

Destruction of Kerogen in the Presence of Pyrite and Cobalt-Based Catalyst

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Abstract

Objectives: The investigation of the process of the kerogen in situ catalytic transformation accompanied by the synthetic oil production. **Methods:** To develop kerogen-rich deposits, such technologies as in situ combustion and retorting, presupposing productive layers warming-up, can be employed. The intensification of the light hydrocarbon generation under the kerogen cracking is achieved while using nano-dimensional catalysts based on the transition metals. **Finding:** The cracking catalyst on the cobalt basis alongside with the impact on the organic substance can promote to the transformation of pyrite into mixed iron oxides, the latter also being the catalysts of the processes under discussion. Under the thermo-catalytic effect on the kerogen-containing rocks, the processes of the destructive hydrogenation with the formation of liquid hydrocarbons take place. The processes above are quite catalytic, accompanied by the hydrocarbons molecules activation with power and chemical methods. Iron-containing minerals of all other ones found in the thermal transformation of kerogen. Pyrite under thermal treatment transforms into hematite which is a hydrocracking process. **Conclusion:** The influence of the nano-dimensional catalyst based on cobalt aims at the organic substance cracking.

Keywords: Catalyst, Kerogen, Pyrite, X-Ray Structural Analysis

1. Introduction

Among the alternative sources of raw materials oil shale is of particular interest for industrial energetics nowadays^{1,2}. Bazhenov formation has most of the Russian oil shale containing a solid organic matter (kerogen), and liquid light oil in a small permeable clay collector. The area of Bazhenov formation makes more than 1 million square km., the depth of formation makes over 2 km with the thickness of 20-30 m. The formation temperature reaches 130 °C. The recoverable oil reserves may reach several tens of billions tons. Kerogen formed as the result of accumulation in sediments under organic matter oxygen isolation³. In Bazhenov formation kerogen content makes 5% - 40% stored in the rock in the form of spherical colloidal particles with the diameter of 20-140 microns. Apparently, shale, characterized by a relatively high content of high molecular hydrocarbon compounds should be

regarded as petrochemical raw materials to obtain a full range of products. However, a high ash content, low reactivity of shale oil kerogen requires the use of new highly efficient production methods. It is necessary to specify fire flooding among the most promising methods of production. The application of this technology on the sediments of Bazhenov Formation is determined by certain features associated with the kerogen properties and a low oil density in considered reservoir rocks. The combustion process is supported by the pumping of plain oxygen-enriched air or oxygen into an injection well. Thus, carbon dioxide and water are developed, which are filtered through the formation and dissolved in oil. In its turn, the filtering of carbon dioxide decreases oil viscosity and increases its volume ratio up to 20-30%. The ground processing experience of oil shale is known according to beyond formation retorting technology (Galoter Process (GALSTER, Russia - Estonia), Benefit

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(the modification of Galoter process), Kiviter (Estonia), Alberta-Taciuk Process (ATP) (Australia), Petrosix (Brazil), etc.). The use of such technologies is limited to environmental issues - the recycling of waste rock and the depth of working layers. Therefore, the attention of researchers is drawn to the implementation of kerogen chemical destruction directly in the reservoir according to so-called transformational retorting technology (Shell ICP, Chevron ICP, ExxonMobil Electrofrac, AMSO EGL Technology). It provides the cracking of kerogen (calorific value makes 29-37 MJ/kg), and the upgrading of bitumen composition - the formation of so-called synthetic crude oil. The thermal conductivity of kerogen is much lower than the thermal conductivity of rocks, which determines the natural limitations of heat loss in a mountain range. The heat generating channel is located within the formation at an equal distance from the boundary surfaces. So, displacing agents are formed at thermal gas impact due to thermal-oxidative processes. Generated heat is used to warm a low permeable matrix, which results in kerogen degradation and the formation of human-made fractures.

2. Research Methodology

The work carried out laboratory simulations of thermo catalytic impact on the kerogen sample of Bazhenov formation. The simulation performed in an autoclave at the pressure of 50 atm and the temperature of 300 °C; the duration made 6 hours. The heat treatment was conducted in an inert atmosphere, supplying inert gas (nitrogen) to the reactor. Catalyst sample used on cobalt basis. The dosage of the catalyst precursor in kerogen makes five Wt. %. The molecular catalyst precursor is synthesized using distilled tall oil as ligand formation - the product of the vacuum rectification of crude tall oil containing no more than 30% of resin acids, and up to 6% of unsaponifiable substances, the rest substances are fatty acids (oleic, linoleic, linolenic ones). The acid number is in the range of 170 - 190 mg KOH/g. Cobalt carboxylate obtained by an inorganic metal salt exchange reaction with the sodium salt of high oil. An active form of the catalyst is formed during the thermal exposure. According to thermal analysis data, an endothermic effect is observed in the temperature range of 160 - 230 °C corresponding to molecular precursor decomposition. The oxidation of the organic ligand is performed at higher

temperatures. Demineralized shale was extracted with chloroform to remove bitumen. Kerogen was extracted sequentially by the processing the crushed rock using the solutions of hydrochloric and hydrofluoric acid. To study the transformation of kerogen composition ¹³C NMR spectroscopy was utilized in a solid body using «AVANCE III TM 400» spectrometer, which allows determining the relative content of functional groups (ether, hydroxyl, carboxyl, carbonyl ones, etc.). The elemental composition of kerogen was determined by the burning method in semiautomatic C, H, N analyzer and by X-ray fluorescence analysis Table 1. X-ray analysis of kerogen was performed using an automatic powder diffract meter Shimadzu XRD-7000S with CuK α radiation at the wavelength $\lambda = 1, 54060$ nm using a nickel monochromatic on a diffracted beam, at the step of 0, 0008A₋₁ and a single exposure in a point for 3 seconds; and D2 PHaser Bruker on CuK α radiation with the wavelength of $\lambda = 1, 54060$ nm. The treatment of diffraction spectra and the diagnosis of presented crystalline phases are performed using the original interactive computer system EVA (version 4.0) that is intended for the study of sedimentary rocks and soils, with the specialized database ICDD-2010.

Table 1. Composition of kerogen sample with complex related pyrite

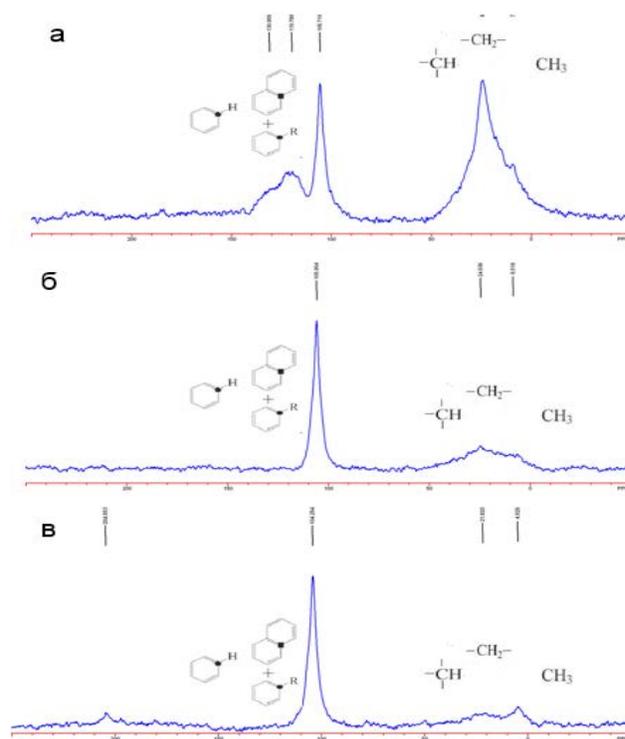
Element composition, wt. %				Microelement composition according to X-ray fluorescence analysis data, %.			Calculated content of pyrite, wt. %	
C	H	N	S	S	Fe	Si	Mo	
54.7	3.9	1.1	26.2	65.8	33.0	1.1	0.2	28.2

3. Study Results and their Discussion

To study the transformation of kerogen during thermal catalytic impact pyrite complexly associated with kerogen was not separated. Pyrite is the precursor of hydrating agents - oxygen compounds of iron. Hematite produced from precursor's exhibit a high efficiency during the laboratory simulation of refining formation processes for highly sulfurous oils^{4,5}. During the decomposition of pyrite, FeS_{1-x} pyrrhotites, hematite and other mixed iron oxides are developed, which are efficient catalysts for the hydrogenation and the decomposition of hydrocarbons Table 1.

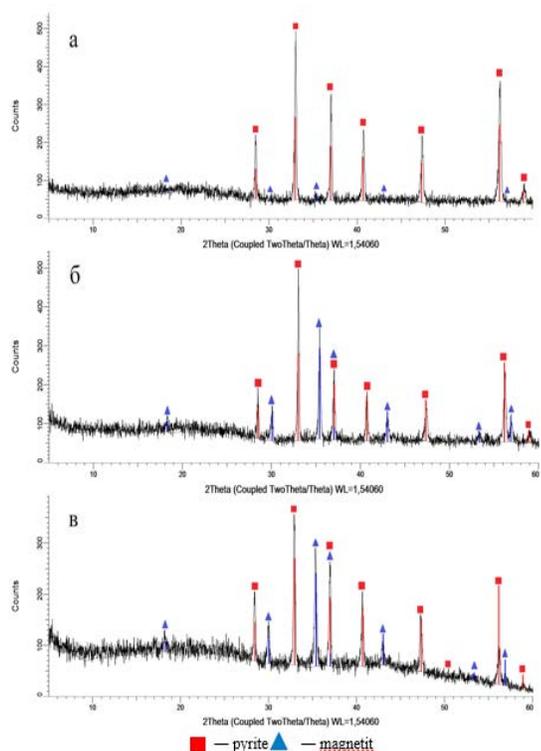
Pyrite is a permanent component of the rocks. Natural iron sulfides - pyrrhotite and pyrite, are often formed during hydrothermal processes and undergo an ongoing transformation in exogenous conditions. The sulfur content reaches up to 30%, most of which is contained in pyrite. The pyrites of an earlier generation is presented in a fine-dispersed form, and develop organ mineral complexes strongly associated with kerogen. The pyrite of a later age (crystalline) is developed unevenly and forms inter-layers and the lens of several centimeters. Pyrrhotite and sphalerite and galantines which retained residual magnetization are presented in lower concentrations. The concentration of many elements (Mo, U, V, Cu, Zn, Ni, As, Sb, Se, Ag, Au, Ba, Br) is high along with a high content of organic matter in oil shale^{6,7}. The comparison of ¹³C NMR-spectroscopy results in a solid body of an original kerogen, and after thermo catalytic impact Figure, 1 shows a significant change of composition. Aliphatic carbon content is reduced as the result of aliphatic substituent cracking and the aromatic skeleton condensation. A poly-condensed aromatic portion is preserved in a solid state. At that, there is a profound transformation Figure1, range B in the presence of a catalyst. The signals in area 114 and 139 ppm are referred to double bonds. The signals in the other areas have an aliphatic nature. The signals in the regions 14 and 16 ppm are assigned to CH₃ groups. CH₂-CH₂- (~ 21-39 ppm), CH-PO (OC₂H₅)₂ (~ 43-46 ppm) and CH-Cl (~ 61 -64 ppm) groups are registered. Kerogen maturation process is in its gradual compaction, which is based on the reaction of longitudinal polymerization and the cross-linking of molecules. At the same time, low molecular weight compounds (liquid and gaseous ones) are extracted from the kerogen and during the late stage, high molecular compounds are removed (like resins). In immature kerogen, resins are strongly related with the kerogen surface, and then they decompose. In vivo, during the process of diagenesis, a fixed residual kerogen continues to coalify, including the compressions of container rocks during their lithification. Thermal catalytic exposure accelerates these processes. X-ray diffraction analysis Figure 2 found that the part of moon mineral pyrite is transformed into a magnetic

form - magnetic after thermal catalytic impact. The processes of destructive hydrogenation take place with the development of liquid hydrocarbons at the thermal catalytic effect on the kerogen containing rocks. This process is quite a catalytic one, accompanied by the activation of hydrocarbon molecule energy and chemical methods. The latter include both the injection of special agents into a productive formation and the use of mineral component catalytic abilities of kerogen-containing rocks. The greatest influence on the thermal conversion of kerogen is provided by iron-containing metal components, the composition of which varies depending on natural or human made hydrothermal effects. Natural hydrothermal processes contribute to geologically instantaneous formation of oil-like substances⁸⁻¹³.



a - original kerogen b - transformed kerogen after thermocatalytic impact, B - converted kerogen after the thermocatalytic impact in the presence of a catalyst

Figure 1. ¹³C NMR spectra of kerogen before and after heat treatment.



a - original kerogen b - transformed kerogen after thermocatalytic impact, B - kerogen converted after thermocatalytic impact in the presence of a catalyst

Figure 2. X-ray patterns of kerogen before and after heat treatment.

4. Conclusions

The development of pyrite and other iron-bearing minerals decomposition mechanism at relatively low temperatures, which can be maintained in productive formations using such techniques as in-situ combustion and the retort, is necessary for the formulation of technological solutions and the development of various agents injected into a developed formation. A research perspective on the activation of acidic aluminosilicate components already contained in a composition and the precursors of hydrogenating compounds - mixed iron oxides, which are the hydrocracking catalysts, the effectiveness of which for the in-situ upgrading of high-viscosity oils is set in some works, including author works. The action of catalysts in the studied processes is aimed at asphalt-resinous compound cracking, similar to kerogen by chemical nature. Bazhenov formation is rich in pyrite, which accompanies an organic substance. The

transformation of pyrite into hematite demonstrated in the paper allows intensifying the in-situ conversion of kerogen with synthetic oil production.

5. Conflict of Interest

The author confirms that the presented data do not contain any conflict of interest.

6. Acknowledgement

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7. References

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