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New method for rapid thixotropic measurement of waxy crude

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Abstract: Waxy crude exhihibits a thixotropic behavior at the temperature closing to the gelation threshold. The thixotropic model is considered to be of crucial importance in the calculation of restart pressure for crude oil pipeline in shutdown. The thixotropic curves at several shear rates are necessary for the determination of the model parameters. The traditional measurement of thixotropic curves is complicated and takes much time, especially, it is impossible to be carried out under the condition of pipeline operation. According to the experimental observation and analysis, an empirical and simple method is developed to solve this problem. The test results show that the average relative error of the two methods is less than 25%.

Key words: waxy crude; thixotropy; measurement; empirical method; stepped shear rate

1 Introduction

Reliable thixotropic model is fundamental for the calculation of pipeline restart pressure[1−5]. In order to ascertain the parameters of thixotropic model, several thixotropic curves of different shear rates under the complete structure condition are necessary. The constant shear rate method is traditionally employed, which requires that the oil sample is newly treated corresponding to every thixotropic curve[6−9]. The thixotropy is related with the thermal and shear history. It is difficult to measure the thixotropic behavior for a crude oil pipeline under multiple operation conditions. This makes the thixotropic models cannot be used effectively. The change of shear stress with time and stepped shear rates was analyzed. An empirical method was proposed for the simple and reliable measurement of waxy crude thixotropy. By this method, the thixotropic curves obtained from the experiment of stepped shear rates can be reverted to the ones tested by the constant shear rate method.

2 Experimental

2.1 Apparatus and samples

The thixotropic measurements were conducted by a controlled-stress rheometer RS150H made by HAAKE Corp. in Germany, being equipped with the coaxial cylinder test system Z41Ti. The Daqing waxy crude oil was used as oil samples, supplied by Daxing pump station of Qinjing pipeline on March 11, 2004.

The differential scanning calorimetry (DSC) test for the oil sample showed that the WPT and the wax content were 42 ℃ and 24% respectively. According to the viscosity-temperature data measured by VT550 rheometer, the abnormal point was defined as 36 ℃ with the preheating temperature being 45 ℃.

2.2 Experimental condition

In order to ensure the repeatability and comparability of test data, the oil samples were pretreated to eliminate the memory effect for the thermal and shear history. Firstly, the oil samples in sealed bottle were heated quiescently to 80 ℃ in water bath. After being kept at this temperature for 2 h, the oil samples became homogeneous because of thermal diffusion, and then were statically placed at the room temperature for 48 h[10]. The shear rates used in experiment were selected as 1, 2, 4 and 8 s^{-1}.

3 Measurement of thixotropic curves

3.1 Constant shear rate method (C method)

Constant shear rate method is a traditional test method of thixotropy. After being stationarily held to form a steady structure, the oil sample was sheared by an invariable shear rate. At the initial shear stage, the shear stress sharply declined with increasing shear time. On further shearing, the shear stress gradually tended to a stable value, being called the dynamic equilibrium. The curve of shear stress decline was therefore obtained. Different shear rates have different influences on the extent of structure breakdown. Then a series of thixotropic curves were achieved.

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3.2 Stepped shear rate method (S method)

The oil sample was continuously sheared by several shear rates in sequence of magnitude of shear rate. The time at each shear rate should be long enough to ensure the oil sample to attain the dynamic equilibrium. Then a step-changed curve was obtained. For the oil sample at 33℃, the change of shear rate and stress with time is plotted in Fig.1.

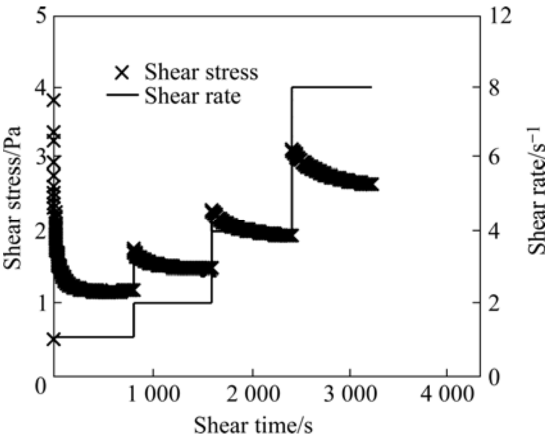

Fig.1 Change of shear stress and shear rate with time

4 Results and discussion

4.1 Experimental phenomenon

The oil samples were cooled from 45 ℃ to the test temperatures. After holding the temperature for 30 min, the thixotropic experiments were conducted by the above two methods. The peak times when the shear stresses reach their maximum values tested by the two methods are close to each other, as listed in Table 1. The dynamic equilibrium stresses tested by the two methods are almost at the same level. Fig.2 shows this tendency of stress change of 32 ℃ at a shear rate of 4 s^{-1}.

4.2 Reverse deduction of thixotropic curve from data tested by S method

After the thixotropic measurement was performed by S method, the test data should be processed. According to the above analysis, some hypotheses were made. First, the yielding time tested by C method is equal to the time when the stress reaches the maximum value by S method. Second, the dynamic equilibrium stress tested by the two methods are at the same level.

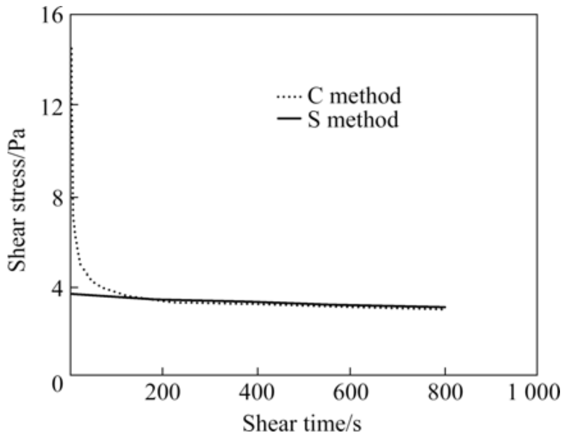

Fig.2 Change of shear stress with time at shear rate of 4 s^{-1}

Based on the above hypotheses, the thixotropic data tested by S method are processed by superposition to obtain the thixotropic curves equivalent to the ones tested by C method. The deduction process can be divided into three steps. First, the shear stress profile over the dynamic equilibrium stress at shear rate of 1 s^{-1} is obtained by the shear stress minus the dynamic equilibrium stress. Second, the yielding time at the other shear rate is considered as the one at which the shear stress reaches its maximum value by S method. After the time correspondence, the above stress profile is superposed on the stress at shear rate except 1 s^{-1} to obtain the thixotropic curve equivalent to the one tested by C method.

4.3 Reliable analysis

The oil sample was cooled from 45 ℃ to different temperatures in the vicinity of pour point. After being statically held for 30 min, the oil samples were sheared at shear rates of 1, 2, 4 and 8 s^{-1} for 800 s respectively by using S and C methods. The change of shear stress with time was recorded during shear action. The thixotropic curves equivalent to the ones measured by C method were deduced reversely by means of superposition. The

Table 1 Comparison between peak times with maximum values of shear stress (unit: s)

Temperature/℃	At shear rate of 2 s^{-1}		At shear rate of 4 s^{-1}		At shear rate of 8 s^{-1}	
	C method	S method	C method	S method	C method	S method
30	8.353	6.329	5.308	5.308	3.407	3.407
31	4.146	2.049	2.049	3.068	1.016	2.049
32	2.375	2.375	2.375	2.375	2.375	3.407
33	1.091	1.091	1.091	0	1.091	1.091

two kinds of curves obtained by different methods are compared with each other and the results show that the curves agree well. The average relative error between the two methods doesn’t exceed 25%. The change of shear stress with time at 29 ℃ tested by the two methods are plotted in Figs.3−5.

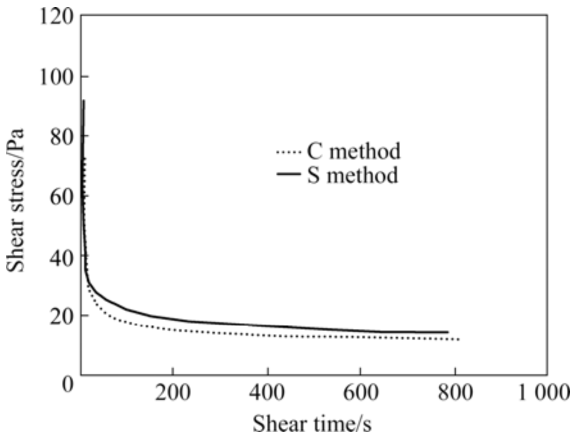

Fig.3 Curves of shear stress vs time at shear rate of 2 s^{-1}

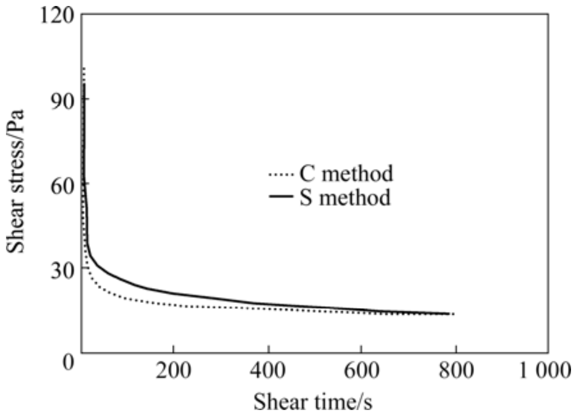

Fig.4 Curves of shear stress vs time at shear rate of 4 s^{-1}

5 Conclusions

1) An empirical method for the measurement of thixotropic curves is developed. It is applicable for the oil samples near the gel point. It facilitates the measurement of thixotropic curves.

2) For Daqing waxy crude, the test results indicate that the average relative error of the two method doesn’t exceed 25%.

3) It should be mentioned that this empirical method need to be validated by theoretical analyses and more actual measurements.

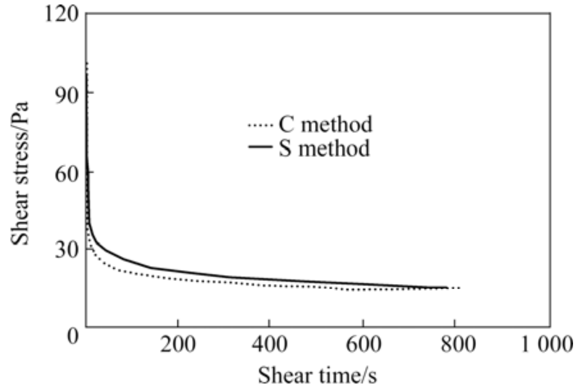

Fig.5 Curves of shear stress vs time at shear rate of 8 s^{-1}

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