THERMOANALYTICAL AND THERMOGASTITRIMETRIC INVESTIGATION OF OIL-SHALES

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From thermoanalytical curves (DTG, TG) recorded in an oxygen atmosphere, the moisture and carbonate contents of oil-shales were determined with acceptable accuracy. The nature of the carbonates was predicted from the shape of the DTG curves above 550°C. Dolomite (ankerite) as found in Gérece oil-shale, and calcite in Pula-9 oil-shale. The clay content was determined from the signal of a water-detector recorded in a nitrogen atmosphere. The peaks at 80°C and 150°C for Gérece oil-shale were attributed to montmorillonite, and the sharp peak at 525°C for Pula-9 oil-shale to kaolinite.

The volatile and fixed carbon contents of the oil-shales were calculated from the thermogastitrimetric curves.

Oil-shale (mineralogically called alignite) has been defined as a compact laminated rock of sedimentary origin which contains 15-50% organic matter [2]. The organic matter can at best be only slightly extracted with ordinary solvents for petroleum [1]. If the organic matter is subjected to heat it yields shale-oil, the composition of which depends on the atmosphere used [3, 4].

Distillation [5], thermogravimetry [2, 6] and NMR spectrometry [7] are commonly used for quantitative determination of the utilizable organic matter, with organic elemental analysis for determination of the total content.

The present paper describes thermoanalytical investigations on raw oil-shales, in which the mass change and the carbon content of the evolved organic matter were determined simultaneously. The investigations were carried out in inert (nitrogen) and in active (oxygen) atmospheres. The total carbon content of the gaseous products (in the presence of the carrier gases mentioned above) was completely converted to carbon dioxide by means of postcatalytic combustion [8, 9] and continuously titrated.
Experiments

Materials

Two kinds of raw, powdered Hungarian oil-shale, found in the vicinity of Gérce and Pula, in Transdanubia, were investigated.

Their total carbon contents (organic and inorganic) were determined with an elemental analyser (CHN–I, Laborator Pristoje, Prague). The total carbon contents (organic and mineral) of the oil-shales were 7.68% (Gérce) and 12.95% (Pula–9). Their mineralogical compositions were estimated with an X-ray diffractometer (Philips, PM 8203, CuKα line). The minerals found were as follows:

Gérce: quartz, chlorite, muscovite, ankerite (dolomite), gypsum, chabazite, calcite and feldspar;

Pula–9: aragonite, quartz, calcite, dolomite, feldspar, mica, montmorillonite and kaolinite.

Instruments

A derivatograph (MOM, Hungary) was used for the thermoanalytical studies. A gas-collecting adapter [10], installed in the oven of the derivatograph, allowed the continuous introduction of carrier gases and the transfer of the gaseous products into the absorbers of the titration apparatus.

A thermogastitrimeter (MOM, Hungary) was used for continuous titration of the carbon dioxide content of the gaseous products. In certain measurements the amount of water released during heating in a nitrogen atmosphere was followed with a water-detector [11].

Thermoanalytical methods

1. The air-dried samples were ground and sieved through a 50 μm sieve. About 150–300 mg of oil-shale was spread on the platinum plates of the “multi-plate” sample holder [12]. During the entire operation, a carrier gas input flow of 25–30 l/h and a suction flow rate of 6–10 l/h were maintained. A heating rate of 9 deg/min was applied up to 900°C.

2. The gaseous products evolved in a nitrogen atmosphere were sucked through the water-detector [11] attached to the derivatograph and the amount of water released was continuously recorded.