Journal of Petroleum Science and Engineering 170 (2018) 374–382

Contents lists available at ScienceDirect

Journal of Petroleum Science and Engineering

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

Experimental study on the viscosity reduction of heavy oil with nano-catalyst by microwave heating under low reaction temperature

Li Hanyong[a,*], Cui Kexin[b], Jin Ling[a], Wang Leilei[a], Yu Bo[a]

[a] School of Mechanical Engineering, Beijing Key Laboratory of Pipeline Critical Technology and Equipment for Deepwater Oil & Gas Development, Beijing Institute of Petrochemical Technology, Beijing, 102617, China
[b] MOE Key Laboratory of Petroleum Engineering, China University of Petroleum, Beijing, 102249, China

ARTICLE INFO

Keywords:
Low reaction temperature
Viscosity reduction of heavy oil
Microwave heating
Nano-catalyst

ABSTRACT

70% global oil reserves are heavy oil. The high viscosity and poor liquidity of heavy oil lead to many difficulties in its development, storage and transportation. In recent years, as a new technology, viscosity reduction with nanotechnology and microwave technology has become a hot spot in heavy oil study. However, because of low selective absorption of microwave, poor dispersion and high cracking reaction temperature of nanoparticles, nanotechnology cannot be widely applied. This project proposes a super heavy oil viscosity reduction method under synergism of carbon nano-catalyst and microwave. In this paper, a new nano-catalyst with low temperature is proposed to reduce viscosity of heavy oil by synergistic microwave action. By using the Jin County's heavy oil sample in Bohai oilfield, the optimum dosage of nanometer catalyst, the temperature of microwave reaction and the reaction time are firstly determined by single factor experiment, and the effect of catalyst type and different heating mode on oil sample viscosity is secondly verified. At last, the changes of the group composition and the structure of the oil samples before and after the experiment are compared and analyzed by means of modern test. The results show that the heavy oil macromolecules can be chemically cracked under low reaction temperature (less than 100 °C) by use of the low-temperature new 6# Nano-catalyst assisted by microwave. The recombination fractions are reduced, and small molecular saturation components and aromatic components increased significantly, which will permanently reduce the viscosity of heavy oil, with a viscosity reduction rate up to 99.7%. The results reveal the non thermal effect mechanism and the activation action of microwave on nano-catalyst to promote viscous oil viscosity reduction under low reaction temperature, which would provide theoretical basis and technical support for future application of nano-microwave synergistic technology in heavy oil piping.

1. Introduction

Heavy oil is a high-viscosity and high-density crude oil. In foreign countries, heavy oil is collectively known as heavy crude oil, and it accounts for a large percentage of the world's oil and gas resources. According to statistics, the reserves of heavy oil, super heavy oil and natural asphalt in the world are about 1000×10^8 t (Yu, 2002). Many countries have rich heavy oil resources, including Canada, Venezuela, USA, former Soviet Union, China and Indonesia, their heavy oil and asphaltic sand resources are about 4000×10^8–$6000 \times 10^8\,m^3$ (predicted resources included), and their annual output of heavy oil reaches up to 1.27×10^8 t (Yu, 2002).

Heavy oil has high viscosity, so the friction between heavy oils, as well as between heavy oil and pipe wall is very high. Transporting such oil will lead to very high pipe pressure drop, so there is strict requirement on pumping equipment which basically cannot be used for normal transportation if it is not treated by special process. Currently, the pipeline transportation of heavy oil often adopts heating crude transportation technology or low-temperature transportation technology like mixing light oil and watering chemical emulsification (Long, 2016). Restricted by local light oil resources, economic benefit, environmental pollution control pressure and other conditions, low-temperature transportation technology often cannot be widely applied. For traditional heating crude transportation technology, fuel oil, fuel gas or electrical heating and other methods are usually adopted, though it only needs low hardware cost, it has the shortcomings of low energy conversion efficiency and great economic loss (Long, 2016). Microwave can be used to heat the heavy oil to reduce its viscosity, with the advantages of fast speed and low pollution, and it also can degrade heavy oil to certain extent (Yang et al. (2016a, 2016b). Through experiment,

* Corresponding author. .
E-mail address: lihanyong@bipt.edu.cn (L. Hanyong).

https://doi.org/10.1016/j.petrol.2018.06.078
Received 8 April 2018; Received in revised form 22 May 2018; Accepted 25 June 2018
Available online 26 June 2018

Bosisi (1977), Balint et al. (1983), Jiang (2004), Wang et al. (2010), Dai et al. (2013) found that with microwave radiation, the temperature of certain local position inside the heavy oil was higher than the thermal cracking temperature of resin and asphaltene, thus resulting in local overheating. Some resin and asphaltene would produce small organic molecules through pyrolysis reaction. In the meantime, it also would increase the content of dispersed media like saturated hydrocarbon and aromatic hydrocarbon, thus changing the original dispersed state of the disperse system, which will reduce the concentration of resin and asphaltene and long-chain alkane on the whole, thereby lowering the viscosity of crude oil. Edward (1983) conducted an experiment to extract viscid crude oil from oil shale with microwave, and found that low-viscosity crude oil could be extracted at low temperature, which is different from the conditions shown in traditional heating reaction (the pyrolysis temperature is greater than or equal to 300 °C, but the experimental temperature was less than or equal to 100 °C, so pyrolysis reaction would not occur in the experiment, and it was not thermal effect produced by thermal cracking). Through experiment, Amoosh (1992), Cheng et al. (2005), Jiang (2004), Dai et al. (2013) also verified that chemical pyrolysis reaction with non-thermal effect would occur when heavy oil was under microwave radiation. Domestic and overseas studies consider that both the "thermal effect" and "non-thermal effect" of microwave can reduce the viscosity of heavy oil, but study on the technology of reducing viscosity with microwave radiation only remain on describing experimental phenomenon at the current stage, and there is not enough high-level analysis on its mechanism.

In addition, Jiang (2004), Shang et al. (2013) used microwave radiation to reduce the viscosity of heavy oil from different regions, and found that different compositions of crude oil showed varied sensitivities to microwave. Long-chain alkane, resin and asphaltene were sensitive to microwave, while aromatic hydrocarbon was insensitive to microwave, so they would absorb microwave selectively. But some catalyst with good dielectric property can be used as strong microwave absorbing medium to improve the efficiency of viscosity reduction by heating heavy oil with microwave (2016). Based on this mechanism, Kirkbride (1981), (Tanner and Ding, 1999, Tanner et al. (2000, 2002)) , Xiang et al. (2005) selected and used charcoal which could absorb metal ion as the catalyst, and studied the influence of microwave on heavy oil's catalytic cracking. According to their research result, microwave enables the catalytic cracking reaction to proceed at low temperature and pressure, and saturated carbon-carbon bond can be ruptured selectively. Researchers believed that this was mainly because microwave could activate the catalyst. Jackson (2002), Zhao (2009) studied the influence of different catalyst combinations on the viscosity reduction of heavy oil with microwave. The experimental result also confirmed that microwave could activate the catalyst, and different catalyst types ensured the local catalytic cracking reaction of hydrocarbon molecules to varying degrees, which was conducive to the cracking and viscosity reduction of heavy oil.

As the study deepened, researchers turned their eyes on nanotechnology to develop more efficient catalyst. Nano particles have many advantages for their unique physicochemical property, e.g. high surface area/volume ratio increases the contact area with heavy oil, thus improving catalytic activity; metal nano-catalyst strengthens heat conduction (Bell, 2003). Therefore, nanotechnology has been applied in heavy oil recovery for catalyzing and viscosity reduction (Angeles et al., 2014; Shokrlu and Babadagli, 2011, 2014). Hyne et al. (1982), Clark and Hyne (1990a); Clark et al. (1990b) pointed out that using water-soluble metal salt as catalyst was conducive to the aquathermolysis. The study of Fan et al. (2006) showed that both water-soluble and oil-soluble dispersed catalysts could facilitate the aquathermolysis of crude oil. The study of Li et al. (2007), Wu et al. (2011) showed that the Ni-nanoparticles synthesized with micro-emulsion method had good catalytic activity to organic reaction when they suspended in the system, and nickel was typical hydrogenation catalyst, so it may transfer hydrogen in water to the super heavy oil. But the study above mainly uses traditional heating method and nano-catalyst to reduce the viscosity of heavy oil, so it has the following problems: firstly, nano-catalyst will take effect in the catalytic cracking reaction of heavy oil when the temperature is high enough (200 °C–350 °C), and it shows poor effect in reducing viscosity when cracking reaction occurs at low temperature; secondly, the steam-driven heating method adopted has the disadvantages of small action range and high energy consumption; thirdly, different heavy oils show varied alkane with different carbon number and content, as well as very different structure and content of resin and asphaltene, so nano-catalyst only selects the most suitable heavy oil.

In recent years, many researchers started to integrate microwave technology and nanotechnology together to study the modification and viscosity reduction rule of heavy oil with the combined action of nano-catalyst and microwave. Shokrlu and Babadagli (2010) put forward using nano-particles as catalyst to enable the catalytic cracking of heavy oil with microwave assisted. Greff and Babadagli (2011, 2013) considered that the unique photochemical effect of microwave not only could heat heavy oil rapidly (reaction temperature is less than 150 °C), but also could produce active hydrogen free radical in situ, which could be used as the hydrogen donor of aquathermolysis. Li et al. (2014) believed that metal nano-catalyst would pollute the crude oil, so they selected carbon nano-catalyst in the pyrolysis for viscosity reduction of heavy oil. The experimental result showed that with microwave assisted, catalyst consumption could be reduced, catalytic efficiency improved, viscosity reducing effect enhanced, and cracking reaction occurred at low temperature (reaction temperature is less than 150 °C). However, in existing studies on mechanism of reducing the viscosity of heavy oil, describing experimental phenomena about thermal effect and thermal cracking accounts for the major part, and there is few in-depth study on the viscosity reduction mechanism with the combined action of nanotechnology and microwave. Therefore, it is highly required to research and develop a new method to reduce the viscosity of heavy oil that can be applied in the future, and the newly integrated nano-catalyst and microwave is also the new method that can be used to reduce the viscosity of heavy oil and decrease its resistance. In this paper, we'll conduct experimental study on reducing the viscosity of heavy oil with low-temperature new 6# nano-catalyst and microwave (reaction temperature is less than 100 °C), and reveal its viscosity reduction mechanism through advanced testing method.

2. Experimental research

2.1. Experimental conditions

2.1.1. Experimental oil sample

The oil sample used is heavy oil from Jin County of Bohai Oilfield (hereinafter referred to as "Jin County oil sample"). Its density is 0.988g/cm^3 (20 °C), and its viscosity-temperature characteristic parameters are shown in Table 1. We determine the oil sample according to *Petroleum Asphalt Four-Component Determination Method* in Standard NB/SH/T 0509-2010, and find asphaltene accounts for 2.1%, resin accounts for 44.9%, saturated hydrocarbon 36.6%, and aromatic hydrocarbon 16.4%.

2.1.2. Experimental instruments and experiment reagents

Main instruments include computerized microwave solid-liquid phase synthesizer/extractor (XH-200A), Fourier infrared spectrometer (TENSOR27), TA rheometer (DHR), four component separation experimental system for heavy oil, and so on (as shown in Fig. 1).

Table 1
Oil sample's viscosity-Temperature characteristic parameters.

Temperature/°C	30	40	50	60	70	80	90
Viscosity/mPa·s	134820	48624	15777	6814	2583	1383	963.8