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Experimental investigation of thermal decomposition of Bazhenov formation kerogen: Mechanism and application for thermal enhanced oil recovery

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ABSTRACT

Bazhenov formation is the key kerogen-bearing oil shale reserve in Russia. Therefore, as recovery from conventional reservoirs decreases, the need to find enhanced oil recovery (EOR) techniques in order to develop Bazhenov formation becomes evident. Despite the huge amount of reserves, oil shales in Russia have not been developed extensively due to the absence of suitable recovery technique. High pressure air injection (HPAI) is one of the recovery techniques that has a potential to become the main recovery method. In order to design this method correctly, different aspects must be investigated. To do that, thermal analysis methods should be implemented. In this work, thermomicroscopy, simultaneous thermal analysis and open system pyrolysis were performed to investigate kerogen conversion process.

The optical thermomicroscopy showed changes in the macrostructure and the morphology of the Bazhenov shale sample during heating up to 720 °C with the heating rate 10 °C/min. It was demonstrated that the conversion of kerogen into hydrocarbons caused increasing in sample porosity. Geometrical characteristics of pores such as size and shape were determined, dynamic events during the heating were investigated. During the air purge, intensive fracturing occurred along the voids formed due to oxidation of organic matter at 450 °C. The simultaneous thermal analysis (STA) revealed linear relationship between TOC and heat value for single well samples. Interval of oxidation reactions was determined.

Bulk-kinetic parameters (activation energy and frequency factor) were calculated by numerical inversion of pyrolysis data using the Kinetics2015 optimization software. Fixing the A factor to a 2×10^{14} s^{-1} and using a spacing of 1 kcal/mole in the discrete activation energy distribution were investigated. In result, solution for different samples along the well was rather stable comparing to traditional approach.

1. Introduction

Because of the decrease in recovery from conventional reservoirs, it is necessary to find new recovery methods to develop unconventional resources. Bazhenov formation is the biggest and the most promising oil-shale reserve in Russia (Henderson, 2014; U.S. Department of Energy, 2013; Jarvie, 2012). Bazhenov formation is Upper Jurassic – Lower Cretaceous organic-rich clay-siliceous shales with carbonate admixture in the West Siberian Basin with more than one million km^2 area. Balushkina et al. (2014) presented a complex lithological typization of the Bazhenov formation rocks. Thickness of the formation varies from 5÷10 to 20÷40 m. The Abalak Formation, represented by alternating carbonated sandstone and siltstone (Upper and Middle Jurassic), lies beneath it, whereas the Achimov terrigenous beds (Lower Cretaceous) are located just above the Bazhenov Formation. Geochemical analysis of core samples showed total organic carbon values of 2–18 wt%, which consist mainly of amorphous kerogen. The main rock section of Bazhenov formation is characterized by very low open porosity and permeability (Chugunov et al., 2015; Vasiliev et al., 2015; Khamidulin et al., 2012; Zumberge and Curtis, 2014). Despite the high hydrocarbon generating potential, it has not been developed extensively due to the absence of suitable recovery technique (Braduchan et al., 1986; Khalimov and Melik-Pashaev, 1980; Yakovleva-Ustinova, 2014).

Experimental research shows that generating hydrocarbons from kerogen requires heating (Tiwari et al., 2013; Zhang et al., 2014; Deng and Li, 2011; Le-Doan et al., 2013; Kibodeaux, 2014; Bondarenko et al., 2016), therefore, thermal EOR methods are the most suitable.

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High pressure air injection is one of the recovery techniques that has a potential to become a recovery method. Although it is a cost effective method, some of its pilots are unsuccessful; statistics of HPAI pilots was shown by Sarathi (1999). The main reason of these failures could be the lack of knowledge regarding the process. It has been acknowledged that the chemical reactions and their kinetics play a critical role on the success of air injection process (Barzin et al., 2010). The classical heavy oil kinetic models consist of three principal types of reactions, namely pyrolysis or fuel deposition, oxygen addition reactions or low temperature oxidation (LTO), bond scission reactions or high temperature oxidation (HTO) (Sarathi, 1999).

In order to make this process be effective in Bazhenov oil shales, it is crucial to understand the mechanism of kerogen conversion process. Kerogen is a cross-linked, high molecular weight solid with complex structure (Kelemen et al., 2006). Moreover, accurate chemical structure of kerogen is unknown. As a result, it has complicated behavior while heating. Therefore, the experimental studies on oil shale should be performed in order to understand mechanisms of Bazhenov Formation kerogen thermal breakdown and identify a number of important physical and chemical processes occurring during this process.

The main purpose of this study was to complete series of different experiments on selected samples of Bazhenov formation to investigate pyrolysis, low temperature and high temperature oxidation reactions, kerogen conversion process and gain valuable data for numerical simulation, namely kinetic parameters of pyrolysis reaction and heating values. In this work, in order to obtain a bigger picture of the processes related to the thermal breakdown of kerogen, we analyzed samples using different techniques. Namely are open-system pyrolysis, simultaneous thermal analysis and thermomicroscopy. Through implementing these methods, we can investigate the process from different perspectives: mass loss, heat output and visual monitoring at micro-scale. In the following section, experimental approach is described in detail.

2. Methodology

2.1. Sample selection

In this study, seven samples of kerogen-bearing Bazhenov Formation from three oil fields of interest were selected for the investigation of thermal decomposition of kerogen. Namely, four samples (1_1, 2_1, 3_1, 4_1) from oil field 1 (Tumen region, West Siberia) from depth of 3046–3066 m, one sample 5_2 from oil field 2 (Tomsk region, West Siberia) from depths of 2611 m and two samples (6_3, 7_3) from oil field 3 (Tumen region, West Siberia) from depth of 2559 m. It should be noted that sample 5_2 is isolated kerogen.

2.2. Test design strategy

This work was performed for better understanding of kerogen decomposition. The complexity of the process is such that there is still not a single test that can provide all the information needed. Therefore, different experiments are required to get a complete picture of the process. Table 1 contains information about samples selected for different experiments. These experiments fall into the following categories:

- open-system pyrolysis and kinetics: to perform geochemical analysis and study the kinetics of pyrolysis;
- simultaneous thermal analysis: to study thermal effects and temperature intervals of low temperature and high temperature oxidation;
- thermomicroscopy: to visually investigate kerogen conversion process during pyrolysis and oxidation.

Table 1
Test design strategy.

Experiment	Oilfield number	Sample ID
Open-system pyrolysis and kinetics	1	1_1, 2_1, 3_1, 4_1
	2	5_2
	3	6_3, 7_3
Simultaneous thermal analysis	1	1_1, 2_1, 3_1, 4_1
	2	5_2
Thermomicroscopy	3	6_3, 7_3

2.2.1. Open-system pyrolysis and kinetics

In this study, HAWK pyrolysis instrument was used to analyze the samples by the breakdown of the kerogen through a programmed temperature pyrolysis and oxidation processes and measurement of the generated hydrocarbons as well as organic and inorganic carbon (Peters, 1986). The programmed temperature method consists of pyrolysis and oxidation cycles. The pyrolysis cycle starts at 90 °C and ends at 650 °C, after that the oven is cooled to 300 °C. The oxidation cycle is initiated to run up to 750 °C. Red sample temperature curve shows precise temperature mode implemented (Figs. 1–7). Pyrolysis experiments were performed on 50–70 mg non-extracted powdered samples. The amount of thermally freed hydrocarbons in the sample in milligrams of hydrocarbons per gram of rock by temperature of 300 °C is designated as S1. Kerogen breakdown is known to start at just about 300 °C and to end at 650 °C. Amount of hydrocarbons that are generated during the pyrolysis process is a measure of the kerogen's capability to generate hydrocarbons under increasing temperatures, which is designated as S2 kerogen yield in mg HC/g rock. This value represents the hydrocarbons source potential of the rock formation. The temperature at which maximum generation of the S2 kerogen yield hydrocarbons (T_{max}) is characteristic of the kerogen type as well as the rock formation's maturity measure. Total Organic Carbon (TOC) is a measure of the organic carbon richness of the rock and is expressed in weight percentage. This characteristic is determined from both pyrolysis and oxidation parameters.

Two approaches was used in generating kinetic data from open-system pyrolysis laboratory experiments. The traditional approach has been to conduct three to five pyrolysis runs on each sample at different heating rates (Benson, 1976; Braun et al., 1991). The purpose is to measure pyrolysis yield as a function of temperature and time over a wide range of thermal histories and to subject these data to mathematical analysis using software programs designed to generate kinetic parameters, such as frequency factor A and activation energy E_a distribution. This approach allows A and the E_a distribution to vary

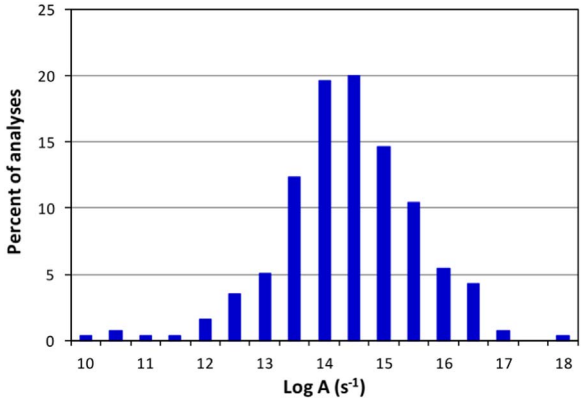

Fig. 1. Logs of A factors shown in histogram form for hydrocarbon-generation kinetics published for 259 source rocks. All these A factors were determined by allowing both A and E_a to vary freely during derivation of kinetic parameters from raw pyrolysis data. Adapted from Waples and Nowaczewski (2014).