on multiple heating rates experiments, where no kinetic model is needed before activation energy is calculated.

FWO method is an integral method independent of the degradation mechanism. Equation (4) has been used and the apparent activation energy of CF can therefore be obtained for the two steps from a plot of lnβ against 1/T for a fixed degree of conversion since the
two C-N bonds attaching –CH₃ groups to the quinonoide nucleus and the breakdown of a C-H bond from ethane molecule formed. The largest weight loss in the first decomposition step includes the loss of 7-methyl xanthine.

In the second step of decomposition, ethylene molecule, as a result of increasing temperature is fragmented and the fragments (gaseous products) leave the crucible without any residue.

The TG, DTG curves results of CF agree with similar results obtained when investigating the thermal stability of anhydrous CF(₂²). In that study, DSC curve has shown a phase transition of CF, from the crystal form α to the crystal form β at a peak temperature 147°C. The mass-loss curve (TG) shows that most of the decompositions occur in the temperature range 181-291°C in a single step and no residue was found in the crucible after the experiment was completed.

In the light of these results, a possible decomposition route of CF is proposed based on the results of mass spectra of xanthines(₂³) and are represented. The two well-defined stages were selected for the study of the kinetics of decomposition of CF.
The activation energy $E$ can be obtained from the slope of the straight line $\ln \left( \frac{\beta}{\tau_p^2} \right)$ versus $1/T_p$. This method provides the value of $A$ apart from the value of activation energy $E$. Here one gets a single value of $E$ using Eq. (8).

**Augis-Bennett's method**\(^{(20)}\)

According to the method suggested by Augis and Bennett,

$$\ln \left( \frac{\beta}{\tau_p - \tau_0} \right) = -\frac{E}{RT_p} + \ln A$$  \hspace{1cm} (9)

where $T_p$ and $T_0$ are the peak temperature and the onset temperature of the DTG peak respectively. The activation energy $E$ can be obtained from the slope of the straight line $\ln[\beta/(T_p - T_0)]$ versus $1/T_p$.

**Results and Discussion**

Thermal analysis of CF was studied starting from room temperature up to 500°C in nitrogen atmosphere. The TG and DTG curves of the decomposition process of CF obtained at different heating rates (5, 15 and 20°C /min) are shown in Figs 1 and 2 respectively. TG curves are shifted to higher temperatures at higher heating rates, although the shapes of curves are quite similar. The first decomposition step in rates 5, 15, 20°C /min occurs in the 155-230, 170-280 and 200-270°C temperature range respectively with a weight loss of about 88% for the three rates. This weight loss occurs at a peak temperature of 220.11 °C, 247.59°C and 253.54 °C for the rates 5, 15 and 20°C /min respectively whereas the melting point of CF is 236°C. This means that the CF decomposes before melting. A weight loss of 88% corresponds to the loss of 7-methyl xanthine nucleus and agrees with the appearance of a peak at $m/z=165$ in the mass spectrum of CF\(^{(21)}\). The loss of 7-methyl xanthine nucleus necessitates the breakdown of
The dependence of $\ln(\beta/T^2)$ on $1/T$, calculated for the same $\alpha$ values at the different heating rates ($\beta$) can be used to calculate the activation energy.

**Friedman method**\(^{(18)}\)

The derivative techniques are based on the comparison of the rates of mass loss $\alpha$ for a given fractional mass loss determined using different linear heating rates ($\beta$). This method utilizes the following logarithmic differential equation:

$$
\ln\left(\frac{d\alpha}{dt}\right) = \ln[Af(\alpha)] - \frac{E_\alpha}{RT}
$$

(7)

Where $d\alpha/dt$ is the rate of conversion and $f(\alpha)$ differential expression of kinetic function. A plot of $\ln(d\alpha/dt)$ versus $1/T$ gives a straight line with a slope of $-E_\alpha/R$.

**Kissinger method**\(^{(19)}\)

This well-known method assumes that the reaction rate reaches its maximum at the temperature ($T_p$) at the DTG peak. This assumption also implies a constant degree of conversion ($\alpha$) at $T_p$. In many cases, the degree of conversion ($\alpha$) at $T_p$ varies with the heating rate and hence raises doubt about grouping this method into isoconversional category.

The Kissinger equation is

$$
\ln\left(\frac{\beta}{T_p^2}\right) = -\frac{E}{RT_p} \ln\left(\frac{AR}{E}\right)
$$

(8)
Flynn-Wall-Ozawa method\(^{(14)}\)

This method is derived from the integral method. The technique assumes that the \(A, f(\alpha)\) and \(E\) are independent of \(T\) while \(A\) and \(E\) are independent of \(\alpha\) then Eq. 2 may be integrated to give the following in logarithmic form:

\[
\log g(\alpha) = \log(AE/R) - \log \beta + \log p(E/RT)
\]  
(3)

Using Doyle’s approximation\(^{(15)}\) for the integral which allows for \(E/RT > 20\), Eq 3 now can be simplified as

\[
\log \beta = \log \left(\frac{AE}{R}\right) - \log g(\alpha) - 2.315 - 0.456
\]

\[
\log \beta = \log \left(\frac{AE}{R}\right) - \log g(\alpha) - 2.315 - 0.456
\]  
(4)

Tang method\(^{(16)}\)

Tang method is an approximation formula for resolution of Eq. 2 where following equation can be obtained

\[
\ln \left(\frac{\beta}{T^{1.894641}}\right) = \ln \left(\frac{AE}{Rg(\alpha)}\right) + 3.635041
\]

\[
-1.894661 \ln E - \frac{1.001450 E}{RT}
\]  
(5)

The plots of \(\ln \left(\frac{\beta}{T^{1.894641}}\right)\) versus \(1/T\) give a group of straight lines. The activation energy can be obtained from the slope \(-4.001450\ E/R\) of the regression line.

Kissenger-Akahira-Sunose method\(^{(17)}\)

This method (KAS) is integral isoconversional methods as FWO

\[
\ln \frac{\beta}{T^2} = \ln \left[\frac{AR}{E g(\alpha)}\right] - \frac{E}{RT}
\]  
(6)
Experimental
Materials
CF was supplied by Sigma (St. Louis, MO). It is used without any further purification.

Physical Measurements
The thermogravimetric (TG) curves were obtained using Shimadzu TGA-50 thermobalance. The measurements were performed with dynamic nitrogen furnace atmosphere at a flow rate of 20 mL min\(^{-1}\) starting at room temperature up to 500\(^{0}\)C. The heating rates used were 5, 15 and 20\(^{0}\)C min\(^{-1}\) and the samples were of masses 1.233, 1.955, 1.689 mg respectively which were contained in an alumina crucible.

Kinetic methods
The rate of solid-state non-isothermal decomposition reactions is expressed as

\[
\frac{d\alpha}{dT} = \left(\frac{A}{\beta}\right) \exp\left(\frac{-E}{RT}\right) f(\alpha)
\]  

(1)

Rearranging Eq. 1 and integrating both sides of the equation leads to the following expression

\[
g(\alpha) = \left(\frac{A}{\beta}\right) \int_{\alpha_0}^{\alpha} \exp\left(\frac{-E}{RT}\right) d\tau = \left(\frac{AE}{\beta R}\right) p(u)
\]  

(2)

Where \(p(u) = \int_{\infty}^{u} -\left(\frac{u}{u^2}\right) du\) and \(u = E/RT\).
amoxicillin complexes of d-block elements\(^{(7)}\), imipramine hydrochloride and trimipramine maleate\(^{(8)}\) penicillin sodium salts\(^{(9)}\), other ones were also done.

Study of the thermal behaviors of some new xanthine derivatives by TG and DSC were used to determine the thermal stability, the purity of the compounds and crystallinity\(^{(10)}\). Thermal decomposition of CF and other methylxanthines was studied by DTA, TG and DTG methods to determine the influence of heating rate and sample size on thermal destruction of the selected methylxanthines\(^{(11)}\). Anhydrous CF thermal behavior was investigated by TG, DTG, DSC where a (solid-solid) and a (solid-liquid) phase transitions of the compound were found at \(T= \) (413.39 and 509.00) \(k\) respectively. Molar enthalpies of these transitions were determined\(^{(12)}\).

The aim of this study is to investigate the thermal behavior and to determine the apparent activation energies of thermal degradation of CF in \(N_2\) atmosphere by isoconversional methods through which the activation energy depends on the conversion degree. Isoconversional methods provide a comprehensive description of the decomposition process of a heterogeneous solid-state reaction. Based on the results of the International Confederation for Thermal Analysis and Calorimetry (ICTAC) kinetics project\(^{(13)}\), the multi-heating rate methods together with isoconversional methods are the most reliable techniques for the analysis of thermal data. In this study, isoconversional methods of Friedman (FR), Tang, Flynn-Wall-Ozawa (FWO) and Kissenger-Alkahira-Sunose (KAS) were used to evaluate the activation energy \((E_a)\) values at different stages of fraction decomposed \((\alpha)\) during the thermal decomposition of CF. The results are compared to the \(E_a\) values calculated using Kissinger method and Augis - Bennett’s methods.
Caffeine (CF) \((1,3,7\text{-trimethylxanthine})\) is the most widely consumed psychoactive substance in the world. While it is present in a number of dietary sources such as tea, chocolate and soft drinks, the largest intake of caffeine has always been through coffee\(^{(1)}\).

\[
\begin{array}{c}
\text{H}_3\text{C} \\
\text{N} \\
\text{O} \\
\text{N} \\
\text{N} \\
\text{O} \\
\text{CH}_3 \\
\end{array}
\]

Caffeine

Caffeine can be used in soft drinks as a flavoring ingredient and recently also in so-called "sports drinks" to increase the basal metabolic rate\(^{(2)}\). They are occasionally components of some over-the-counter pharmaceutical preparations. As a central nervous system stimulant, caffeine can also stimulate the cardiac muscle\(^{(3)}\).

Thermal decomposition helps in studying the drug behavior at various temperatures, which is important for the prediction of storage conditions for drug formulations. It also gives important information on temperatures, at which the drug substance can be subjected to technological processes without loss of its specific physico-chemical and pharmacological properties\(^{(4)}\). Decomposition reactions are carried out in order to obtain the solid products, which are characterized by proper phase composition and activity for further technological applications.

In literature, there are many examples treated with the application of thermal methods of analysis, especially DSC, DTA, TG and DTG, in the studies of thermal stability and decomposition of organic and inorganic compounds used in medicine. Studies on allopurinol\(^{(5)}\), Mn(II), Co(II) and Fe(III) norfloxacin complexes\(^{(6)}\),
COMPARATIVE STUDY FOR ACTIVATION ENERGY OF THERMAL DEGRADATION OF CAFFEINE USING DIFFERENT METHODS

Laila T. Kamel*

The thermal decomposition of caffeine was studied by thermogravimetry in nitrogen atmosphere from room temperature up to 500°C at three different heating rates 5, 15 and 20°C min⁻¹. Two main steps were observed for the thermal decomposition. The activation energies, E_a, of decomposition were calculated by means of isoconversional methods using Tang, Flynn–Wall–Ozawa (FWO), Kissenger–Akahira–Sunose (KAS) and Friedman (FR). Results show that the methods used were in good agreement with each other. Activation energy results were compared by using Kissinger’s and Augis-Bennett (AB) methods. The activation energy values obtained using Kissinger and AB methods showed higher values in both steps than that calculated using isoconversional methods. Results showed that the activation energies of the first step are greater than the second step.

Introduction
In recent years the food, nutrition, and pharmaceutical industries have devoted increasing attention to methylxanthine derivatives because of their various physiological effects.

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