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KINETICS OF EVOLUTION OF INDIVIDUAL GASES IN THE COURSE OF SHALE THERMAL DECOMPOSITION

I. Experimental results

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The results are presented of an experimental investigation of the kinetics of evolution of C_nH_m, CH_4, CO and H_2 in the course of shale thermal decomposition. The experiments were carried out with a complex experimental set-up consisting of a derivatograph, a chromatograph and a spectrophotometer, with shale samples of different fractions from different seams of basic commercial deposits. In spite of the differences in the sites of taking the samples and in their characteristics, the reaction rate curves for each gas are close to one another.

The thermal decomposition of shale is a matter of current interest in a number of countries. Soviet and American scientists are paying special attention to this question [1, 2] as there are large shale deposits in their countries (such as the Pribaltic shale in the U.S.S.R. and the combustible shale of the Green River deposits in the U.S.A.). One of the most interesting problems is the kinetics of evolution of the individual gases. This article is devoted to an investigation of Pribaltic shale and is a continuation of a series dealing with shale combustion and its mineral matter behaviour in the course of shale thermal decomposition, e.g. [3, 4].

Pribaltic shale finds very large use in the chemical and energetics industries in the European part of the U.S.S.R., but the processes of its thermal decomposition not have yet been studied sufficiently deeply. The dynamics of total volatile matter production are studied in the majority of the works, but publications devoted to determination of the kinetic parameters are few and contradictory [5]. The most interesting and the most complicated question in the study of solid fuel pyrolysis is the kinetics of evolution of the individual gases. We know of no publication devoted to this question with reference to Pribaltic shale, except [6]. In [6] we presented the dependences of the weight change and the rate of weight change of the sample as

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functions of temperature in the course of shale thermal decomposition. The temperatures and kinetic constants were determined for the processes of resinification, resinification with gas evolution and carbonate decomposition (formation of CO_2). In this work, detailed experimental data are presented on the kinetics of production of C_nH_m, CH_4, CO and H_2.

Experimental

The experiments were carried out with samples of Estonian shale, taken from four seams of commercial deposits: from the "Akhtme" mine (seams E and B), and from the "Leningradskaya" mine (seams I and III). The results of chemical analysis:

seam B: $\gamma = 1.62\ 10^{-3}$ kg m^{-3}, $A = 46.6\%$, $W = 7.8\%$, $Q = 1.26\ 10^4$ kJ kg^{-1};

seam E: $\gamma = 1.88\ 10^{-3}$ kg m^{-3}, $A = 44.7\%$, $W = 12.8\%$, $Q = 0.9\ 10^4$ kJ kg^{-1};

seam I: $\gamma = 1.69\ 10^{-3}$ kg m^{-3}, $A = 42.9\%$, $W = 10.3\%$, $Q = 1.02\ 10^4$ kJ kg^{-1};

seam III: $\gamma = 1.59\ 10^{-3}$ kg m^{-3}, $A = 43.2\%$, $W = 8.1\%$, $Q = 1.16\ 10^4$ kJ kg^{-1}.

For all samples $S = 1.4\%$ (γ = density, A = ash content, W = moisture content of shale, Q = low heat value, and S = sulphur content).

The samples were milled in the laboratory roller mill, with separation into the following fractions: 0.00–0.05, 0.05–0.10, 0.10–0.315, 0.315–1.0 and 1.0–2.5 mm, which were used for the investigation.

Complex thermal analysis was used to study the kinetics of individual gas evolution. This system was described in detail in [7] and consists of a derivatograph (the total output of volatile matter and CO_2 from carbonate decomposition was determined), a chromatograph (the output of H_2 and C_nH_m was determined) and a spectrophotometer (the output of CO, CO_2 and CH_4 was determined). Three experiments were carried out on each fraction and statistical mean curves were plotted for each fraction too. As noted in [6], these curves are close to each other: the deviation in the experimental data is within 10%. Accordingly, one statistical mean curve is given below for all the fractions. An exception is the fraction

1.0–2.5 mm, for which diffusional complications were noted. The cause of this was apparently the large particle size, so that a considerable layer of reaction product blocked the diffusion of evolved gases, particularly at the end of the reaction. Thus, the experimental data on this fraction were not used for plotting of the statistical mean curves or for kinetic parameter computation.

The experiments were carried out with a sample mass up to 0.3 g, which was put on a multiplate sample holder (5 plates). A dynamic inert atmosphere of N_2 with a flow rate of 10^{-5} m^3 s^{-1} was used. The samples were heated up to 1173 K at a heating rate of 0.167 K s^{-1}. Al_2O_3 was used as reference material.

Such experimental conditions made it possible to eliminate the diffusional complications arising because of the large particle size, the "gas jacket" effect around the decomposed individual particles and the influence of the sample layer thickness (a monolayer arrangement of the sample particles was used). These effects have been reported to be observed from a sample mass of ~1 g [8]; our data suggested that they are observed from a sample mass of 0.5 g. All the above findings indicate that the experiments were carried out in the kinetic region.

Results and discussion

The experimental statistical mean curves of the reaction rate of individual gas formation are presented in Figs 1–4. The value of α was calculated by analogy with formal kinetics, i.e. as the fraction of evolved gas: $\alpha(t) = \frac{m(t)}{m_0}$, where m_0 and $m(t)$ are the total and variable mass of evolved gas, respectively, and t is time. Thus, it

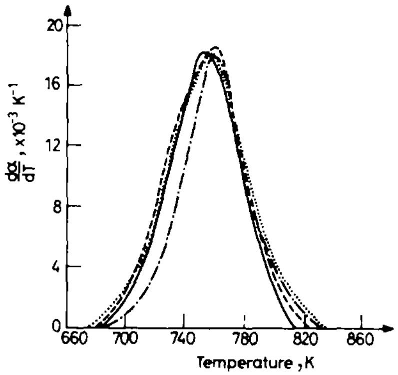

Fig. 1 C_nH_m outlet rate dependence on the temperature in the course of shale thermal decomposition.
— — — - B seam; — · — - E seam;
— · · — - I seam; — ∘ — - III seam

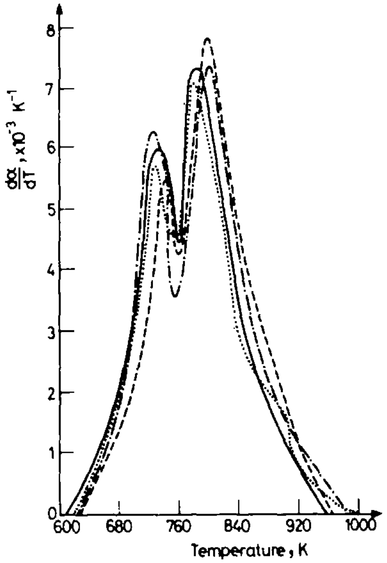

Fig. 2 CH_4 outlet rate dependence on the temperature in the course of shale thermal decomposition.
— — — - B seam; — · — -- E seam;
— · · — - I seam; — ○ — - III seam

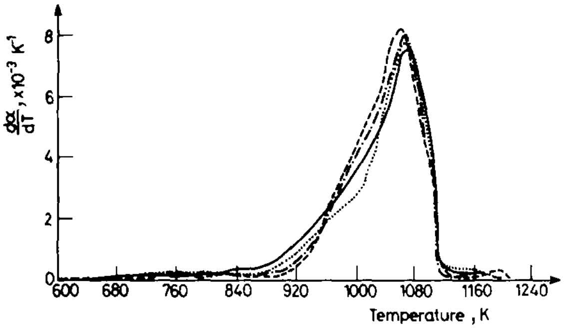

Fig. 3 CO outlet rate dependence on the temperature in the course of shale thermal decomposition.
— — — - B seam; — · — E seam;
— · · — - I seam; — ○ — - III seam

was assumed that $\alpha = 1$ at the final temperature of the reaction (when the evolved gas could not be determined with our experimental methods). Three representative reaction temperatures are presented in Table 1: T_m = the reaction rate maximum temperature; T_1 = the temperature corresponding to $\alpha = 0.01$; and T_2 = the temperature corresponding to $\alpha = 0.99$. The initially evolved gas traces emerge significantly earlier. Thus, CO formation begins at ≈ 603 K and H_2 formation at 640 K (Figs 1–4). However, the quantity formed in this range is very small in

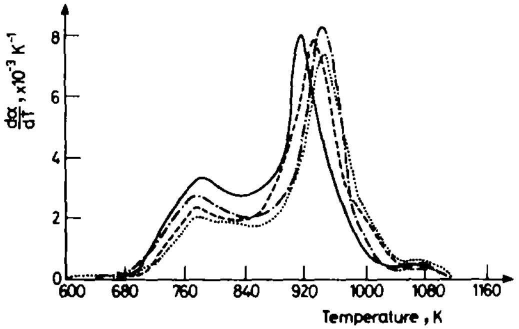

Fig. 4 H_2 outlet rate dependence on the temperature in the course of shale thermal decomposition.
— -- — - B seam; — · — - E seam;
— ·· — - I seam; — ○ — - III seam

comparison with the total output. It is necessary to note some of the main features in the experimental results. The kinetic curves for the individual gases are close to one another for all of the investigated seams. The reactions begin with CH_4 evolution, followed by C_nH_m, H_2 and CO (Fig. 5). The reaction rate curves for C_nH_m have a clear beginning and end. The formation of these gases is obviously determined by one reaction or by a group of parallel reactions proceeding simultaneously. The reaction rate curves for CH_4 have two peaks and indicate at least two different overlapping reactions. The situation is similar for H_2 formation. The small peak at ≈ 775 K shows that one more reaction takes place. It is obvious that, after the end of the basic reaction of H_2 evolution, further processes take place which lead to the formation of a small amount of H_2 up to ≈ 1150 K. The kinetic curves for CO have no clear initial and final temperatures. A very weak CO formation is noted in the temperature range 603–873 K. An analogous situation occurs after the end of the basic reaction (or the group of reactions) in the temperature range 1123–1193 K. Unknown weak processes leading to CO formation proceed in this range.

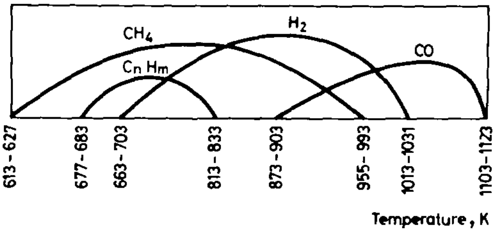

Fig. 5 Temperature ranges of separate gases evolution in the course of shale thermal decomposition

Table 1 The characteristics of separate gases outlet

Place of sampling	Seam	T_1, K				T_m, K				T_2, K				α_m			
		C_nH_m	CH_4	CO	H_2	C_nH_m	CH_4	CO	H_2	C_nH_m	CH_4	CO	H_2	C_nH_m	CH_4	CO	H_2
“Akhtme”	B	681	628	897	703	760	802	1059	933	822	967	1117	1023	0.740	0.510	0.675	0.620
mine	E	681	620	903	673	760	805	1066	943	830	983	1123	1013	0.675	0.650	0.660	0.750
“Leningradskaya”	I	677	623	873	663	757	781	1064	944	833	993	1103	1031	0.550	0.475	0.760	0.630
mine	III	683	613	881	693	750	790	1066	913	813	955	1113	1013	0.725	0.565	0.725	0.475

Accordingly, for all the studied samples from all the seams the reaction rate curves are very close both qualitatively and quantitatively. All these facts permit the assumption of a single reaction mechanism determining the formation of each gas in the course of shale thermal decomposition. Independently of the deposits, it is suggested that unique kinetic constants are sufficient to describe the kinetics of evolution of each gas.

References

1 K. Lonvik, K. Rajeshwar and J. B. Dubow, Thermochim. Acta, 42 (1980) 11.

2 B. I. Tyagunov, G. P. Stelmakh, V. I. Chugul, A. B. Gavrilin, Yu. V. Aronovich and B. M. Dolgopolov, Khim. Tverd. Topl., 3 (1982) 26.

3 V. Yu. Zakharov, Yu. A. Rundygin and I. A. Shchuchkin, In: Using of modern physical-chemical methods of the processes and products for chemical and coal-chemical processing, Irkutsk, 1976, p. 29.

4 V. Yu. Zakharov, V. V. Pomerantsev and Yu. A. Rundygin, Joint Power Generation Conference, 82-JPGC Fu-2, N.Y., 1982.

5 Yu. N. Korchunov and K. D. Syrkina, In: Transactions of All-Union Conference on theory of combustion, v. 2, Moscow, Published by Academy of Sciences, 1960, p. 21.

6 V. Yu. Zakharov, V. V. Pomerantsev, Yu. A. Rundygin and I. A. Shchuchkin, Proceedings of universities of USSR, Power Engineering, 5 (1980) 56.

7 B. V. Nelyubin and G. P. Alaev, Khim. Tverd. Topl., 1 (1969) 44.

8 S. M. Dolgikh and Ya. A. Belikhmaer, Khim. Tverd. Topl., 4 (1984) 137.

Zusammenfassung — Ergebnisse einer experimentellen Untersuchung der Kinetik der Freisetzung von C_nH_m, CH_4, CO und H_2 im Verlaufe der thermischen Zersetzung von Schiefern werden mitgeteilt. Die Versuche wurden mit einer komplexen, aus einem Derivatograph, einem Chromatograph und einem Spektrophotometer bestehenden Ausrüstung vorgenommen. Untersucht wurden Schiefer von verschiedenen, kommerziell abgebauten Lagerstätten. Obwohl sich die Schieferproben hinsichtlich der Lage und der Charakteristik des Vorkommens unterscheiden, verlaufen doch die Reaktionsgeschwindigkeitskurven für jedes Gas nahezu gleich.

Резюме — Представлены результаты экспериментального исследования кинетики выхода C_nH_m, CH_4, CO, H_2 при термическом разложении сланца. Опыты проводились на комплексной экспериментальной установке, состящей из дериватографа, хроматографа и спектрофотометра, с образцами сланца различных фракций из различных пластов основных промышленных месторождений. Показано, что кривые скорости реакции для каждого газа близки друг к другу независимо от различий в местах отборов образцов и их характеристиках.