Journal of Petroleum Science and Engineering 167 (2018) 241–248

Contents lists available at ScienceDirect

Journal of Petroleum Science and Engineering

journal homepage: www.elsevier.com/locate/petrol

Experimental study on H_2S and CO_2 generation capacities of the Bohai bay heavy oil

Kongyang Wang, Wei Yan*, Jingen Deng**, Hao Tian, Wenbo Li, Yangang Wang, Luyao Wang, Sutao Ye

State Key Laboratory of Petroleum Resources and Engineering, China University of Petroleum, Beijing, 102249, China

ARTICLE INFO

Keywords:
Heavy oil
Thermal recovery
Pyrolysis
H_2S and CO_2 generation
Partial pressure

ABSTRACT

Thermal recovery is a conventional technology for heavy oil development. During thermal oil recovery the reservoir could generate H_2S and CO_2. They will potentially threat the safety of downhole tubing regarding the sweet or sour corrosion. In some Bohai heavy oil fields CO_2 and H_2S under thermal recovery conditions lead to some corrosion problems of the tubing and equipment. Therefore, to determine the corrosive gas generation capacity is crucial for anti-corrosion design of downhole tubing and casing. Heavy oil samples from Bohai, China were experimentally studied for their pyrolysis characteristics using high-temperature-high-pressure autoclaves. The gases were collected when autoclaves cooled down to the in situ formation temperature. Effects of temperature, water chemistry and core mineral on corrosive gas generation were investigated. The results show that total pressure increase significantly when temperature reached 250°C-280 °C under the single heavy oil condition. The additional water facilitates the reaction process, after more SO_4^{2-} added in the mimic formation water, higher H_2S content is obtained. Under the condition of multiphase of oil, formation water and cores, both of the H_2S and CO_2 content increase obviously, and the cores' effect on CO_2 is greater than H_2S. Anti-corrosion design usually concerns only the highest corrosive gas concentration without further analysis. The highest concentration does not always correspond to the best corrosive gases generation capacities of heavy oil. Comprehensive analysis of both the total pressure of reaction process and the quality of the reaction heavy oil is carried out, then the corrosive gases volume per unit mass of heavy oil is calculated. These can determine the strongest corrosive formation environment and the maximum gases generation capacities of heavy oil.

1. Introduction

In the recent era, conventional fossil fuel depletion and the alternative energy source is a crucial problem all over the world. Some studies paid attention to the experiments of the alternative source like biofuels to solve the problem of conventional fossil fuel depletion (Dhinesh et al., 2016a; Annamalai et al., 2016; Parthasarathy et al., 2016). On the other hand, besides focusing on finding alternative source (Isaac et al., 2016; Dhinesh et al., 2016b, 2017), the development of unconventional fossil fuel resources may be a new solution. Crude oil is a fossil fuel formed by organic, thermal, and bacterial processes that transform sediments into hydrocarbons, water and carbon dioxide. It becomes an unconventional petroleum resource-heavy oil, if environmental conditions are appropriate (Chang and Robinson, 2006). Based on American Petroleum Institute (API) gravity and viscosity values, crude oil can be divided into light oil, medium oil, heavy oil and extra heavy oil (Smalley, 2000; Hart et al., 2015). The key properties of heavy oil are density, viscosity, and chemical composition. Here are several methods for heavy oil thermal recovery injection, including cyclic steam stimulation (CSS), also known as Huff and Puff (Shah et al., 2010; Haan and Lookeren, 1969), steam flooding/steam drive or steam stimulation (Zhao et al., 2014), steam-assisted gravity drainage (SAGD) (Zhao et al., 2015; Butler, 1985; Butler and Stephens, 1981), and in-situ combustion (ISC) or fire flooding (Chu, 1977, 1982; Guo et al., 2016a). All the methods will directly or indirectly heat the heavy oil reservoir.

Under the conditions of mentioned thermal recovery methods, heavy oil decomposes to produce corrosive gases such as H_2S and CO_2. It is important to know the origin of H_2S and CO_2, which is toxic and corrosive. According to the reference, three causes of H_2S production are: (1) Bacterial sulfate reduction (BSR), (2) Thermochemical sulfate reduction (TSR), (3) Thermal decomposition of Sulfide (TDS) (Mi et al.,

* Corresponding author.
** Corresponding author.
E-mail addresses: yanwei@cup.edu.cn (W. Yan), dengjg@cup.edu.cn (J. Deng).

https://doi.org/10.1016/j.petrol.2018.03.100
Received 7 December 2017; Received in revised form 19 March 2018; Accepted 27 March 2018
Available online 12 April 2018
0920-4105/

2017; Zhu et al., 2010; Aali and Rahmani, 2012). These reactions also generate a large amount of CO_2.

The inorganically genetic H_2S is produced primarily by TSR, water will participate in the reaction following the reaction equations below (Wang, 2008):

$$2CaSO_4 + 4C + 2H_2O = 4CO_2\uparrow + Ca(OH)_2 + Ca(SH)_2 \quad (1)$$

$$Ca(SH)_2 + CO_2 \rightarrow CaCO_3 + H_2S\uparrow \quad (2)$$

$$CaSO_4 + 4H_2 = Ca(OH)_2 + H_2S\uparrow + 2H_2O \quad (3)$$

$$FeS_2(\text{pyrite}) + HCl \rightarrow FeCl_3 + H_2S\uparrow \quad (4)$$

The organically genetic H_2S is generally related to Mercaptan and thioether, Mercaptan is prone to reacting with other substances to generate H_2S following the reaction equations below (Wang, 2008):

$$2CuCl_2 + 4RSH = RSSH + 2RSCu + 4HCl \quad (5)$$

$$RCH_2CH_2SH \rightarrow H_2S\uparrow + RCH = = CH_2 \quad (6)$$

Mercaptan can provide high recovery of H_2S and heavy oil will be cracked easily by catalyst (Alaei et al., 2017).

Thioether is produced when the oxygen atom in an ether molecule is replaced by a sulfur atom, the structural formula is R-S-R′. Some thermal decomposition of thioether reaction equations are like below (Wang, 2008):

$$C_{19}H_{19}SC_{19}H_{19} \rightarrow C_9H_{19}SH + C_9H_{18} \quad (7)$$

$$C_{19}H_{19}SH \rightarrow H_2S\uparrow + C_9H_{18} \quad (8)$$

$$C_2H_5SC_2H_5 \rightarrow H_2S\uparrow + CH_3CH_3 \quad (9)$$

$$C_2H_5SC_2H_5 \rightarrow C_2H_5SH + C_2H_4 \quad (10)$$

$$C_2H_5SH \rightarrow H_2S\uparrow + C_2H_4 \quad (11)$$

These reactions of H_2S and CO_2 generation are related to the properties of the heavy oil itself, different regions may cause great difference, regarding reaction temperature, SO_4^{2-} ions concentration in formation water and mineral in formation, and the effect of formation water (Lin et al., 2016).

Thermal recovery methods will inject steam to reduce the viscosity of heavy oil which the temperature ranges from 180 to 350 °C (Liu et al., 2016; Romanov and Hamouda, 2011; Szasz and Thomas, 1965). The mercaptan (R-SH) is completely decomposed when the temperature reaches 300 °C, so the experiment chose the temperature condition of 280 °C and 350 °C to compare the effect of temperature on the corrosive gas generation.

The combined effect of corrosive gas, high temperature and salty water has a great potential threat on the production tubing integrity of heavy oil (Zhong et al., 2013; Xiang et al., 2017; Guo et al., 2016b). For now, corrosive gas concentration is used to indicate the capacities of heavy oil, but this engineering method may come with error when the gas is of low concentration. The conditions of the highest measured concentrations of H_2S or CO_2 in laboratory may not always represent the best corrosive gas generation ability for a heavy oil sample (Pahlavan and Rafiqul, 1995). The experiment under this condition may show a false concentration of corrosive gases. Therefore, to determine the quantity of corrosive gas formation properly and accurately is significant for downhole tubing design during the heavy oil thermal recovery. For this case, a new comprehensive method considering gas concentration and gas volume per unit mass of heavy oil has been proposed.

In this paper, pyrolysis experiments are conducted under three kinds of conditions (oil, oil + water, oil + water + rock) and two situations in different temperature and SO_4^{2-} concentration. By using a certain amount of single heavy oil (200g), formation water(50g) and cores (100g) from Bohai bay block, China. The relationship between temperature and pressure during the reaction process is recorded, which is affected by water or core added to the reaction. Analysis of corrosive gas concentration and volume per unit mass of heavy oil is made to identify the condition of maximum corrosive gas generation capacity. The gas generation capacity of Bohai heavy oil is compared under different temperatures and SO_4^{2-} concentration. And we conducted repeat-heat experiments to simulate cyclic steam stimulation (CSS) process used in Bohai oil fields.

2. Experimental

2.1. Apparatus

The stainless-steel autoclave (FYXD, Haian, China) with an internal volume of 2L, has been designed for a maximum operating temperature of 380 °C [653 K] and a pressure of 33 MPa [4786 psi]. The stainless-steel autoclave was placed in an electrically heated furnace with electronic regulation and high heating power, permitting the vessel to be heated from ambient temperature to the experiment temperature condition within a few hours. A thermocouple was placed inside the vessel to record the temperature during the test. The apparatus was equipped with pressure gauge and a valve system to control the gas inlet and outlet. Different tests can be carried out with the stainless-steel autoclave being dynamic or stagnant. Because the in-situ heavy oil pyrolysis reactions could be recognized as static reactions, thus, the following laboratory tests were performed under stagnant condition. The stainless-steel autoclave was connected with an exhaust gas treatment device. When the test is finished, the air in the exhaust gas treatment device is swept by the exhaust gas and then gathered by gas packing (Tedlar PVF gas packing, Dalian Delin Gas packing Co.,Ltd, China). Other exhaust gases will be treated with NaOH solution before letting into the air (Fig. 1).

2.2. Materials

The heavy oil samples were all collected from the Guantao formation (1000–1035 m) of Bohai bay block, China. They were from the exploratory wells and Guantao formation (1000–1035 m) temperature is about 64.6 °C. The properties of the heavy oil were given in Table 1 and the samples for the experiment were shown in Fig. 2(a) and b. Heavy oil viscosity is more than 10000 mPa s and density is more than 1 g/cm^3. Sulfur content is about 0.43%, indicating that the sample itself is easy to produce H_2S. Chemical properties are stable, not as easy to volatilize as light oil. All experimental oil samples are heavy oil. The main chemical composition of the heavy oil in this formation consists of 31% saturated hydrocarbon, 27% aromatic hydrocarbon, 21% asphalt and 21% non-hydrocarbon (Shan, 2001; Kong et al., 2009). Because of the high viscosity of heavy oil, after it was poured into the autoclave, the residual oil in the cup was around 10g, so a total mass of about 210g heavy oil was needed.

Three core samples were collected from the same in-situ formation with heavy oil. The core samples were used in the heavy oil aquathermolysis and TSR experiment to compare the capacity of the heavy oil to generate corrosive gas under different conditions. The core and mimic formation water influence on gas generation were considered in the tests. The elements content analysis of each core samples is quantified by using a microscope and software QUANTAX7.0 (TM3030, HITACHI & Bruker, Japan). And the mineral contents of each three core samples are quantified using an X-ray diffractometer (Miniflex II, Rigaku, Japan). The elements and mineral contents analysis of all the samples are listed in Tables 2 and 3, respectively.

Formation water samples were collected from eight different sampling points of exploratory wells, and analyzed by the Drilling Engineering Research Institute Bohai Experimental Center. The formation water ion concentration for this experiment by the Institute is shown in Table 4. For the #3 test, the SO_4^{2-} ion concentration was 10 times higher than others.