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Effect of asphaltenes on the stratification phenomenon of wax-oil gel deposits formed in a new cylindrical Couette device

Chuanxian Li, Jinyang Cai, Fei Yang*, Ying Zhang, Fan Bai, Yangyang Ma, Bo Yao

College of Pipeline and Civil Engineering, China University of Petroleum, Qingdao, Shandong 266580, People's Republic of China

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ABSTRACT

Based on a newly developed cylindrical Couette device, the stratification phenomenon of wax deposit formed by synthetic waxy oils was investigated through direct observation, DSC test, composition analysis, rheological test and microscopic observation. When no asphaltenes present in waxy oil (oil sample 1), the formed wax deposit is a thick wax-oil gel (4.6–5 mm) and no stratification phenomenon is found. A clear two-layer stratification phenomenon of wax deposit occurs after the addition of asphaltenes (oil sample 2–4). The two layers could be clearly identified based on the outstanding structural strength difference: the outer deposit layer is very loose and soft and is easy to be scraped off; while the inner deposit layer is so compact and hard that it could not be scraped off unless using some sharp instruments. The thickness of outer deposit layer is 0.7–0.8 mm and changes little with increasing asphaltene content, while the thickness of inner deposit layer decreases with increasing asphaltene content from 1.2 mm at 0.75 wt% to 0.7 mm at 1.5 wt%, then to 0.4 mm at 3 wt%. The wax appearance temperature (WAT) and wax content of outer deposit layer is similar to those of wax deposit formed by oil sample 1 and change little with increasing asphaltene content; while the WAT and wax content of inner deposit layer are very high and increase with increasing asphaltene content. For the inner deposit layer formed by oil sample 3 (1.5 wt% asphaltenes), (a) the critical carbon number (CCN) is relatively high (C26); (b) the rheological property is greatly aggravated; (c) the inner deposit layer is filled with large spherical-like wax crystals and is rich of asphaltenes (3.4 wt%). The increased asphaltenes amounts facilitate nucleation and growth of wax crystals in the inner deposit layer, causing a significant reduction of wax concentration in the inner deposit layer and a fast wax diffusion rate from bulk oil and outer deposit layer to inner deposit layer. Therefore, the inner deposit layer has very high WAT, wax content and yield stress. With increasing asphaltene content, the formed wax crystals become smaller and more compact, favoring the formation of a thinner inner deposit layer.

1. Introduction

One of the problems faced by the petroleum industry is the wax deposition in pipelines during transportation of crude oils. Most of crude oil contains a substantial amount of paraffin waxes, which are mainly composed of n-alkanes heavier than $C_{18}H_{38}$ (Garcia, 2000; Singh et al., 1999; Kelland, 2009). When the crude oil is transported through pipelines in cold ambient temperature well below wax appearance temperature (WAT), wax crystals appear and deposit on the inner cooler wall of pipe and form a layer of wax-oil gel deposit. The resulting wax deposit causes significant transportation problems by progressively restricting the flow of crude oil, increasing the pressure drop, or even plugging the pipeline (Singh et al., 1999; Kelland, 2009). Pigs are commonly used to scrape off the wax deposits and ensure safe flow of crude oil in pipeline. However, if the wax deposits become too thick or too hard, pigs will be unable to break the deposits and will get stuck in pipeline, causing further blockage. A better understanding of the deposition mechanism, deposition rate and deposition aging is crucial in order for one to make a suitable pigging schedule.

Four possible mechanisms have been identified and considered for wax deposition, that is, molecular diffusion, shear dispersion, Brownian movement, and gravity settling (Burger et al., 1981; Azevedo and Teixeira, 2003). Most researchers considered that molecular diffusion played a critical role on wax deposition. The molecular diffusion approach is based on the premise that the deposition process is driven by a radial concentration gradient of wax molecules created by the radial temperature gradient in pipeline. The Fogler group (Venkatesan, 2004) proposed a five step process for wax deposition based on molecular diffusion approach. A lot of wax deposition models for the prediction of deposition

* Corresponding author.
E-mail addresses: lchxian@upc.edu.cn (C. Li), yf9712220@sina.com, yangfei@upc.edu.cn (F. Yang).

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rate were developed according to experimental data and molecular diffusion mechanism (Ramirez-Jaramillo et al., 2004; Edmonds et al., 2008; Huang et al., 2011). There are also some researchers (Mehrotra and Bhat, 2010; Arumugam et al., 2013; Haj-Shafiei et al., 2014) modeling wax deposition based on the premise that the deposition process is thermally driven, i.e., the deposition of solids is controlled primarily by heat transfer.

Some kinds of wax deposition system, such as cold finger system (Shasha and Qi yu, 2014; Wang et al., 2013), flow loops system (Valinejad and Nazar, 2013; Zheng et al., 2013), parallel plate deposition cell system (Tinsley and Prud'homme, 2010), Couette system (Akbarzadeh and Zougari, 2008; Zougari, 2010; Zougari et al., 2006), and oscillatory baffled tube system (Ismail et al., 2008) were developed to carry out laboratory investigation of wax deposition under different flow regime (laminar flow and turbulent flow). The results showed that variables such as oil temperature, flow rate, the inside pipe-wall temperature, the wax layer composition and concentration, greatly affect the deposit-layer thickness and deposit properties. The aging process of wax deposit, which causes the hardening and compositional changes of wax deposit with time, was also well investigated (Singh et al., 2000; Singh et al., 2001; Paso and Fogler, 2003).

The structural characteristics of wax deposit, including the macrostructure (such as stratification, hardness of the deposit) and microstructure (morphology of wax crystals), are also important for better guidance of pigging operation. Several experimental investigations studied the morphology of wax crystals in deposit (Ismail et al., 2008; Singh et al., 2001; Masoudi et al., 2010; Bai and Zhang, 2013). In a recent work, Bai and Zhang (2013) studied the thermal, macroscopic, and microscopic characteristics of wax deposits in field Pipelines through DSC, yield stress measurement and optical microscopy.

In some Chinese field pipelines transporting waxy crude oils, a two-layer structure wax deposit may occur (Yang, 2006): the inner deposit layer attached on the inner wall of pipes is a thin and hard layer with large amounts of wax, while the outer deposit layer attached on the surface of inner deposit layer is a thick and gel-like layer with large amounts of oil phase entrapped in the wax crystal network. In a pigging process, the outer gel-like wax deposit layer is easier to be broken into liquid colloidal dispersions. However, the hard inner wax deposit layer is difficult to be broken into pieces. It is liable to accumulate at the head of pigs and finally causes stuck of the pigs in pipeline. Therefore, a better understanding of the formation mechanism and hardness of the outer/inner wax deposit layer are important for the guidance of pigging operation in pipelines transporting waxy crude oils. Studies on the stratification of wax deposit are scarce. Toma et al. (2006) investigated the deposition property of a crude oil with the aid of a newly developed axial wax deposition apparatus. They found that a two-layer paraffin deposition structure forms under turbulent flow instead of laminar flow. The inner layer is a hard layer with more long chain length n-alkanes, while the outer layer is gel-like with more short chain length n-alkanes. They did not explain the mechanism of the stratification phenomenon.

In this paper, the deposition behavior of 6.7 wt% synthetic waxy oils in a newly developed Cylindrical Couette Device was investigated. A clear two-layer stratification phenomenon of the wax deposit was observed after the addition of a small amount of asphaltenes. The effect of asphaltene content (0–3 wt%) on the stratification phenomenon was studied based on direct observation and DSC test. The n-alkanes composition and hardness of the two different deposit layers were measured by high temperature gas chromatography (HTGC) and rheological test, respectively. In addition, the wax crystal morphology of the two different deposit layers was observed through polarized microscopy. The purpose of this paper is to clarify the stratification phenomenon of wax deposit induced by asphaltene addition and to discover the compositional and structural differences between the two deposit layers, both of which favor the better guidance of pigging operation.

2. The new cylindrical Couette device for wax deposition test

A newly developed wax deposition testing device (Yang et al., 2014) was designed based on Couette flow principals to simulate the hydrodynamic and thermal characteristics encountered in crude oil pipelines. As seen in Fig. 1, the cylindrical Couette device is mainly composed of a hot bath, a cold bath, a torque sensor, a lifter, a sample barrel (R_1=52 mm), a wax deposition barrel (R_2 =25.5 mm) and a conveyor. In a wax deposition test, the sample barrel rotates at a fixed rotating speed, while the inner wax deposition barrel is stationary. According to Couette's study (Li, 2007), the Reynolds number of the flow field in a Couete device is calculated as follows:

$$\mathrm{Re} = \frac{\Omega R(R_1 - R_2)\rho}{\mu}$$

where R_1 is the radius of outer barrel, R_2 is the radius of inner barrel, R is the radius of rotary barrel, Ω is the rotating speed of rotary barrel, μ and ρ are the viscosity and density of oil phase respectively. For the cylindrical Couette device (see Fig. 1), R_1 $=R=0.052$ m, $R_2=0.0255$ m, $\Omega=15.7\ \mathrm{rad\cdot s^{-1}}$ (fixed at 150 r/min). Imaging the $\rho=\rho_{water}=10^3\ \mathrm{kg\cdot m^{-3}}$ (ρ is normally smaller than ρ_{water}) and the $\mu=\mu_{min}=0.005$ Pa · s (μ is normally larger than 0.005 Pa · s), the calculated $\mathrm{Re}_{max}=4326.92$. When the inner cylinder (wax deposition barrel) is stationary while the outer cylinder (sample barrel) is rotary, the critical Reynolds number is greater than 50,000 (Wazer and van, 1963). Because the Re_{max}

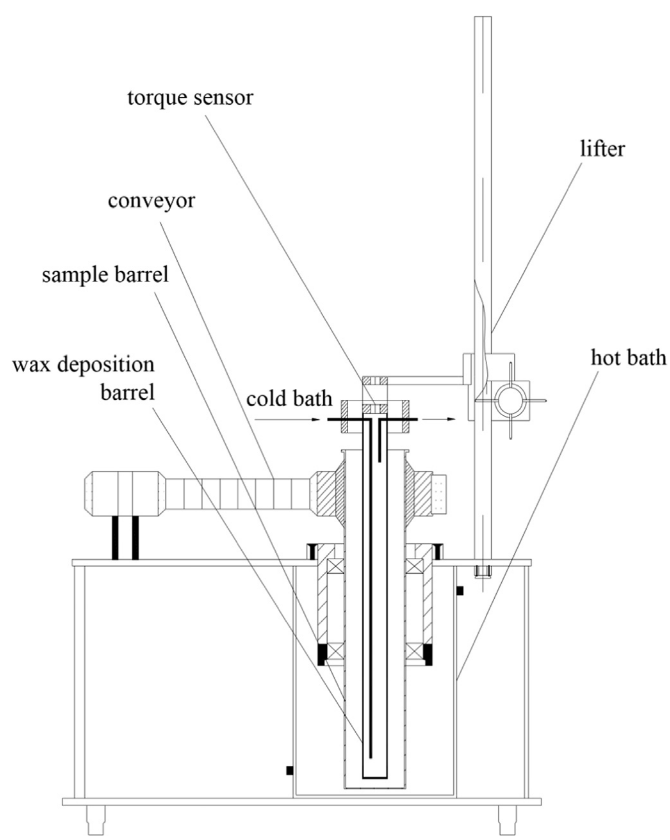

Fig. 1. Schematic diagram of cylindrical Couette device for wax deposition test.