Journal of Thermal Analysis, Vol. 17 (1979) 39—44

INITIAL INVESTIGATION OF THE THERMAL DECOMPOSITION KINETICS OF THE VACUUM-DISTILLATION RESIDUE OF CRUDE OIL

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(Received July 18, 1978, in revised form February 15, 1979)

The equation $\frac{d\alpha}{\alpha^p(1-\alpha)^q} = k\,dt$ was used for an investigation of the mathematical description of the kinetics of the thermal decomposition of the residue remaining after vacuum-distillation of Romashkino crude oil.

The investigations were carried out at 573, 623, 673, 723, and 773 K. Various methods were used for the calculation of the function $F(\alpha)$ using polynomials of different degrees and solving the integrale of precise and approximate methods.

Thermal analysis finds more common application in investigations of the properties of various substances both inorganic and organic. The development of the theoretical basis of thermal analysis and the considerable improvement of the apparatus permits utilization of these methods not only in phase analysis but also in the investigations of reaction kinetics [1 – 5].

Changes of the energy and mass of a sample during heating are strictly connected with the physical and chemical properties of the investigated substance.

Finding a suitable relation between the experimental data obtained from thermal analysis has been and still is the subject of much work.

In investigations of some chemical processes involving changes in mass (depending on the temperature), thermogravimetric methods are used. The change in mass is strictly connected with the reaction kinetics.

Thermogravimetry provides many pieces of information about the course of reactions occurring during heating.

For solid-state reactions the reaction kinetics are described by the general relationship:

$$\frac{d\alpha}{dt} = k \cdot t^m f(\alpha) \tag{1}$$

in which $f(\alpha)$ is a function depending on the mechanism of the reaction: m the exponent may be a function of α.

In more complicated reactions, it often happens that the value of k is not constant, but changes with the progress of the reaction. The most frequently used equation is that given by Zsakó [6]:

$$\frac{d\alpha}{dt} = k\alpha^p \cdot (1-\alpha)^q \tag{2}$$

where p and q are the homogeneity factor; q can formally be called the reaction order.

The aim of the present work was to find an equation suitable for the mathematical description of the thermal decomposition of the vacuum distillation residue of crude oil.

Experimental

The vacuum-distillation residue obtained from petroleum from Romashkino crude oil was used for the investigations. The characteristics are given in Tables 1 and 2. The thermal investigations were carried out by using a derivatograph (MOM Hungary) under dynamic conditions, with argon flowing at 2 l/min, under isothermal conditions at 573, 623, 675, 723 and 773 K. The deviation was ± 2 K. The thermal curves are given in Fig. 1. Because of the complexity of the thermal decomposition of the investigated substance, it seemed proper to use the equation given by Zsakó for the mathematical description of this process and to choose the suitable values of p and q in Eq. 2.

Table 1

Physical and rheological properties of investigated substance

Property		Sample No. 1
Fusing point	K	315.5
	°C	(42.5)
Brittle point	K	261
	°C	(−12)
Penetration under load 0.05 kg at 293 K (25°)		152
Penetration under load 0.1 kg at 298 K (25°)		248
Ductility at 298 K	m	1
Evaporativeness	%	0.30
Density d_{277}^{298}	kg/m³	1012.2
Volatile matter content	%	87.8
Dynamic viscosity	Ns/m²	
at 323 K (50°)		143.80
at 343 K (70°)		13.20
at 373 K (100°)		1.45
at 393 K (120°)		0.41

Polynomials of various degrees ≤ 7 were approximated to the function $\alpha = \alpha(t)$. The polynomials smoothed the experimental values and served for the calculation of the derivative $\frac{d\alpha}{dt}$ (the reaction rate).

The calculated values of the derivatives made it possible to obtain the parameters of p, q and k in relationship 2.

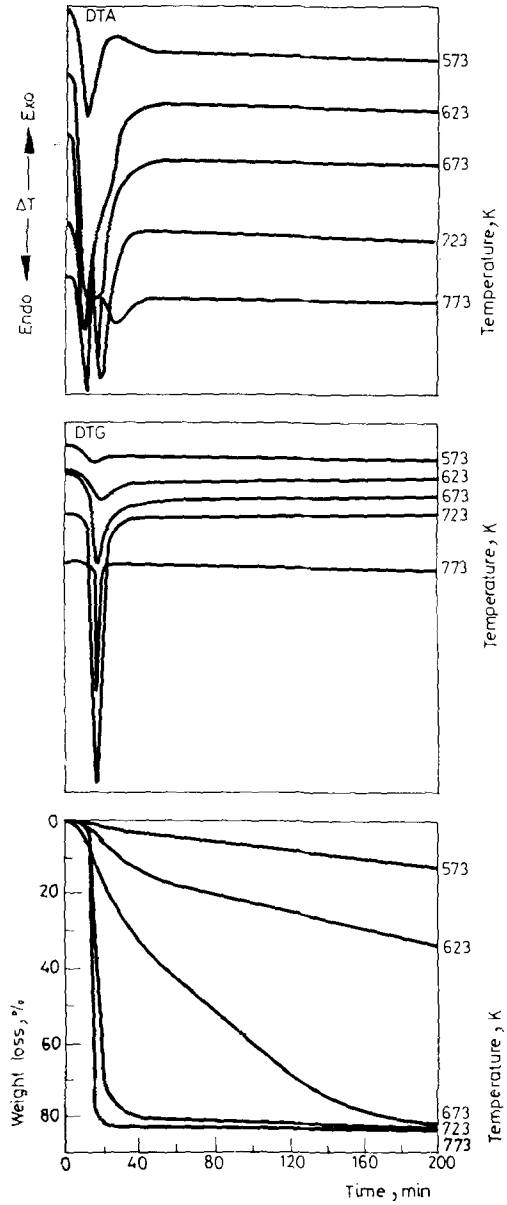

Fig. 1. Thermal analysis curves of vacuum-distillation residue of crude oil at various temperatures. Mass weight 0.5 g; argon atmosphere (2 l/min); ceramic sample holder

Table 2

Chemical properties of the investigated substance

Property		Sample No. 1
Elementary analysis	C %	85.25
	H %	10.54
	S %	2.90
	N %	0.73
Atomic ratio	C/H	0.68
Molecular weight	M	613
Content of		
oils	%	39.3
resins	%	51.4
asphaltenes	%	9.3
Paraffin content	%	4.0
Hydroxyl group content	%	3.8
Carbonyl group content	%	0.7

The programme* was prepared in such a way that on the basis of the calculated values of the derivative and the smoothed values, the optimum parameters p, q and k could be found. The method of least squares was used: this means the criterion of minimalization of the sum:

$$\sum_{i=1}^{n}\left[\frac{d\alpha}{dt_i} - k \cdot \alpha_i^p(1-\alpha_i)^q\right]^2$$

First, efforts were made to determine the optimum values of all the parameters p, q and k; different results were obtained depending on the chosen time and the degree of the polynomial. The great inconstancy of the derivative values made precise calculation impossible.

Consequently, generality was limited and the programme was used with the following restrictions:

1. The probable values of p and q were determined, choosing optimum k.

Analogously:

2. The probable value of p was determined, choosing optimum q and k,
3. The probable value of q was determined, choosing optimum p and k.

The above-mentioned investigations did not give satisfactory results, except for the information about the probable orders of parameters p and q. From the physical interpretation, we have

$$q \geq 1 \text{ and } 0 \leq p < 1$$

In consideration with the accuracy of the solution from the derivative value of function α, test methods were used regarding the optimum choice of p and q (k was fixed for each p and q pair).

* The programme was written in Algol language for an Odra 1204 computer.

The excepted criterion of correctness of choice for p and q consisted of the minimalization of the average deviation of the real time reaction t_i from the suitable calculated moment

$$\frac{1}{k}\int_0^{\alpha_i}\frac{d\xi}{\xi^p(1-\xi)^q}$$

where ξ is the integration variable (in connection with the formula):

$$t(\alpha)=\frac{1}{k}\int_0^{\alpha}\left\{\frac{d\xi}{\xi^p(1-\xi)^q}\right\}.$$

The integral was calculated precisely for the values given below:

$p = 0$	$q =$ optional
$p = 0.25$	$q = 1$
$p = 0.5$	$q = 1$
$p = s$	$q = 2 - s$

where $s = 0.15$; 0.5; 0.75. The approximate method was used for many other pairs of values of p and q. The tests suggested the following orders of parameter values (depending on the temperature of the decomposition reaction):

for $T = 573$ K:	$p = 0$;	$q = 1.5$;	$k = 0.0098$ min^{-1}
$T = 623$ K:	$p = 0$;	$q = 1.75$;	$k = 0.0187$ min^{-1}
$T = 673$ K:	$p = 0$;	$q = 1.75$;	$k = 0.0202$ min^{-1}
$T = 723$ K;	$p = 0$;	$q = 1.8$;	$k = 0.6570$ min^{-1}
$T = 773$ K:	$p = 0.1$;	$q = 2$;	$k = 0.9720$ min^{-1}.

Results according with the experimental data were also obtained for quite other parameters of p and q at 723 K:

for $T = 723$ K:	$p = 0.4$;	$q = 1$;	$k = 0.200$
	$p = 0.4$;	$q = 1.1$;	$k = 0.227$
	$p = 0.3$;	$q = 1.3$;	$k = 0.283$

Conclusions

The equation given by Zsakó was used for a mathematical description of the kinetics of thermal decomposition of the residue remaining after vacuum-distillation of crude oil. Various methods were used for calculation of the function $F(\alpha)$: the method of choosing parameters p and q by using polynomials of various degrees, and methods of choosing some parameters and calculation of the others by solving the integrals by precise and approximate methods.

Good results such as those obtained for decomposition at lower temperatures, e.g. 573, 623 and 673 K, were not obtained at 723 and 773 K (different parameters p, q and k). At these temperatures the process occurs very quickly and is more complicated.

References

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RÉSUMÉ — Afin d'étudier la description mathématique de la cinétique de la réaction de décomposition thermique du résidu obtenu après distillation sous vide de l'huile brute de Romashkino, l'équation

$$\frac{d\alpha}{\alpha^p(1-\alpha)^q} = k dt \text{ a été utilisée.}$$

Les mesures ont été effectuées aux températures de 573, 623, 673, 723 et 773K. La fonction $F(\alpha)$ a été calculée à l'aide de diverses méthodes, en utilisant des polynômes de différents degrés et en résolvant les intégrales de façon précise et par approximations.

ZUSAMMENFASSUNG — Die Gleichung $\frac{d\alpha}{\alpha^p(1-\alpha)^q} = k dt$ wurde zur Untersuchung der mathematischen Beschreibung der Reaktionskinetik der thermischen Zersetzung des Rückstandes nach Vakuumdestillation des Romaschkiner Rohöls angewandt.

Die Untersuchungen wurden bei den Temperaturen von 573, 623, 673, 723 und 773 K durchgeführt. Verschiedene Methoden wurden zur Berechnung der Funktion $F(\alpha)$ unter Verwendung der Polynome verschiedener Ordnung und Lösung des Integrals von präzisen und Näherungsmethoden eingesetzt.

Резюме — При исследовании математического описания кинетики реакций термического разложения остатка, получаемого после вакуумной перегонки сырой нефти ромашкинского месторождения, использовали уравнение $\frac{d\alpha}{\alpha^p(1-\alpha)^q} = k dt$. Исследования были проведены при температурах 573, 623, 673, 723 и 773 К. Применяли различные методы для вычисления функции $F(\alpha)$, используя полиномы различных степеней и интегральные решения точных и приближенных методов.