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Evaluation of gas products emission kinetic constants under sulfur oil shale thermal decomposition

Simonov V.F.[a], Selivanov A.A.[a]*, Mrakin A.N.[a], Morev A.A.[a]

[a]*Yuri Gagarin State Technical University of Saratov, 77, Politechnicheskaya Str., Saratov 410054, Russian Federation*

Abstract

The paper deals with the evaluation issues of kinetic constants (activation energy and preexponential factor) characterizing gas products emission process under sulfur oil shale semi-coking in units with solid (ash) heat-carrier.

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Keywords: oil shale; ash heat-carrier; activation energy; semi-coking; gas

1. Introduction

A brief papers review on oil shale organic matter thermal decomposition kinetics studying carried out in [1-4] shows that the mathematical model development making possible to predict thermolysis process proceeding and to determine products composition on the basis of oil shale chemical composition and its structure is nowadays one of the fuels thermal decomposition studying main problems.

To develop the mathematical model of sulfur shale thermal decomposition process (semi-coking) according to the formal chemical kinetics laws, it is necessary: 1) to define the kinetic parameters system describing the kinetics of shale semi-cocking total volatile products yield; 2) to determine the original composition of shale functional groups; 3) to find out the shale particles temperature dependence on time.

* Corresponding author. Tel.: +7-987-322-7656.
E-mail address: selivanych-86@mail.ru

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2. The study subject (Model, Process, Device, Sample preparation etc.)

There is currently no rigorous theory that would make it possible to predict thermolysis process proceeding and to determine products composition on the basis of oil shale chemical composition and its structure. Therefore, in most cases the thermolysis of each particular shale is experimentally studied, the process parameters impact on its products composition and yield is investigated. Subsequently, a qualitative interpretation of obtained results is given and more or less adequate process model is developed by means of the theory.

In some studies [5, 6] the attempts to develop the general principles of pyrolysis modeling in which a wide variety of chemical characteristics is used for oil-shale kerogen structure reproducing have been made.

However, it is generally accepted that shale organic matter macromolecule structure considerably depends upon the sulfur, nitrogen, oxygen content and their ratios. These elements most commonly form side radicals of hydrogen and carbon macromolecule base and define the products composition of primary thermal decomposition. Generally, shale organic matters of different deposits greatly differ on these parameters.

3. Methods

In this paper model kinetic parameters were chosen to give quantitative interpretation of available experimental data on sulfur oil shale semi-coking. The parameters values are not connected with the shale structure, its elementary composition and cannot be used for shale thermolysis modeling of different deposits.

The technological effectiveness of the vapor-gas mixture (VGM) catalytic conversion subsequent process is mainly defined by qualitative and consumption characteristics of shale semi-coking vapor-gas products supplied into this process. The available experimental material on sulfur shale semi-coking in the solid heat-carrier unit (SHCU) is nonrecurring and accidental one and cannot be applied for the deep analysis of original substance influence on thermocatalytic conversion parameters. In this regard, the sulfur shale semi-coking process in SHCU on the basis of formal chemical kinetics ratios was described by the authors at the first stage of work. The description is based on experimental material by Kazakov E.I. and other authors.

The experiments were carried out on the stand unit with a solid heat-carrier having capacity of 15 kg/hr of shale. This unit models semi-coking circuit of industrial process and its scheme is represented in Fig. 1.

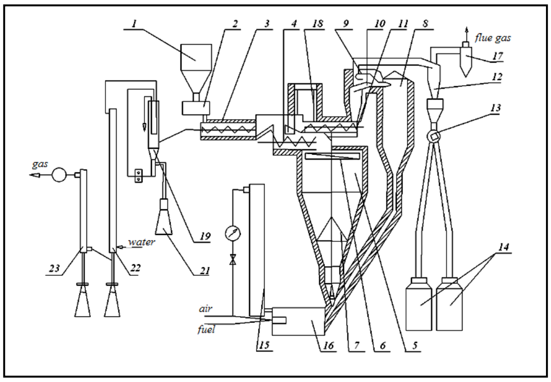

Fig. 1. Stand scheme designed for technological characteristics studying of oil shale and other high-ash fuels under reprocessing in SHCU: 1 - feed bin, 2 - disk feeder, 3 - dry shale screw, 4 - mixer, 5- reactor, 6 - level regulator, 7 - distributing cone, 8 - aerofountain furnace, 9 - by-pass, 10 - heat-carrier separator, 11 - heat-carrier screw, 12 - first-stage ash separator, 13 - switching device, 14 - receiving bin, 15 - air heater, 16 - firing furnace, 17 - second-stage ash separator, 18 - fine filter, 19 - scrubber, 20 - sparging pump, 21- receiving vessel, 22 - condenser, 23 - electric precipitator.