EXPERIMENTAL ASSESSMENT OF THE HYDROCARBONS YEILDS FROM BAZHENOV SHALE FORMATION BY KEROGEN CONVERSION IN THE PRESENCE OF SUPERCRITICAL WATER

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ABSTRACT

The study presents experimental results on the use of supercritical water (SCW) as an Enhanced Oil Recovery (EOR) agent for Bazhenov formation. Bazhenov formation is the biggest potential shale reserves in Russia. Therefore, as the world's oil supply decreases, the need to find EOR techniques in order to develop Bazhenov formation becomes evident. The experimental studies on oil shale performed in the work will help to advance the move to large scale oil production from the hydrous pyrolysis of shale. The main purpose of the study was to estimate experimentally a potential of hydrocarbon recovery from oil shales and to evaluate technique of kerogen conversion in the presence of supercritical water. In order to investigate a temperature influence on hydrocarbon recovery during kerogen conversion in the presence of supercritical water, a series of experiments were conducted on non-extracted crushed samples at 300, 350, 400 and 480°C and at pressure of 27 MPa in a pressure vessel. In result, only gaseous products were received at temperature below 400°C, whereas liquid hydrocarbons in state of films on the rock sample and the vessel's walls were detected only starting from temperature of 400°C. For the sake of evaluating amount of converted kerogen, open-system pyrolysis on rock samples before and after experiments with SCW were carried out. Results indicate almost total recovery of free hydrocarbons (S1) and 82% decrease in the amount of hydrocarbons generated through thermal cracking of non-volatile organic matter (S2) after SCW injection at 480°C. Gaseous products were analyzed by gas-chromatography. Significant amount of methane was detected in the gas products at 480°C. It suggests that secondary oil cracking and coke production may starts at temperatures around 480°C. The samples' matrix porosity and matrix permeability before and after SCW injection were measured by GRI method [8]. Analysis revealed negligible porosity increase and sufficient growth in permeability when temperature is raised. We attribute this to the start of core destruction process with formation of multiple microfractures. The investigation

determined the “hydrocarbon generation window” within temperature range of 400°C and 480°C for the general Bazhenov formation rocks with low kerogen maturity at western part of West Siberian Petroleum Basin. Preliminary results show that supercritical water is a promising EOR agent for Bazhenov formation rocks.

INTRODUCTION

As recovery from conventional reservoirs decreases, the need to find a new EOR technique to develop unconventional resources becomes necessary. Bazhenov formation (BF) is the biggest oil-shale reserve in Russia. The Upper Jurassic organic-rich clay-siliceous shale occurs in the West Siberian Basin. Geochemical analyses of its core samples showed total organic carbon (TOC) values of 2 to 18 wt. %, consisting mainly of amorphous kerogen, and where the level of maturity varies within the range of 429° - 446°C. The main rock section of BF is characterized by low open porosity (up to 2 %) and absolute gas permeability ranging from a microdarcy to a nanodarcy, and even less than 1 nanodarcy. [1, 2].

Despite of the huge amount of reserves, oil shales in Russia have not been developed extensively due to the absence of suitable recovery technique [3, 4]. There has been extensive research and field pilots in the Bazhenov shale using different methods by different research groups and companies [5, 6, 7]. Nevertheless, none of them has been establish as a development method. The potential of supercritical water as an EOR agent is not fully investigated for Bazhenov formation. Therefore, the experimental studies on oil shale performed in this work will help to advance the move to large-scale oil production from the hydrous pyrolysis of shale. The main purpose of the study was to estimate the potential of hydrocarbon recovery from oil shales and to evaluate the mechanism of kerogen conversion in the presence of supercritical water.

Open-system pyrolysis and closed system hydrous pyrolysis were used to evaluate the effectiveness of SCW method. Since measurements of reservoir parameters cannot be done with standard conventional techniques because of the extremely low permeability and porosity of Bazhenov shale, GRI Analysis methods were used [8]. To analyze products, gas and liquid compositional analysis was performed using gas chromatography.

MATERIALS AND METHODS

Four rock samples from a well drilled in Krasnoleninsky vault in South-West Siberian Petroleum Basin were chosen to represent the Bazhenov Shale (Fig.1), the samples depth range is 2558-2561 m. The samples were crushed and homogenized to 0.5-2 mm.

The following instruments were used: monel alloy pressure vessel with pressure and temperature control, volume of the experimental cell is 200 cc (Fig. 2); HAWK Pyrolysis

Instrument; gas chromatograph "Kristall – 2000"; CoreLab SMP-200 matrix permeameter.

The GRI method for measuring permeability uses sized crushed rock samples and detects the pressure pulse response in the sample cell. Permeability is then calculated through the analysis of the pressure decay over time.

Figure 1. Disintegrated sample of Bazhenov shale.

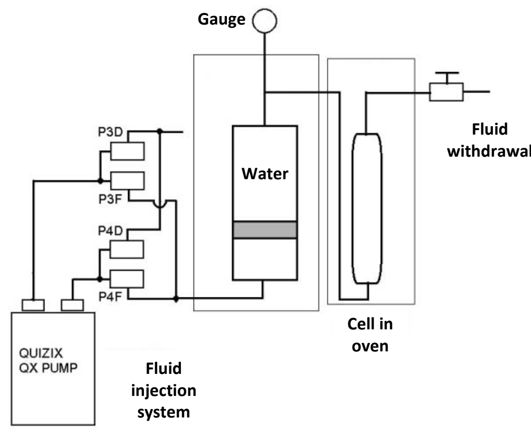

Figure 2. Hydraulic Scheme of the experimental setup.

PROCEDURES

The experiments were designed to investigate the influence of temperature on hydrocarbon recovery during kerogen conversion in the presence of supercritical water. A series of experiments was conducted on non-extracted crushed samples at pressure of 27 MPa in Monel alloy pressure vessel fully filled with deionized water and 55 g of crushed rock sample. The reactor was sealed and the chamber then evacuated for one hour. The hydrous pyrolysis experiments were performed at temperatures 300, 350, 400 and 480°C with heating rate of 20°C/h. Time of treatment was 30 hours for all samples at the test temperature. After that, the pressure vessel was cooled down to room temperature and depressurized to atmospheric pressure.

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 submitted 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 SCW extraction, 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 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 SCW extraction to investigate the change.

RESULTS

Only gaseous products were collected in the tests under 400°C, whereas very small volumes of liquid hydrocarbons were released from the organic matter during SCW extraction and were detected in the form of films on the rock sample and on the vessel's walls in the test at 400°C. The hydrous pyrolysis test on 55g of sample at 480°C generated 1350 scm^3 of gas. According to the gas chromatography results (Fig. 3), methane production increased at higher temperature. Significant amount of methane was determined in the gas products at 480°C. This suggests that secondary oil cracking and coke production started near 480°C. Oil extract was 0.308 g. The content of the polar resin-asphaltene compounds was 21.0%. Content of saturated and unsaturated hydrocarbons, aromatic and other compounds was 77.5%, 3.9% of them were n-alkanes (C10-C35).

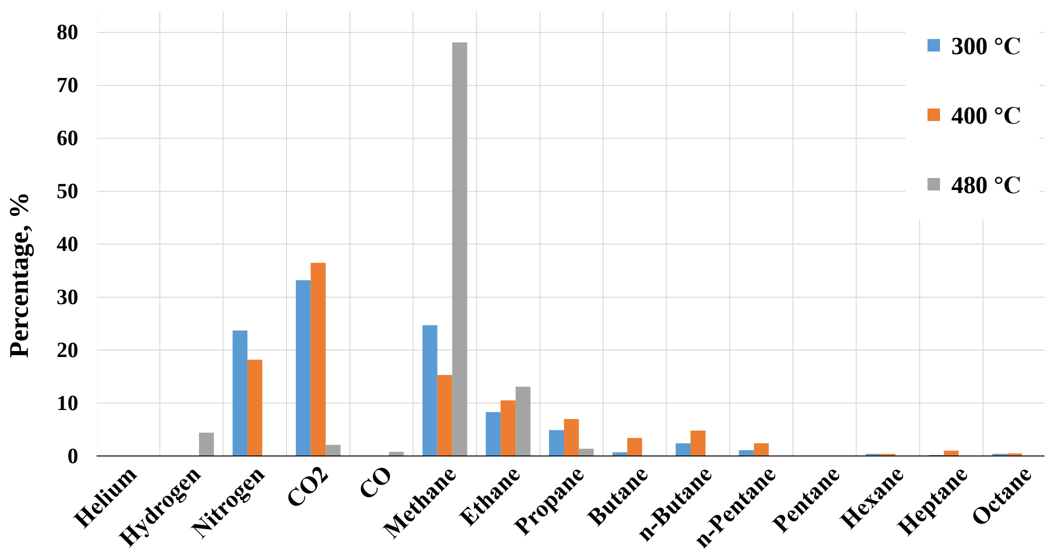

Figure 3. Produced gas compositional analysis.

GRI analysis of the rock chips revealed negligible porosity increase when temperature is raised and sufficient growth in permeability in the test #4 (Table 1). Open-system pyrolysis analysis results indicate almost total recovery of free hydrocarbons (S1) and 82% decrease in the amount of hydrocarbons generated through thermal cracking of non-volatile organic matter (S2) after SCW injection at 480°C (Table 2). Porosity of the core after extraction is unknown and therefore original oil in place and recovery factor cannot be calculated accurately. Nevertheless, we can estimate recovery factor according to the open-system pyrolysis analysis, namely by change in S1 and S2 parameters after SCW extraction. At temperature of 480°C recovery factor is around 83%, which confirms that SCW might be a suitable EOR agent for Bazhenov formation shales.

Table 1. GRI (Crushed Shale) Analysis results.

Sample ID	Temperature, °C	Before the SCW extraction		After the SCW extraction		Percentage change, %	
		Porosity, %	K, nD	Porosity, %	K, nD	Porosity	K
1	300	1.07	20	1.14	23.3	7	17
2	350	0.75	14.4	0.97	17.8	29	24
3	400	1.40	37	1.56	45.2	11	22
4	480	1.04	28	1.55	244	49	771

Table 2. S1 and S2 parameters before and after the SCW extraction

Sample ID	Temperature, °C	Before the SCW extraction		After the SCW extraction		Percentage change, %	
		S1, mg HC/ g rock	S2, mg HC/ g rock	S1, mg HC/ g rock	S2, mg HC/ g rock	S1, mg HC/ g rock	S2, mg HC/ g rock
1	300	8.40	78.30	4.70	75.50	-44.0	-3.6
2	350	5.20	66.80	2.93	64.13	-43.7	-4.0
3	400	6.30	107.60	2.52	97.50	-60.0	-9.4
4	480	9.03	77.07	0.29	13.83	-96.8	-82.1

CONCLUSION

In this study, we evaluated a technique of kerogen conversion in the presence of supercritical water. The investigation determined the “hydrocarbon generation window” within temperature range of 400°C and 480°C for the general BF rocks with low kerogen maturity of South-West Siberian Petroleum Basin. The compositional analysis of evolved products indicated that secondary oil cracking and coke production starts at 480°C. Open-system pyrolysis results indicate almost total recovery of free hydrocarbons and 82% decrease in the amount of hydrocarbons generated through thermal cracking of kerogen after SCW extraction at 480°C. GRI analysis on crushed rocks revealed negligible porosity increase and sufficient growth in permeability when temperature is raised above 400^{o}C, which can be attributed to the start of core destruction with formation of microfractures. Preliminary results show that supercritical water could be a promising EOR agent for Bazhenov formation shales. Obtained data might be a very useful in numerical simulation of supercritical water injection in BF. Due to the small number of hydrous pyrolysis experiments conducted, future work therefore should include different temperatures experiments to determine an accurate temperature of kerogen conversion in Bazhenov formation. In addition, effects of heating rate and minerals on hydrous pyrolysis of kerogen should be investigated.

ACKNOWLEDGEMENTS

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