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 C₉Hᵥ, CH₄, CO and H₂ 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
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$_n$H$_m$, 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: $\gamma = 1.62 \times 10^{-3}$ kg m$^{-3}$, $A = 46.6\%$, $W = 7.8\%$, $Q = 1.26 \times 10^4$ kJ kg$^{-1}$;
- seam E: $\gamma = 1.88 \times 10^{-3}$ kg m$^{-3}$, $A = 44.7\%$, $W = 12.8\%$, $Q = 0.9 \times 10^4$ kJ kg$^{-1}$;
- seam I: $\gamma = 1.69 \times 10^{-3}$ kg m$^{-3}$, $A = 42.9\%$, $W = 10.3\%$, $Q = 1.02 \times 10^4$ kJ kg$^{-1}$;
- seam III: $\gamma = 1.59 \times 10^{-3}$ kg m$^{-3}$, $A = 43.2\%$, $W = 8.1\%$, $Q = 1.16 \times 10^4$ kJ kg$^{-1}$.

For all samples $S = 1.4\%$ ($\gamma$ = 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$_n$H$_m$ 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

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