

Composition of pyrolysis gas from oil shale at various stages of heating

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Abstract. Underground, the pyrolytic conversion of an oil shale in the nearest future may become an alternative source of a fuel gas and a synthetic oil. The main scientific problem in designing this technology is to provide a methodology for determination of the optimal mode of heating the subterranean formation. Such a methodology must allow predicting the composition of the pyrolysis products and the energy consumption at a given heating rate of the subterranean formation. The paper describes the results of heating of the oil shale fragments in conditions similar to the underground. The dynamics of composition of the gaseous products of pyrolysis are presented and analyzed.

1. Introduction

Retorting of an oil shale has long been regarded as a source of alternative energy and chemical technology raw materials. The main its products are a synthetic oil and a combustible gas. Before retorting the extracted shale, the rock is ground to a desired fractional composition and charged to a specific reactor. There the oil shale is exposed to heat and thermal degradation.

The composition and yield of the pyrolysis products is dependent on the process parameters of retorting – the fractional composition of raw rock, the heating rate, the slag removal rate, the technological scheme of movement of the rock in the retort. Many technological regimes have been developed for processing of the oil shale in retorts - a number of designs and processing parameters to achieve the maximum yield of products are already known [1-4].

At the same time, the necessity of extraction of the rocks on the surface is an inevitable limitation of the retorting. This operation determines the cost of obtained products. In this regard, the underground pyrolytic conversion, which consists in a direct heating of the rocks in situ, looks promising. However, in this case, obtaining the gas with constant composition is practically impossible. Heating the continuous medium, which takes place in a subterranean formation, a temperature gradient and the movement of liquid and gaseous products of pyrolysis are unavoidable. Calculation of such heating requires taking into account many factors [5].

Heating of the subterranean formation by an electric current can be used for the conversion of the underground reservoirs of the oil shale. In this case, electrodes connected to the surface generator are placed into two wells. The source of heat is the cylindrical area between the electrodes through which the current flows. The heat spreads from the source due to the thermal conductivity and the motion of



pyrolysis products. The gaseous pyrolysis products are selected directly in the heating process through the wells, and the shale oil may be selected from the reservoir after extraction of the electrodes.

At the initial stage of heating of the underground formation, the electric current forms a thin conductive channel, which has a high temperature because of the high energy density. Then, the conductive channel expands and the heat is being distributed in the surrounding space. The paper describes an experimental simulation of the heating of the subterranean formation on a laboratory scale. The purpose of the study is a definition of the dynamics of the composition of pyrolytic gas during the heating of the oil shale at different stages of heating.

2. Experiment conditions

Experimental studies were carried out for the oil shale of Huadian deposit (China). A sample of the rock was heated under conditions, similar to the underground.

The sample was placed in a concrete shell, which simulated the effect of enclosing rocks. For creating the shell, the sample with the rebar cage was placed into a pouring form and poured by a concrete. The sample was covered with a thin layer of polyethylene film for waterproofing from the concrete. The concrete was reinforced by a fiberglass rebar of 5 mm thick. The fiberglass is an insulator and does not affect the distribution of the field and the current flow. The poured sample was dried to a constant weight under room conditions (about 30 days).

The temperature of the sample was measured by tungsten-rhenium thermocouples, which were inserted into the sample in the ceramic covers. The covers were used as dielectric insulators to prevent the damage of a measuring unit and thermocouples.

The electrodes were made as graphite rods of 10 mm diameter, spaced 250 mm apart and inserted into the sample till a depth ~120 mm. The temperature was measured at 4 points. The first point was located in the center of the inter-electrode distance. The second, third, and fourth point were removed from the axis between the electrodes at 30 mm, 60 mm, and 90 mm, respectively (Figure 1).

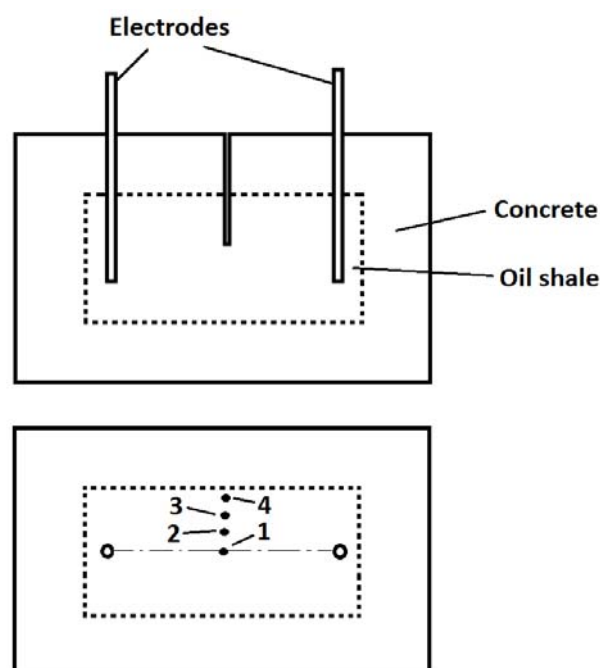


Figure 1. A diagram of thermocouples placing (a side view and a top view): 1, 2, 3, 4 – thermocouples

The graphite conductive paste was used to improve an electric contact between the electrode surface and the rock surface. The sample was placed inside a chamber, which was evacuated to

remove oxygen and then, filled with nitrogen to a pressure of 5 kgf/cm². The increased pressure inside the chamber simulated the pressure of fluids in the underground reservoir.

During heating, the gas was sampled from the chamber without stopping the process. The gas was filtered from an aerosol and disintegrated by the filter-reducer LFR-1/4-D-5M-MINI (Festo, Germany) with a pore size of 5 microns. The gas chromatograph was supplied, under a slight positive pressure (about 0.01 kgf/cm²). A gas was cooled directly during movement of the sample through the tubes, thus, the gas got the chromatograph at room temperature. We used Festo valves and tubes.

Gas analysis was performed using a gas chromatograph analyser Agilent 7890A, with a thermal conductivity detector using a column "ShinCarbon ST 100/120 mesh" 2 m long and of 1 mm diameter, according to the standard method for an absolute calibration. The chromatograph was calibrated using a standard gas mixture.

3. Results

In a given experiment, the heating power was about 500 W during all heating time. If we assume a cylindrical heating channel, it is reasonable to act with the power density, divided by the length of the inter-electrode gap. In the described experiment, this value was 2 kW/m. The resulting heating characteristics are shown in Figure 2. The heating was carried out continuously for 19 hours.

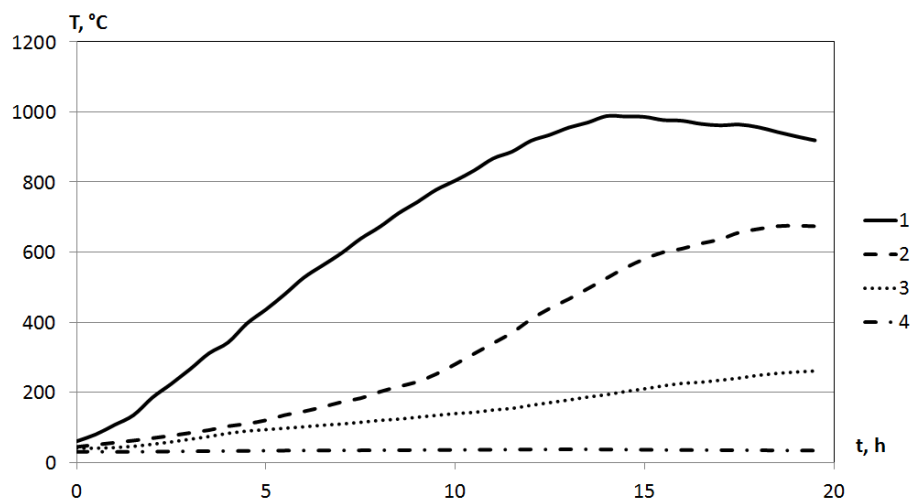


Figure 2. Heating characteristics at points 1, 2, 3, 4, shown in Figure 1

The gas was sampled from the chamber at intervals of about 1 hour. The dynamics of the gas composition is shown in Figure 3.

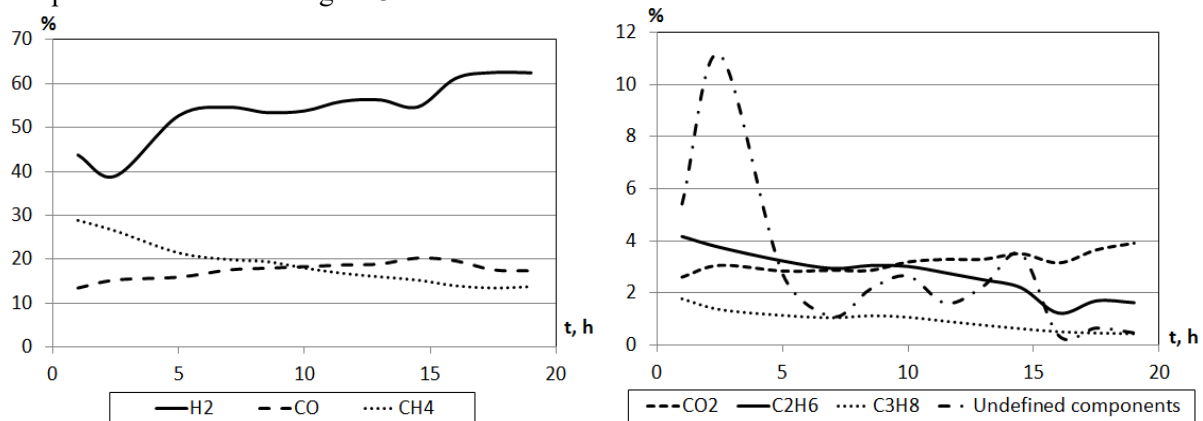


Figure 3. Pyrolysis gas composition dynamics

With the change of the gas composition, its calorific value also changes. The dynamics of the calorific value during heating is shown in Figure 4.

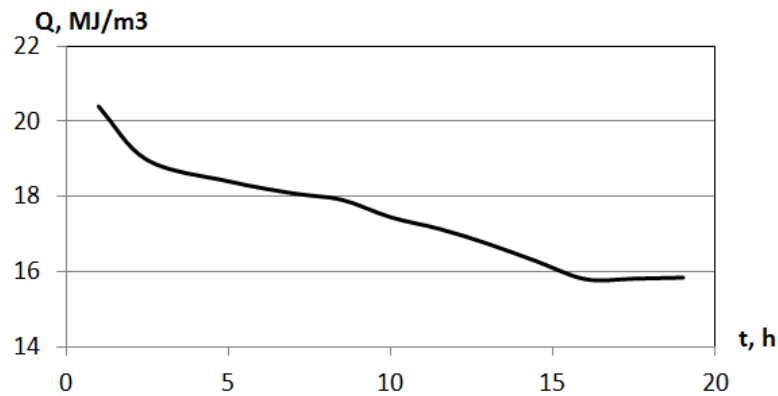


Figure 4. A changing calorific value of the pyrolysis gas

4. Discussion

The experimental data confirmed the estimates of the low rate of thermal energy distribution in an oil shale [5, 6]. In this experiment, the temperature in the center of a heated zone at the time, when a temperature at 90 mm apart from the channel center did not reach 100°C, exceeded 900°C. In such a situation, the increasing input power will reduce an efficiency for the following reasons:

- an unproductive temperature rise in the center of a channel, which has been already depleted;
- a consumption of thermal energy in the power-consuming reactions of decomposition of rock mineral components in the channel center, which occurs at temperatures above 900°C;
- an oxygen release due to mineral decomposition and oxidation of the fuel conversion products.

Thus, a viable option for heating and pyrolysis of large volumes of the rock under underground conditions is to increase the heating time at a fixed power. Calculations based on a mathematical model and experimental studies have shown that to achieve a temperature of 400°C at a point distanced 1 m apart from the center of the channel takes about 40 days.

The pyrolysis gas consists mainly of such combustible components as hydrogen, carbon monoxide, and methane. At the beginning of heating, only a small area in the vicinity of the electro breakdown channel undergoes the pyrolysis. The temperature in this channel is high, then, as far as the larger rock volume heats, it begins to decrease. According to the results, the number of undetectable by chromatograph components decrease during the heating. Most likely, these are the sulfur compounds (sulfur dioxide, hydrogen sulfide), the output of which is associated with a decay of the weak bond C=S, and also a water steam.

At the first stage of the heating, the gas contains an abnormally high volume fraction of methane, which is not typical gas for the pyrolysis from solid fuels. This gas is not a product of thermal decomposition of the organic part of the rock, but it is mainly a gas desorbed from the oil shale by high temperature. This is confirmed by an approximately constant fraction of methane in the final stage of the experiment, when the heating is close to a thermodynamic balance.

The component composition diagram allows concluding that the composition of the gaseous products is appropriate for the production of liquid synthetic fuels due to the Fischer-Tropsch process. The most suitable ratio H_2/CO has a value, which is equal to or greater than 2. In this experiment, the H_2/CO ratio was about 3.5.

During heating, the balance of carbon monoxide and dioxide is shifted towards CO. At the same time, the content of alkanes is reduced, resulting in a reduction of the calorific value, since they are the

most calorific components of the gas. The increase of the ratio of hydrogen/alkanes can be explained by the decay of alkanes by an increasing temperature.

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