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Study on the aging and critical carbon number of wax deposition with temperature for crude oils

Qing Quan, Jing Gong*, Wei Wang, Ge Gao

Beijing Key Laboratory of Urban Oil and Gas Distribution Technology, China University of Petroleum, Beijing 102249, China

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ABSTRACT

The aging of wax deposition with time and temperature was investigated by a series of experiments using cold finger device and carbon number distribution of the deposit samples was analyzed by high temperature gas chromatography. Deposition experiments were performed with the waxy crude oils from oil field in China, containing 18.6 wt% wax content. In the process of wax deposition aging, wax molecules with carbon number higher than critical carbon number (CCN) would diffuse into the deposit, while those with carbon number less than CCN would diffuse out from the deposit during the experiments. In this study, it is found that the wax content and higher carbon number in deposit all increase as time increases from 3 h to 48 h, so the hardness of deposit increases during the aging of wax deposition. In addition, the higher temperature range has an active effect on the aging of the wax deposition. Comparing the effect of the different temperature conditions, it could be concluded that temperature differential mainly determines the wax content and that hardness of the deposit mainly depends on the bulk oil temperature. Moreover, in this study, it is found that the temperature has only a little effect on critical carbon number (CCN) as change in CCN does not exceed one carbon number under different temperature conditions.

1. Introduction

For the exploration of the deepwater oil fields and the construction of subsea pipelines, wax deposition is growing to be a major issue of flow assurance. As waxy crude oil flows through the ocean floor (the bottom temperature of the ocean can reach 4 °C) from subsea reservoirs(70–120 °C)(Huang et al., 2011), wax molecules dissolved in waxy crude oil will crystallize out and then precipitate on the pipe wall due to the fact that actual temperature of the pipe wall is well below wax appearance temperature (WAT). Molecular diffusion is the dominant mechanism in wax deposit formation (Burger et al., 1981; Majeed et al., 1990; Svendsen, 1993; Creek et al., 1999). The wax deposition containing gel oils refers to n-paraffin molecules with carbon numbers ranging from 10 to 50 (Roehner et al., 2002). The n-paraffin molecules precipitated on the pipe wall create a radial concentration gradient due to radial temperature gradient from the bulk oil to the pipe wall, and this concentration gradient will in turn drive more n-paraffin molecules to precipitate on the pipe wall and form wax deposition. In recent years, the scholars found that the components of deposit change with time, and this phenomenon is called aging (Hsu and Santamaria, 1994; Singh et al., 2001, 2000; Paso and Fogler, 2003). During the process of "aging", the heavy n-paraffin components diffuse into the deposit layer, while the light n-paraffin components diffuse out of the deposit layer, so the deposit layer hardens with time, and the highest n-paraffin components diffused out of the deposit is defined as the critical carbon number (CCN).

The wax deposited in pipelines can increase pressure drop by reducing the area open to flow, which would result in an increase of the transportation cost. In the worst case, pipes would get plugged and have to be replaced. To avoid this, pigging is perhaps the most conventional remediation technique to scrape off wax deposition. The difficulty and efficiency of pigging is closely related to the deposit thickness and hardness of deposit (Wang et al., 2005, 2008; Pengyu et al., 2013). Deposit thickness can be acquired by calculation of pressure drop or directly weighing, and the hardness of wax deposition can be described by carbon number distribution and wax content in deposit, especially the amount of the relatively higher carbon number components. The aging process of wax deposition causes deposit to harden and become difficult to remove by pigging. Singh et al. (2000) found the continuous diffusion of long-chain n-paraffin molecules from the bulk oil into the gel layer during the aging process.

In the past few decades, deposit thickness has been studied extensively, the aging process have been studied for the past few decades by many researchers in this field, and only few papers have been

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* Corresponding author.
E-mail address: ydgj@cup.edu.cn (J. Gong).

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published. Researchers from University of Michigan used model oils consisting of a commercial paraffin wax dissolved in a mineral oil (Singh et al., 2000), in a single component solvent such as dodecane (Singh et al., 2001), or in a commercial model oil consisting of only n-alkanes (Paso and Fogler, 2003), and avoided complications of aromatics, naphthenics, resins, and asphaltenes in crude oils. Components such as aromatics, naphthenics, resins, and asphaltenes certainly influence the crystallization kinetics and solid–liquid equilibrium of *n*-paraffin components in crude oils. So the carbon number distribution of a simple model oil does not reflect the n-paraffin distribution of the real crude oils, especially the high wax content crude oils in China. Singh et al.'s (2001) depositional studies only discussed the effect of wall temperature with constant oil temperature on CCN. While in the actual crude oils' pipelines, the wall temperature (ambient temperature) is a basically stable along the pipe flow, and the bulk oil temperature decreases along the pipe flow. So the studies of the relationship between the CCN and operating bulk oil temperature are much more important. In this study, the crude oils with 18.6% wax content were used to explore the aging process and CCN of wax deposition for crude oils, and the changing of CCN along with the wall temperature and bulk oil temperature. The cold finger apparatus was used and the carbon number distribution of deposit was analyzed by high temperature gas chromatography (HTGC).

2. Experimental section

2.1. Waxy crude oil sample

During the experiments, the waxy crude oil from oil field in China was used. The crude oil has a density of 863.4 kg/m^3 at 40 °C, a pour point temperature (PPT) of 30 °C and a WAT of 44 °C, measured by Differential Scanning Calorimetry (DSC) with the model TA2000/MDSC2910. The DSC curve of the crude oils has been shown in Fig. 1. Its wax content is approximately 18.6% by weight of n-paraffin components.

2.2. Experimental apparatus

Cold finger is a method to simulate warm oil in contact with the cold pipe wall. The oil is stored in a stainless-steel vessel with circulating hot water to keep warm, while the cold finger is maintained by circulating cold water. The bulk oil temperature (T_{oil}) and the cold finger surface temperature (or coolant temperature, T_{coolant}) can be maintained by circulating the water. Thus, a radial temperature gradient forms between the bulk oil and the cold finger surface, which would drive the wax molecules to diffuse and deposit on the surface. The photos of cold finger apparatus during experiments are shown in Fig. 2. The volume of the crude oil in all experiments is set to be 300 ml, and the diameter of cold finger is 2 cm.

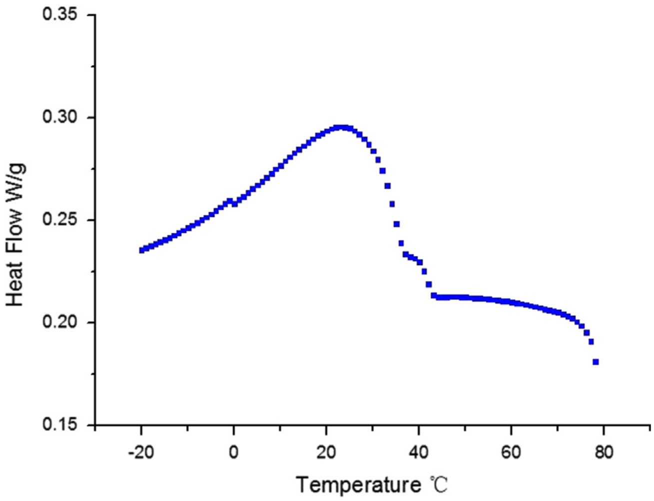

Fig. 1. The DSC curve of crude oils.

2.3. Experimental procedure and method

Before the experiments, oil samples were maintained in stainless-steel vessel at 60 °C to dissolve the wax crystal and eliminate the thermal history for 6 h, and the cold finger was maintained at the desired temperature. Cold finger was then put into warm oils as the time and desired temperature were reached. After the experiments, the cold finger was carefully removed from the stainless-steel vessel, and the deposit was scraped from the cold finger for further weighing and analyzing. Deposit samples were obtained at deposit time of 3, 6, 9, 12, 24 and 48 h.

The deposit was analyzed by HTGC to get the wax content and carbon number distribution. Fig. 3 shows the carbon number distribution of waxy crude oil. As it is known, wax refers to the n-paraffin, so all the carbon number distributions in this study are the n-paraffin carbon number distribution, which would not be explained again. The wax content in analysis refers to sum of C19+n-paraffin in deposit.

3. Results and discussion

3.1. Aging of wax deposition

Fig. 4 shows the changing of deposit versus time curves. From the results in Fig. 4, it can be seen that wax content and the higher carbon number components in deposit increase as the deposit time increases. In addition, for each experiment, the wax content and the higher carbon number components in deposit increase slightly when time varies from 3 h to 12 h and the deposit rate increases sharply when time varies from 12 h to 48 h.

Fig. 5 shows the absolute difference values between the carbon number distribution in deposit and waxy crude oil. It can be seen from Fig. 5 that the CCN is 26 under the given temperature condition.

During the experiments, the wax molecules with carbon number higher than 26 diffuse into the deposit, while the wax molecules with carbon number lower than 26 diffuse out from the deposit (which is called as counter-diffusion). This phenomenon will be more obvious as the experimental time increases. The efficiency of pigging mainly depends on the deposit hardness, for which the CCN can be used as a criteria, as a higher CCN yields a mechanically harder wax with a higher melting point, as well as a lower solubility in typical wax solvents (Singh et al., 2000; Paso and Fogler, 2003).

3.2. Effect of temperature range

For the purpose of studying the effect of temperature range on aging of wax deposition, the deposit samples at different temperature range were analyzed by HTGC and are shown in Figs. 6 and 7.

It can be seen from Fig. 6 that the amount of lower carbon number components in deposit decreases and the amount of higher carbon number components in deposit increases as the deposit time increases at higher temperature range.

The results compared in Figs. 4 and 6 show that the variation of wax content in deposit for higher temperature range (T_{oil}=WAT+5 °C, T_{coolant}=WAT–10 °C) is higher than that for lower temperature range (T_{oil}=WAT, T_{coolant}=WAT–15 °C). Under the same temperature difference, the amount of higher carbon number components in deposit increases with the increase in the temperature range (i.e., the amount of higher carbon number components at higher temperature range is more than that at lower temperature range, while the amount