Full Length Article

A two-phase model of shale pyrolysis

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ABSTRACT

There are various methods of oil shale thermal processing with the purpose to generate primary energy product – so-called shale gas. However, methods that do not require the extraction of rock to the surface (in-situ methods) are of special interest. In these methods, shale gas is extracted directly from the stratum as it is heating up, in one way or another.

This paper presents a model of in-situ oil shale heating. In comparison to known papers, this model describes processes under "non-equilibrium" conditions. The model takes into account chemical reactions, the flow of the gaseous decomposition products of in pores, concentration expansion phenomenon and interphase heat and mass transfer. Examples of the numerical realization of two individual tasks are provided. The problems on the reaction initiation in shale plate by heat flux from surface and plane shale layer decomposition under electric heating were examined. It was shown that chemical heat release essentially changes the summary heat balance in the system. The work unveiled several ways of reaction development, including explosion and slow decomposition.

1. Introduction

Shale is sedimentary rock formed by the accumulation of pelagic sediments, minerals and their further transformation. Typically, the boundaries of the content of the organic matter (hereinafter OM) in shale constitute 10–40% [1]. The density of different shale of various places of origin ranges from 1172 to 2257 kg/m^3, with a porosity from 0.02 to 0.043 [2,3]. The OM of shale consists of: carbon, hydrogen, oxygen, and sulfur [4]. Most of the OM of shale is insoluble in organic solvents and is called kerogen, and the lesser part, that is soluble, is called bitumoid. The mineral part of shale is formed of silica, carbonate, and clay formations.

Nowadays there are methods that actively being developed for producing shale of liquid hydrocarbons and combustible gas with the help of pyrolysis, which could be used as energy commodities and for the needs of the chemical industry. It is possible to distinguish ground and underground methods of shale processing. In the first case crushed shale is heated in special plants to temperatures of 250–800 °C. Underground processing methods consist of prolonged heating of shale formations. For example, in the technology of Shell ICP production of the products of pyrolysis begins after 2–4 years from the start of heating. The heating itself can be carried out using electrical heaters, hot gas, etc. Another method was developed in [4]. This method implies the boring in the area of reprocessing of straight holes, where the

electrodes if form of roods are dipped in the shale layer. Then electric current heats the shale to temperature 300–500 °C. The products of thermal decomposition are recovered through other special holes. Similar method was developed by ExxonMobil company (it is bil's Electrofrac Process) [5]. However the principal distinction of the ExxonMobil's Electrofrac Process consists in the employment of the liquid electroconductive substances discharge into the fracturing between holes.

This paper is aimed at constructing a model for numerical investigation of possible regimes of thermal shale decomposition in the technology [4]. In this research, the literature on the kinetics of decomposition is analyzed in order to generate a model for shale heating. A model of the flow of the products of decomposition in pores, taking into account chemical reactions and interphase heat- and mass exchange, is formulated. Examples of the numerical realization of individual problems are provided.

2. Kinetics of the thermal decomposition of shale

The thermal decomposition of shale has been studied by several researchers using the methods of thermogravimetry, differential thermal analysis, bomb calorimetry, etc. [6,7]. During the thermal processing of shale resin, gas and ash residue (char) are formed [1]. It is difficult to show the exact composition of the products of thermal

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decomposition since it essentially depends on the initial composition of the shale (which varies depending on the place of origin) and the pyrolysis conditions [8]. Methane, hydrogen, carbon monoxide, carbon dioxide, nitrogen, and various hydrocarbons are typical products of the decomposition of shale [9]. Studies of the transformation process of the structure of the OM of shale [10] showed that, when heated to 200 °C in the air, the molecular structure of kerogen does not change significantly (according to X-ray analysis). Starting from 200 °C the ordering of the structure of organic matter decreases.

The nature of the thermal decomposition of the OM of shale essentially depends on the environment in which the process takes place. Taking this into account, experiments on the decomposition of shale in a vacuum or inert atmosphere are of particular interest for us.

During the thermal degradation of shale in an argon atmosphere there are three typical steps: preheating (to 250 °C); intensive destruction of the OM (250–520 °C); coking to the end and decomposition of mineral components (520–1000 °C). During the stage of preheating, which ended at 120 °C, water evaporated and the reaction of intermolecular rearrangements took place [10]. The active decomposition of kerogen did not yet occur during this. It was during the stage of intensive destruction of organic substances in the range of 250–520 °C that the most significant change in the structure of the OM of shale occurred.

The maximum decomposition temperature varied in the range of 344–384 °C and was dependent on the structure of the OM. Calorimetric measurements of thermal decomposition of the shale in a nitrogen atmosphere, using differential scanning calorimetry (DSC), showed two distinct endothermic effects [11]. The first takes place at a temperature of about 145 °C and is associated with the evaporation of water. The second is expressed at 500 °C and is apparently caused by the decomposition of kerogen. At temperatures of above 500 °C the exothermic phase begins, which reaches its maximum speed at 800 °C, and coincides with secondary gasification. Experiments on the thermal decomposition of shale in an average vacuum (pressure ranging from $2 \cdot 10^2$ to $8 \cdot 10^2$ Pa) [12] showed that in such conditions there is a higher yield of liquid and gas which has low average molecular weights in comparison with the thermal decomposition at normal pressure.

The process of intensive decomposition of the OM during the thermal destruction of all the studied shale is characterized by the proceeding reactions, whose kinetic parameters are governed by a reaction equation of the first order. The activation energy of the decomposition process of the OM is also determined by the type of its structure. Thus, Baltic shale characterized by a homogeneous and low-defect structure had a value of activation energy of 107–108 kJ/mol [13]. Structure of Volga shale is not homogeneous, and this shale is characterized by lower values of activation energy of 47–48 kJ/mol. There are processes of coking to the end of solid remains and the decomposition of mineral components in shale at above 520 °C. According to A.J. Arna [14], the activation energy is 259.93 kJ/mol, and the rate constant decreases during the deepening of the process. A.K. Miturev [15], analyzing the data of experiments by K.A. Kask and A. J. Arna, inclined toward 220.92 kJ/mol. Estimation of Burnham [16] for the activation energy is 241 kJ/mol, and for the rate constant is $1.1 \cdot 10^{15}$ min^{-1}. According to Braun [17], the activation energy is 221 kJ/mol, and the rate constant is $5 \cdot 10^{13}$ min^{-1}. Data of Q. Liu et al. [18] lead to the activation energy 54.62–277 kJ/mol, and to the rate constant $5.246 \cdot 10^2$–$2.225 \cdot 10^{14}$ min^{-1}. Skala [19] suggested describing the kinetics of shale with the following kinetic model:

$$K^* \xrightarrow{K_1(T)} f_1 B_1 + f_2 P_1 \xrightarrow{K_2(T)} f_3 R_1 + f_4 P_2$$
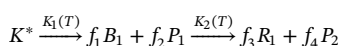
where K^* is kerogen, B_1 and R_1 are condensation products, P_1 and P_2 are volatile pyrolysis products, and f_1, f_2, f_3, f_4 are stoichiometric ratios. The values of the model parameters were: $f_1 = 0.4$, $f_2 = 0.6$, $f_3 = 0.65$, $f_4 = 0.35$.

According to the Arrhenius law, for speeds of reactions we write

$$K_1 = k_1 \exp\left(-\frac{E_1}{RT}\right), K_2 = k_2 \exp\left(-\frac{E_2}{RT}\right).$$

The activation energies and pre-exponential factor were gained from experimental data as $k_1 = 82.17 \cdot 10^5$ c^{-1}, $E_1 = 127.14$ kJ/mol, $k_2 = 49.84 \cdot 10^9$ c^{-1}, $E_2 = 192.79$ kJ/mol.

Broun and Rothman [20], based on the experimental results, proposed a model for the thermal decomposition of shale consisting of two successive reactions:

$$K \xrightarrow{K_1} B + G_1 + C_1$$

$$B \xrightarrow{K_2} A + G_2 + C_2$$
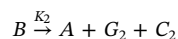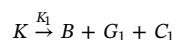
where K and B are the proportion of kerogen and bitumoid, G_1 and G_2 are the proportions of gaseous products, C_1 and C_2 are the proportion of carbon-containing products, A is the proportion of the shale oil, K_1 and K_2 are the speeds of reactions which satisfy the above ratios. The activation energies and pre-exponential factors derived gained on the basis of experimental data differ from the previous data:

$$k_1 = 14.4 \, \text{c}^{-1}, E_1 = 44.56 \, \text{kJ/mol}, k_2 = 2.025 \cdot 10^{10} \, \text{c}^{-1}, E_2 = 177.58 \, \text{kJ/mol}.$$

More complicated kinetic schemes are suggested in [19,21,22]. Summarizing the data, it is possible to say that shale is porous layered rock whose heating involves solid substances decomposing with gassing. Moreover, the total heat effect of the reactions is positive, however, during the initial stages of decomposition endothermic effects occur. It can be assumed that the total thermal effect of the decomposition reaction of the solid phase is negative, the gas product reacts exothermically, and exothermic heat effect prevails.

3. Mathematical model

We shall assume that the porous body of the shale is formed by reagent AS. We assume that initially the pores contain a certain amount of reactant gas GR. During heating the reagent AS decomposes into solid product BS and gas BG, entering the pores with a mass transfer coefficient α_m and mixing with gas of the same composition GR. In turn, GR during heating transforms into gas GP. Therefore, the chemical reactions during the decomposition of the shale can be represented by the following schematic diagram:

$$AS \xrightarrow{K_1} BS + BG$$

$$GR \xrightarrow{K_2} GP$$
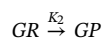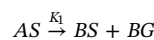
where K_1 and K_2 are speeds of reactions.

Mathematical model of decomposition process is based on ideas of the mechanics of heterogeneous media [23]. We have two phases – solid and gas that occupies the pores. Between phases, the heat and mass exchanges are possible.

Let us assume that the thermal effect of the decomposition reaction of the solid phase is negative, the gaseous product reacts exothermically, and the exothermic heat effect prevails. The heat equation for the solid phase has the form

$$c_s \rho_s \frac{\partial T_s}{\partial t} = \nabla \cdot (\lambda_s \nabla T_s) + W_s - \frac{\alpha_T}{1-\varsigma}(T_g - T_s), \tag{1}$$

where T_s, s, ρ_s is the temperature, heat capacity and density of the solid phase, t is time, λ_s are the thermal coefficient of the solid phase, $W_s = W_s^{ch} + \Phi_s^{out}$ is the summary source or a heat sink in the solid phase, the first is responsible for the contribution of chemical reactions, the second for external action, α_T is the heat transfer coefficient between the gas and solid phases, ς is porosity, and T_g is the gas temperature.

The relation $\eta_{BS} + \eta_{BG} + \eta_{AS} = 1$ reflects mass balance in solid phase. If decomposition reaction rate depends on the amount of solid reagent, the kinetic equations for solid reagent and solid product take the forms