A novel method of testing the pour point of waxy crude oil at high pressure

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Abstract. A novel method to measure pour point at high pressure is presented. This approach uses the pour point and viscosity data at atmospheric pressure as the basic data. The viscosity data at certain high pressure are also used. The results show that, at the pressure of 0.1, 6.9, 13.79 and 24.14 MPa, the pour point is 45, 45.56, 46.76 and 48.98°C respectively. The pour point increases by about 0.17°C respectively when the pressure increases per 1 MPa. The method presented in this paper makes up for the shortage of the existing methods which can only measure the pour point at atmospheric pressure.

1. Introduction
Paraffin deposition in subsea pipelines and oilfield production is a serious problem in the oil industry. When the temperature drop, the wax crystals may separate from the liquid phase and interlock, forming a network structure that entraps the solvent molecules, and the waxy oil end the flow at a certain stage. Once 1 to 2% of separated crystals are thus formed, cessation of the free flow of the waxy crude oil may result, the temperature at which this occurs is called the pour point (PP) [1]. The PP is defined as an important indicator that describes the degree of paraffin deposition and defines expenditures of oil recovery and pipeline transportation [2-5].

There are several standard methods for estimating pour points of petroleum products [6-9]. The PP is considered as the highest temperature at which the sample loses its movement. During this process, the sample is required to stand stationary in a test jar surrounded by a cooling bath. The PP is the highest temperature at which a sample does not flow for certain time determined by a given standard. Waxy crude oil is a complex mixture, and its PP can be influenced by a variety of factors. A large number of experimental studies on PP of waxy crude oil have been conducted. Some studies reported that the waxy inhibitors affect the PP of waxy crude oil [10-15]. Variation in thermal history and shear history are the dominant factors affecting the PP of waxy crude oil observed by many researchers based on laboratory experiments [16-19].

Although some affecting factors of the PP were studied by many experiments. The PP relies on the n-paraffin concentration (PC) and the length of the n-paraffinic chain (CL). Meanwhile, some experiments show that the pressure can change the components and concentration of n-paraffin. Thus we see that the PP of waxy crude oil will change due to pressure change. Since the pressure will change greatly during the process of exploitation and transportation, the effect of pressure change on PP of waxy crude oil cannot be ignored. Further, there have been hardly studies on the effect of pressure. The main reason is the limitation of experiment instruments. The conventional pour point tester has only been able to measure the pour point at atmospheric pressure, and there are no relevant standards and testers for measuring the pour point of crude oil at high pressure. To solve this problem,
this work proposed a novel computing method by using the viscosity data and the pour point at atmospheric pressure. The tests were performed at pressures from stock tank conditions to the initial reservoir conditions (6.9, 13.79, and 22.14 MPa).

2. Experimental

2.1. Sample
Waxy crude oil samples taken from Kingfisher field are used in the tests. Its density is 0.836 g/cm\(^3\) at 20 °C. Its wax appearance temperature (WAT) is 64.08 °C and its wax content is 29.95%.

2.2. Experiment Apparatus
A WFY-131A pour point tester (Wuzhou, China) is used to measure the pour point at atmospheric pressure (approximate 0.1 MPa). A RS600 rotatory viscometer (HAAKE, Germany) is used to obtain the viscosity at 0.1MPa. A high-pressure PVT capillary viscometer which is a part of PVT-2730 (RUSKA, USA) is adopted to obtain the viscosity at high pressure.

2.3. Experimental procedure
The experimental steps are as follows.
   (1)The pour point at 0.1MPa for the oil sample is measured with pour point tester.
   (2)The viscosity data at 0.1MPa are measured by rotatory viscometer. The temperatures are 85, 80, 75, 70, 65, 60, 55, 50, 45 and 40 °C. The shear rates are 5, 10, 20, 50 and 100s\(^{-1}\).
   (3)The viscosity data at three pressures (6.9, 13.79 and 24.13MPa) are detected by high-pressure PVT capillary viscometer. The temperatures are the same as Step 2. For the issue of precision, the selected shear rates of this high-pressure PVT capillary viscometer can not be too small compared with the ones selected for the rotatory viscometer. In this paper, the shear rates are 384.34, 576.51, 768.68, 960.85 and 1153.02s\(^{-1}\). The shear rates is regulated by changing the flow of the sample.

3. Results and discussion

3.1. Pour point and viscosity data
The pour point is 45 °C at 0.1MPa measured by pour point tester. The viscosity data at 4 pressures are shown in Tables 1-4 measured by rotatory viscometer and high-pressure PVT capillary viscometer.

| Table 1. Viscosity data (0.1 MPa) |
|---------------------------------|
| Temperature, °C | Viscosity, mPã·s | 5s\(^{-1}\) | 10s\(^{-1}\) | 20s\(^{-1}\) | 50s\(^{-1}\) | 100s\(^{-1}\) |
|----------------|------------------|--------------|--------------|--------------|--------------|--------------|
| 85             | 8.86             | 8.86         | 8.86         | 8.86         | 8.86         |
| 80             | 10.72            | 10.72        | 10.72        | 10.72        | 10.72        |
| 75             | 13.08            | 13.08        | 13.08        | 13.08        | 13.08        |
| 70             | 16.64            | 16.64        | 16.64        | 16.64        | 16.64        |
| 65             | 18.53            | 18.53        | 18.53        | 18.53        | 18.53        |
| 60             | 38.9             | 38.9         | 38.9         | 38.9         | 38.9         |
| 55             | 57.87            | 57.87        | 57.87        | 57.87        | 57.87        |
| 50             | 72.76            | 70.87        | 69.04        | 66.69        | 64.97        |
| 45             | 766.24           | 570.71       | 425.1        | 287.98       | 214.5        |
Table 2. Viscosity data (6.9MPa)

| Temperature, °C | Viscosity, mPa·s |
|----------------|-----------------|
| 85             | 15.74           |
| 80             | 17.63           |
| 75             | 21.37           |
| 70             | 25.98           |
| 65             | 30.90           |
| 60             | 41.78           |
| 55             | 59.67           |
| 50             | 90.34           |
| 45             | 195.35          |

Table 3. Viscosity data (13.79MPa)

| Temperature, °C | Viscosity, mPa·s |
|----------------|-----------------|
| 85             | 17.47           |
| 80             | 19.98           |
| 75             | 24.61           |
| 70             | 29.81           |
| 65             | 35.5            |
| 60             | 50.0            |
| 55             | 66.84           |
| 50             | 102.84          |
| 45             | 319.27          |

Table 4. Viscosity data (22.14 MPa)

| Temperature, °C | Viscosity, mPa·s |
|----------------|-----------------|
| 85             | 18.20           |
| 80             | 22.74           |
| 75             | 25.79           |
| 70             | 34.74           |
| 65             | 42.85           |
| 60             | 58.44           |
| 55             | 76.47           |
| 50             | 171.84          |
| 45             | 551.86          |

3.2. Pour point calculation at high pressure

The waxy crude oil is a complex mixture, and it does not have fixed PP from a serious physical quantity view. In the oil industry, the PP refers to the peak temperature at which the crude oil just dries up, which does not mean that each oil composition turns into solid. The viscosity is taken as a macroscopic parameter to characterize the liquidity of the crude oil. The smaller the viscosity is, the
stronger the liquidity and vice versa. Thus, we can use the viscosity to represent the liquidity of the crude oil. When the viscosity increased to a certain value (\(\mu_{PP}\)), the crude oil loses its liquidity, namely, the \(\mu_{PP}\) is defined as a viscosity under the condition of solidification. If we know the \(\mu_{PP}\), we can calculate the PP under certain pressure based on the viscosity-temperature data. Take calculating the PP at 6.9MPa for an example, we show you how this method works detail in the following section. At first, the \(\mu_{PP}\) should be determined. In Table 1 (0.1 MPa), we can choose the \(\mu_{PP}\) which is 766.24 mPa·s (at 5s\(^{-1}\)) under PP (45 °C). To determine the PP at 6.9MPa, the temperature corresponding to the 766.24 mPa·s (at 5s\(^{-1}\)) should be calculated. In Table 2, there is no viscosity data at 5s\(^{-1}\). Then we should develop the relationship between viscosity and shear rate. For waxy crude oil, the viscosity and shear rate obey the power-law equation as follow.

\[
\mu = K\gamma^{n-1}
\]  

Where \(\mu\) is viscosity; \(\gamma\) is shear rate; \(K\) is consistency coefficient; \(n\) is non-Newtonian index.

The viscosity data at Table 2 (6.9MPa) are calculated by the Equation (1). The fitting equations and viscosity date (at 5s\(^{-1}\)) are shown in Table 5.

| Temperature, °C | Power-law equation | Viscosity(5s\(^{-1}\)), mPa·s |
|-----------------|--------------------|-------------------------------|
| 50              | \(\mu = 170.54\gamma^{0.1078}\) | 143.38                        |
| 45              | \(\mu = 1420\gamma^{0.3227}\)  | 844.75                        |

The viscosity-temperature data (Table 5) are dealt with linear regression to get the temperature corresponding to the 766.24 mPa·s, which is the PP of 6.9 MPa, obtained in Figure 1.

![Figure 1. Calculation pour point of 6.9MPa](image)

As shown in Figure 1, we put 766.24 mPa·s to the linear regression equation to get the PP at 6.9MPa which is 45.56 °C. The above approach is used to calculate the PP under 13.79 and 24.14MPa, all the results are shown in Table 6. As shown in Table 6, different pressures have different pour points. The bigger the pressure is, the higher the PP. The pressures and pour points are analyzed by linear regression statistics which shows the PP increases by about 0.17°C respectively when the pressure increases per 1 MPa, obtained in Figure 2.
Table 6 Fitting equations and results

| Pressure, MPa | Power-law equation | Viscosity \((5s^{-1})\), mPa·s | Linear regression equation | PP, °C |
|---------------|-------------------|-----------------------------|-----------------------------|--------|
| 6.9           | \(\mu=170.54\gamma^{0.1078}\) (50°C) \(\mu=1420\gamma^{0.3227}\) (45°C) | 143.38 (50°C) 844.75 (45°C) | \(\mu=-140.27T+7157.1\) | 45.56 |
| 13.79         | \(\mu=188.63.54\gamma^{0.1024}\) (50°C) \(\mu=1721.7\gamma^{0.2814}\) (45°C) | 159.97 (50°C) 1094.63 (45°C) | \(\mu=-186.93T+9506.6\) | 46.76 |
| 24.14         | \(\mu=712.68\gamma^{0.2423}\) (50°C) \(\mu=2934.9\gamma^{0.2788}\) (45°C) | 482.70 (50°C) 1873.79 (45°C) | \(\mu=-278.22T+14394\) | 48.98 |

Figure 2. Relationship between pressure and PP

4. Conclusions

(1) This novel method presented in this paper has effectively made up for the shortage of the existing standards and methods which can not measure the pour point of waxy crude oil at high pressure. This method only needs conventional instruments. The process is simple and suitable for the rapid calculation of oilfield.

(2) The result shows that the PP increases by about 0.17 °C as each 1MPa increase.

(3) When the pressure is not very high, it will be accepted that the PP at high pressure is replaced by the PP at 0.1MPa. If the pressure is very high, significant errors will occur by which the PP at high pressure is replaced by the PP at 0.1MPa. Take the waxy crude oil in this paper for an example, the PP at 10MPa merely differs by approximately 2°C from PP at 0.1MPa. The PP at 100MPa differs by approximately 17°C from PP at 0.1MPa, and this big difference cannot be ignored.

(4) The problem of the PP for live oil has yet to be satisfactorily solved. The approach is presented in this paper which can solve this problem based on the same idea.

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