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Laboratory investigations of hydrous pyrolysis as ternary enhanced oil recovery method for Bazhenov formation☆

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A R T I C L E I N F O

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A B S T R A C T

Significant amount of different maturity kerogen in Bazhenov oil-shale formation are reserves of hydrocarbons to be recovered by enhanced oil recovery methods in nearest future when the conventional oil field development drops crucially. A technology of in-situ kerogen conversion into synthetic oil in Bazhenov formation opens broad perspectives in development of Bazhenov formation, West Siberia, Russia.

Laboratory investigation of in-situ kerogen conversion process in the presence of supercritical water performed on Bazhenov formation rocks is presented in this study. A feasibility of the tertiary hydrous pyrolysis hydrocarbons (HC) recovery method was accessed. Study helped to obtain reliable data to validate the numerical simulation model for that enhanced oil recovery method.

First tests of hydrous pyrolysis extraction were conducted on crushed oil shale samples at temperatures of 300, 350, 400 and 480 °C and under formation pressure of 30 MPa. Liquid HC extraction from sample started from 400 °C. The secondary hydrocarbons conversion process was detected at reaction temperature of 480 °C.

Second stage of laboratory tests allowed to find optimal parameters for in-situ kerogen conversion – optimal conversion temperature, time of the conversion. The experiments on Bazhenov formation cores with low kerogen maturity were conducted in closed vessel at formation pressure and in temperature range of 250–400 °C. It was found that oil synthesis starts at 300 °C. Amount of liquid products increased at temperatures above 350 °C, but the secondary cracking processes had been observed also.

It was discovered that hydrous pyrolysis and cracking caused an increase in rock porosity and permeability. Results obtained in this study were used in numerical simulation.

1. Introduction

In-situ retorting technology (In-situ Conversion Process - ICP) is a hybrid technology, which is based on thermal impact and coupled with physical and chemical impacts on the hydrocarbon-bearing formation (Kokorev et al., 2014; Vashkevich et al., 2014a). It was reported about commission tests of an equipment for ICP (ground super critical water generator) in 2015 (Kiryachek and Chernov, 2015).

In the most general form in-situ retorting is aimed at solving the following problems of oil industry:

- increase oil recovery in natural bitumen and heavy oil formations, that are already under development at the productive depth of less than 1200 m, by using high-performance working agent, mainly in the form of superheated steam;
- in-situ irreversibly decrease viscosity and density of hydrocarbons (HC) due to in-situ retorting/molecular modification through hydropyrolysis, which results in extracting a larger volume of high grade and modified oil to the surface;
- intensify oil recovery in low permeability rock formations of oil-bearing shales and simultaneously generate synthetic liquid and gaseous HCs from kerogen by in-situ catalytic hydropyrilization using super critical water (SCW) (Brunner, 2014) or superheated steam,

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followed by an increase in permeability of the reservoirs (Tiwari, 2013; Deng et al., 2011).

In-situ retorting technology is a complex technology. This combination of different impact methods is able to achieve the most out of ICP. The ideological basis of ICP is to process HC formed in the formation directly in the reservoir. Then heat it up with a catalyst (water and matrix minerals) to high temperatures. Thus, making a high-temperature catalyst retort, and complex processes are initiated. These processes increase the permeability of the productive formation, increasing its internal energy and mobility of liquid HCs:

- to reduce its viscosity, intensify its production and to increase oil recovery factor;
- to improve its quality, reducing its density in the reservoir immediately before production;
- to carry out in-situ generation of synthetic crude oil from solid organic matter - kerogen and/or heavy oils.

In this research, we conducted laboratory studies aimed at assessing the prospects of this technology applied to Bazhenov formation (BF), the largest low-permeable rocks containing a significant amount of HC in Russia (Braduchan et al., 1986). The organic-rich clay-siliceous shales are located in the West Siberian Basin. Geochemical analyses of the core samples showed total organic carbon (TOC) values of 2–18 wt%, consisting mainly of kerogen, and where the level of maturity varies within the range of 419°–446 °C from immature to beginning of oil window. The main rock section of BF is characterized by low open porosity (up to 2%) and absolute gas permeability ranging from nanodarcy (nD) to millidarcy (mD) (Bondarenko et al., 2016; Kokorev et al., 2013).

Oil shales in Russia have not been developed actively due to the absence of suitable recovery method (Vashkevich et al., 2014b). Different techniques by different research groups and companies were used for studies and field pilots on the Bazhenov formation. (Andrew et al., 2013). Nevertheless, none of them has been establish as a development method. The potential of supercritical water or hydrous pyrolysis treatments as EOR method has not been investigated for Bazhenov formation. The experimental studies on oil shale performed in this work will help to develop new large-scale technology based on the hydrous pyrolysis for the shale.

Open-system and closed-system hydrous pyrolysis were used to evaluate the effectiveness of the method. Since measurements of reservoir parameters cannot be done with conventional techniques because of the extremely low permeability and porosity of Bazhenov shale, GRI Analysis method was used (Development of laboratory and petrophvsical techniques for evaluating shale reservoirs, 1996). To analyze gas and liquid products compositional analysis was performed using gas chromatography method.

2. Samples and methods

The laboratory experiments were conducted in an autoclave on crushed core samples using HC extraction with SCW or superheated steam. The perspective of ICP enhanced oil recovery (EOR) technology was accessed (Deng et al., 2011; Li et al., 2015).

The data obtained from the experimental study, were put into the numerical model of the EOR under study. Experimental studies were carried out in two stages. At the first stage, we experimentally simulated SCW impact over a wide temperature range on BF rock. At the second stage, based on the experimental results obtained along the first step and numerical simulation results, the procedures were conducted again with the specified parameters and pursuing the task to determine the parameters and dependencies, which cast the greatest uncertainty into modelling results (Erofeev et al., 2016).

Four rock samples from a well, drilled in Krasnoleninsky vault in South-West Siberian Petroleum Basin, were chosen to represent the Bazhenov Shale, the samples depth range is 2558–2561 m, TOC – 13.8%, T_{max} – 435 °C. The samples were clay-siliceous carbonaceous rock with thin layering and spots of pyrite. For the second stage of investigation the samples were taken from the Archinsk oil field in the West Siberian region as the target reservoir in the BF. The interval of selection was 2611–2614 m, average TOC – 10%, T_{max} – 419–426 °C. The samples were represented by clay-siliceous carbonaceous rock with small inclusions of pyrite also. Before the tests the samples were crushed and homogenized to the size of 0.5–2 mm.

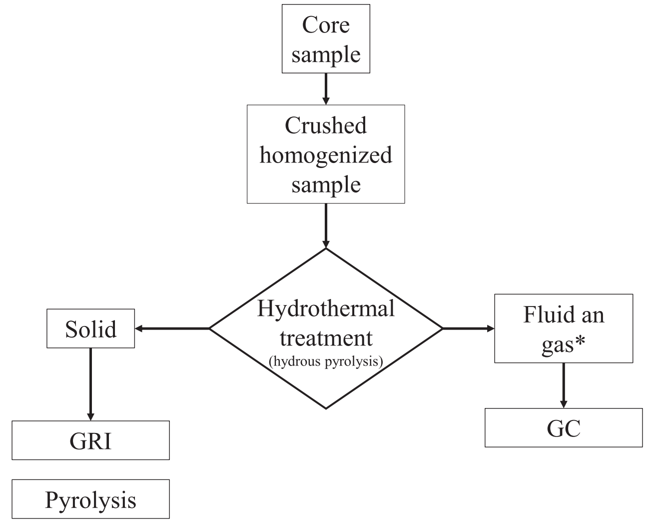

Fig. 1. Basic scheme of the experiments (*- gaseous HC were analyzed in first stage only).

Basic scheme for all laboratory experiments is represented in Fig. 1. The following instruments were used along the tests: in the first stage - Monel alloy pressure cell with pressure and temperature control, in the second stage – cells without pressure control, a high temperature oven. Analysis was performed with HAWK pyrolysis instrument; gas chromatographs (GC) and CoreLab SMP-200 matrix permeameter.

Cumulative volume of produced gas was measured using a wet test meter and was collected for further evaluation using gas chromatography. Liquid samples were collected into graduated cylinders and were sent to a compositional analysis. Organic solvent dichloromethane was used to extract oil from the oil-in-water emulsion and remove adsorbed hydrocarbons from the vessel's walls and the core crushed sample surface. The extracted oil was separated from the solvent using rotary evaporation and compositional analysis was performed. Then the rock chips were removed from the vessel and dried in an oven at 105 °C to constant weight. GRI Analysis was used to evaluate the changes in shale samples' permeability and porosity after extraction with supercritical water.

In order to get percentage of kerogen converted to hydrocarbons after hydrous thermal reaction, open-system pyrolysis was performed. Two main parameters S1 and S2 were measured using HAWK pyrolysis instrument. S1 is the amount of thermally freed hydrocarbons in the sample in milligrams of hydrocarbons per gram of rock by temperature of 300 °C. S2 is the amount of hydrocarbons generated through thermal cracking of non-volatile organic matter. S2 is an indication of the quantity of hydrocarbons that the rock has the potential of producing under increased burial and maturation, namely it is the kerogen yield. Samples were analyzed before and after extraction to investigate the change.

3. Results and discussion

At the first stage the experiments were carried out to investigate the influence of temperature on hydrocarbon recovery during kerogen conversion of hydrothermal treatment. A series of experiments were conducted on non-extracted crushed samples at pressure of 27 MPa in a