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A STUDY OF THE MIXTURE OF COAL AND RESIDUE OF THE VACUUM DISTILLATION OF CRUDE OIL BY THERMAL ANALYSIS

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Thermal analysis was used for investigating the effect of the addition of the residue obtained from crude oil vacuum distillation on the carbonization process of brown coal. The kinetic analysis of the experimental TG curves was carried out by using the Coats-Redfern equation and then to select the most likely mechanism (function $g(\alpha)$) for particular decomposition stages of brown coal and its mixture with the residue. In the brown coal carbonization process the nucleation of a new solid phase is predominant. In the temperature range of the decomposition of coal (620–820 K) the addition of residue results a change in the mechanism of the thermal decomposition process – in the mixture three-dimensional diffusion processes and one-dimensional diffusion occur, depending on the composition. Above 730 K (secondary carbonation processes) the most likely mechanism involves the nucleation of a new solid phase as well as diffusion processes.

Keywords: brown coal, crude oil, kinetic analysis

Introduction

Thermal analysis enables physical and chemical phenomena occurring in the substance investigated during heating to be investigated. The theoretical principles for calculating kinetic parameters are based mainly on investigations into the energy and mass changes at a constant temperature (isothermal conditions) or at a variable temperature (non-isothermal conditions). The kinetic equation describing the thermal decomposition rate of solids is as follows:

$$g(\alpha) = k \cdot t$$

where $g(\alpha)$ is the function describing the mechanism of the reaction, k – is the rate constant and t the time.

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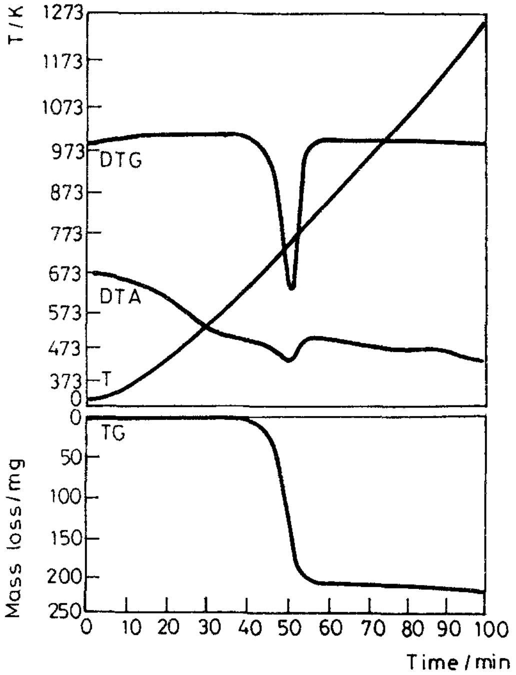

Fig 1. Thermoanalytical curves of the residue obtained after the vacuum distillation of crude oil

The result of kinetic investigations obtained experimentally is the relationship between degree of conversion (α) and time (t). The above relationship is the function of three kinetic parameters: A – preexponential factor in the Arrhenius equation, E_A – activation energy and the form of the expression $g(\alpha)$ – theoretically depending on the reaction mechanism of the thermal dissociation. Several dozen theoretical equations are known to have been obtained [1–13]. Three basic types of the function $g(\alpha)$ may be distinguished depending on the kind of stages limiting the total rate of the process, which may be as follows:

- formation of nuclei of a new solid phase
- reaction at the boundary of product-substrate phases
- diffusion of gaseous reaction products.

The present study was aimed at utilizing thermal analysis for investigating the effect of the addition of the residue obtained from crude oil vacuum distillation on the carbonization process of brown coal.

Experimental

The subject of the study was brown coal from Lubstów Coal Mine, residue after vacuum distillation of crude oil and their physical mixtures (coal:residue = 88:12; 78:22 wt.% respectively). The thermal investigations were carried out using a derivatograph (MOM Hungary) under dynamic conditions with nitrogen flowing at a constant rate, the heating rate being 10 deg·min^{-1}, mass of sample: 300 mg.

Results

The results of the thermal analysis of the material investigated are shown in Figs 1-4. On the basis of the thermal curves of brown coal four temperature ranges may be distinguished (Fig 2):

I 323–473 K temperature range indicating the water loss

II 559–760 K temperature range in which the decomposition of coal occurs with an appreciable weight loss (44 wt.%), the primary carbonization process

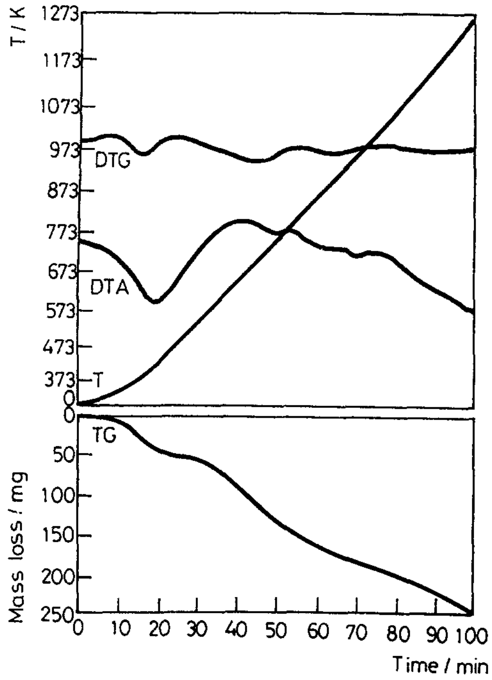

Fig 2. Thermoanalytical curves of brown coal from Lubstów Coal Mine

III 791–958 K temperature range, in which an endothermic peak accompanies an appreciable weight loss of the substance; according to the literature [14] this is connected with the start of hydrogen release

IV 968–1228 K temperature range containing an endothermic peak connected with the increase of hydrogen release

III and IV temperature ranges connected with the secondary carbonization process.

The residue decomposes in one stage in the narrow temperature range between 685–773 K, the peak minimum is at 748 K. The peak is accompanied by an appreciable weight loss of the residue (about 70 wt.%) (Fig. 1).

It may be stated that all the DTA curves of the mixtures of coal with the residue investigated are of similar nature (Figs 3 and 4).

Based on the thermal analysis and the equation proposed by Coats-Redfern, as well as by making use of the mathematical apparatus applied to the description of the kinetics of the thermal decomposition reaction of solids an investigation was made into the mechanism of the thermal decomposition of Lubstów brown coal and its mixtures with the residue. The kinetic analysis of the experimental TG curves was carried out using the Coats-Redfern equation [5]:

$$\frac{\ln g(\alpha)}{T^2} = \ln\left[\frac{AR}{\beta E_a}\left[1 - \frac{2RT}{E_a}\right]\right] - \frac{E_a}{RT}$$

where

α – degree of conversion

A – preexponential factor

R – gas constant

β – heating rate

T – temperature

E_a – activation energy

$g(\alpha)$ – function determining the thermal decomposition mechanism.

The above equation was used for determining the E_a – activation energy and for selecting the most likely mechanism for the particular decomposition stages of a few samples chosen (according to Table 2). The criterion of the division of TG curves were minimum temperature peaks on DTA and DTG curves (the peak displaying coal moisture was disregarded).

For the residue (Fig. 1) one stage of the decomposition in the 685–773 K temperature range was determined.

For brown coal (Fig. 2) the TG curve was divided into three temperature ranges:

Table 1 Characteristics of brown coal and of the residue obtained after vacuum distillation of crude oil

Sample	Moisture W_a /wt.%	Ash A_d /wt.%	Volatile matter V_{daf}* /wt.%
brown coal	9.8	13.4	34.4
residue	0	0.036	87.8

* daf means dry and ash free

I 559–760 K
II 791–958 K
III 968–1228 K

The TG curve of the mixture of brown coal with 12 wt.% residue (Fig. 3) was also divided into three temperature ranges:

I 501–718 K
II 733–946 K
III 983–1225 K

The TG curve of the mixture of brown coal with 22 wt.% residue (Fig. 4) was divided into two temperature ranges:

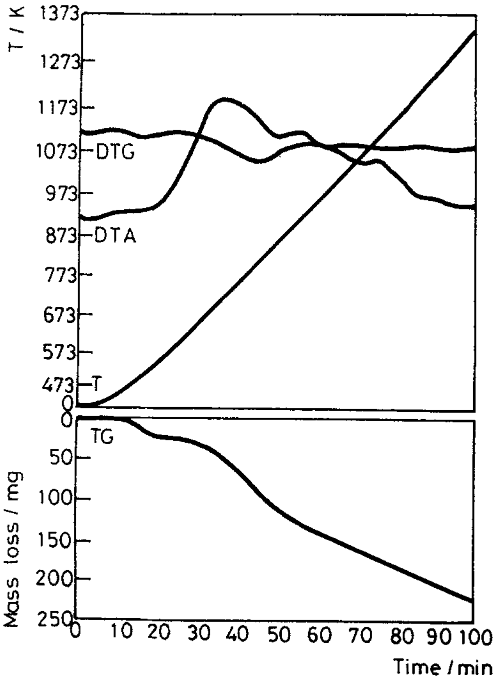

Fig 3. Thermoanalytical curves of brown coal mixed with 12 wt.% residue

I 493–746 K
II 768–1245 K

For each stage, the degree of conversion α depending on temperature was calculated in the following way:

$$\alpha = \frac{\Delta m_T}{\Delta m_c}$$

where

Δm_T – weight loss at temperature T
Δm_c – final weight loss in the stage

10 $g(\alpha)$ functions were calculated for each value of the conversion degree and temperature, and the dependence of $\ln g(\alpha)/T^2$ on $1/T \cdot 10^3$ was determined to verify the linearity of the function.

Table 2 $g(\alpha)$ function for various reaction mechanisms of solid thermal decomposition

Symbol	$g(\alpha)$	Reaction rate determining process
D_1	α^2	one-dimensional diffusion
D_2	$(1-\alpha)\ln(1-\alpha)+\alpha$	two-dimensional diffusion cylindrical symmetry
D_3	$\frac{3}{2}\left[1-(1-\alpha)^{2/3}\right]$	three-dimensional diffusion spherical symmetry, Jander's equation
D_4	$\frac{3}{2}\left[1-\frac{2}{3}\alpha-(1-\alpha)^{2/3}\right]$	three-dimensional diffusion spherical symmetry, Ginstling and Brounstein's equation
F_1	$-\ln(1-\alpha)$	random nucleation, only one nucleus on each molecule
A_2	$-\ln(1-\alpha)^{1/2}$	random nucleation Avrami's equation I
A_3	$-\ln(1-\alpha)^{1/3}$	random nucleation Avrami's equation II
R_2	$2\left[1-(1-\alpha)^{1/2}\right]$	reaction at the boundary of phases, cylindrical symmertry
R_3	$3\left[1-(1-\alpha)^{1/3}\right]$	reaction at the boundary of phases, spherical symmetry
R_1	α	reaction at the boundary of phases, one-dimensional (zero order), Polany-Wigner's reaction

Snedecor test (F) was used as a measure of significance of the function $g(\alpha)$

$$F = \frac{r^2 \cdot (N-2)}{1-r^2}$$

where

r – linear correlation factor

N – number of measured points

It has been assumed that for $F > F_{cr}$ the function $g(\alpha)$ is significant as it determines the most likely mechanism of decomposition. F_{cr} – the critical value of Snedecor random variable satisfying the condition $P(F > F_{cr}) = 0.01$. The values of the activation energy E_a, linear correlation factor r, Snedecor test F as well as of the standard error S obtained from the TG curves of the above mentioned stages of the analysis of chosen samples are given in Tables 3-6. Calculations were carried out by means of computer programme in Pascal language.

Table 3 Kinetic analysis of the thermal decomposition of the residue ($F_{cr} = 11.3$; $\alpha = 0.024 - 0.939$; $T = 685 - 773$ K)

Mechanism	E_a / kJ·mol^{-1}	Statistical parameters		
		r	F	S
D1	375.3	0.973755	109	0.635617
D2	401.8	0.981307	156	0.571073
D3	436.6	0.969145	271	0.470050
D4	413.2	0.984249	185	0.537799
F1	231.4	0.993974	493	0.184958
A2	109.7	0.993192	436	0.093207
A3	69.2	0.992281	384	0.062643
R1	181.5	0.971929	102	0.318477
R2	203.6	0.984815	193	0.260152
R3	212.3	0.988549	257	0.234846

Kinetic calculations on the basis of thermoanalytical measurements are useful for determining a probable reaction mechanism. The calculations carried out for a given temperature range indicate different reaction mechanisms. By comparing the value of E_a* for lower temperature ranges

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* E_a – the activation energy calculated may be referred to as the apparent activation energy

Table 4 Kinetic analysis of the thermal decomposition of brown coal

Mechanism	E_a / kJ·mol^{-1}	Statistical parameters		
		r	F	S
Stage I (F_{cr} = 9.33; α = 0.027–0.916; T = 559–760 K)				
D_1	101.8	0.946242	85	0.655658
D_2	110.7	0.959429	115	0.612826
D_3	121.1	0.970903	164	0.562468
D_4	114.4	0.964329	132	0.591696
F_1	61.7	0.978540	225	0.244563
A_2	25.3	0.965878	139	0.128055
A_3	13.4	0.945924	85	0.086539
R_1	45.5	0.932609	66	0.331782
R_2	52.8	0.9590607	114	0.293861
R_3	55.6	0.966329	141	0.2789
Stage II (F_{cr} = 11.3; α = 0.062–0.937; T = 791–958 K)				
D_1	172.1	0.880486	21	0.871551
D_2	192.5	0.902944	26	0.862071
D_3	220.3	0.931429	39	0.809765
D_4	201.9	0.913978	30	0.843218
F_1	118.9	0.947894	53	0.376029
A_2	52.2	0.93098	39	0.192464
A_3	29.9	0.908369	28	0.12974
R_1	78.8	0.861097	17	0.437519
R_2	96.2	0.907198	28	0.419798
R_3	103.2	0.921287	34	0.409792
Stage III (F_{cr} = 9.65; α = 0.043–0.913; T = 968–1228 K)				
D_1	186.9	0.946599	77	0.578164
D_2	204.3	0.953655	90	0.585436
D_3	228.1	0.973607	163	0.485595
D_4	215.2	0.968446	120	0.527592
F_1	117.3	0.979161	209	0.220948
A_2	49.4	0.967909	133	0.116515
A_3	26.8	0.947723	79	0.081903
R_1	87.3	0.935259	63	0.300188
R_2	99.2	0.960308	106	0.261789
R_3	104.8	0.967663	132	0.248215

Table 5 Kinetic analysis of the thermal decomposition of brown coal mixed with 12 wt.% residue

Mechanism	E_a / kJ·mol^{-1}	Statistical parameters		
		r	F	S
Stage I (F_{cr} = 9.65; α = 0.03–0.94; T = 501–718 K)				
D_1	83.0	0.992844	760	0.220519
D_2	90.1	0.997057	1860	0.153045
D_3	99.3	0.998175	3005	0.132621
D_4	93.1	0.997962	2691	0.131496
F_1	49.6	0.994241	946	0.118105
A_2	19.8	0.991942	674	0.05595
A_3	9.9	0.986908	412	0.035692
R_1	36.5	0.98976	529	0.116268
R_2	42.4	0.997538	2225	0.0658176
R_3	44.6	0.997714	2397	0.066759
Stage II (F_{cr} = 9.33; α = 0.077–0.923; T = 733–946 K)				
D_1	96.5	0.903503	44	0.608912
D_2	109.6	0.924074	58	0.6000105
D_3	125.2	0.945848	85	0.571834
D_4	114.3	0.932501	67	0.58904
F_1	64.6	0.952649	98	0.274616
A_2	25.5	0.925448	59	0.138939
A_3	12.5	0.870159	31	0.939016
R_1	41.4	0.873586	32	0.306948
R_2	51.5	0.919517	35	0.292787
R_3	55.8	0.932549	67	0.28777
Stage III (F_{cr} = 9.33; α = 0.042–0.917; T = 983–1225 K)				
D_1	203.8	0.932969	67	0.677622
D_2	223.0	0.944931	83	0.665695
D_3	247.9	0.959999	117	0.623042
D_4	231.2	0.950473	93	0.651507
F_1	128.2	0.966811	143	0.291953
A_2	54.9	0.954603	103	0.147872
A_3	30.6	0.935177	69	0.09993
R_1	92.6	0.916464	52	0.348519
R_2	108.7	0.945209	83	0.323712
R_3	114.8	0.953239	99	0.313641

(Tables 5 and 6 – I stage) it can be seen distinctly that addition of then of the residue to brown coal reduced the reaction rate which determines the diffusion processes. For coal, however, the most likely mechanism is the nucleation of a new solid phase (Table 4). In the higher temperature ranges (Table 5 – stages II and III and Table 6 – stage II) the reaction mechanism for mixtures is the same as that for coal. The value of the apparent activation energy for a mixture with 22 wt.% residue is lower as compared with the E_a value for 12 wt.%. residue. This difference results from an increase in the mass loss for mixtures with a higher content of residue. The above given kinetic data cannot be approached indiscriminately. The thermal decomposition reaction of coal and its mixtures with the residue is a complex process taking place in the heterogeneous system the course of which is affected by a number of external parameters as well as by those characteristic of the sample being investigated.

In spite of the difficult interpretation of the kinetic data they account, to a certain degree, for the existing phenomena given above.

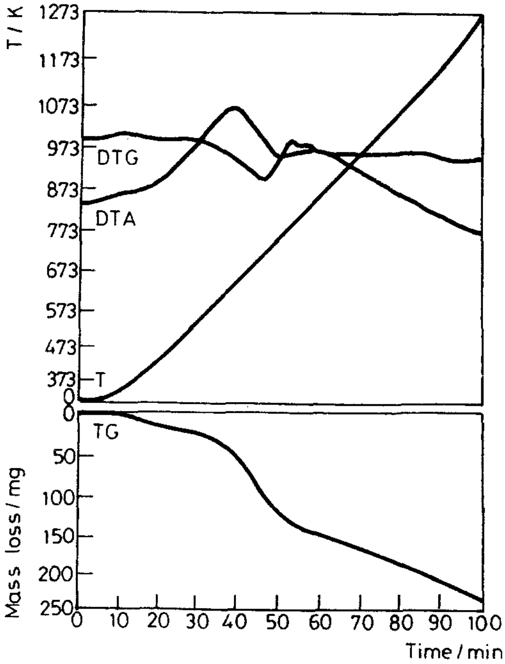

Fig 4. Thermoanalytical curves of brown coal mixed with 22 wt.% residue

Table 6 Kinetic analysis of the thermal decomposition of brown coal mixed with 22 wt.% residue

Mechanism	E_a / kJ·mol^{-1}	Statistical parameters		
		r	F	S
Stage I (F_{cr} = 8.68; α = 0.022–0.888; T = 493–730 K)				
D_1	82.9	0.999512	13317	0.064433
D_2	88.1	0.998629	4730	0.114765
D_3	94.8	0.995337	1387	0.228323
D_4	90.3	0.997768	2903	0.150168
F_1	45.9	0.988547	558	0.174417
A_2	17.9	0.983802	392	0.081391
A_3	8.6	0.973397	234	0.050549
R_1	36.2	0.999346	9931	0.032607
R_2	40.7	0.996861	2061	0.080412
R_3	42.4	0.99473	1224	0.108611
Stage II (F_{cr} = 8.18; α = 0.033–0.928; T = 768–1223 K)				
D_1	76.9	0.925811	108	0.591774
D_2	86.3	0.950118	167	0.533198
D_3	90.5	0.928707	113	0.699198
D_4	89.7	0.956158	192	0.517319
F_1	46.9	0.966713	242	0.229059
A_2	15.0	0.919663	99	0.121029
A_3	4.7	0.721604	19	0.085212
R_1	31.0	0.894909	72	0.291182
R_2	37.8	0.938877	134	0.261197
R_3	40.4	0.949836	166	0.25041

Conclusions

– In the decomposition process (carbonization) of brown coal processes of the nucleation of a new solid phase (mechanism F_1, i.e.: $g(\alpha)) = -\ln(1-\alpha)$ are prevailing. In the temperature range of the coal decomposition (620–820 K) the addition of residue gives rise to a change in the mechanism of the thermal decomposition process – in the mixture three-dimensional diffusional processes are prevailing (mixture containing 12 wt.% residue) and one-dimensional diffusion (mixture with 22 wt.% residue).

– Above 730 K (secondary carbonization processes) the most likely mechanism involves the nucleation of a new solid phase as well as diffusion processes.

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Zusammenfassung — Mittels Thermoanalyse wurde der Einfluß des Zusatzes eines Destillationsrückstandes aus der Vakuumdestillation von Rohöl beim Verkokungsprozeß von Braunkohle untersucht. Die kinetische Analyse der TG-Kurven wurde mittels der Coats-Redfern-Gleichung ausgeführt um dann den bestpassenden Mechanismus (Funktion $g(\alpha)$) für die einzelnen Zersetzungsschritte von Braunkohle bzw. deren Gemisches mit dem Rückstand auszuwählen. Beim Verkokungsprozeß der Braunkohle herrscht der Keimbildungsvorgang der neuen Festphase vor. Im Temperaturbereich der Zersetzung der Kohle (620-820 K) verursacht der Zusatz des Rückstandes eine Änderung des Reaktionsmechanismus des thermischen Zersetzungsprozesses - in Abhängigkeit von der Zusammensetzung des Gemisches verlaufen drei- bzw. eindimensionale Diffusionsvorgänge. Oberhalb von 730 K (sekundärer Verkokungsprozeß) beinhaltet der passendste Mechanismus sowohl die Keimbildung einer neuen Festphase als auch Diffusionsvorgänge.