Wax Inhibitor Screening by Differential Scanning Calorimeter for High Wax Content Crude Oil

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Abstract. In order to investigate the wax inhibition performance of various inhibitors different scanning calorimetric (DSC), a powerful and quickly technique having no request of sample pretreatment, has been used for investigation the thermal characteristics of the wax remover. According to the parameters such as wax appearance temperature (WAT), content of wax and rheology, it is found that the best wax removing rate can be reached to 457mg/L•h under 40℃ with 150mg/L surfactant combination (fatty alcohol polyoxyethylene ether + calcium petroleum sulfonate + mixed alcohol).

Keywords: waxy crude; DSC; wax remover, wax appearance temperature, surfactant.

1. Introduction
The research of crude oil paraffin remover has a history of more than 70 years. Screening the basic formula of paraffin remover still needs a lot of repetition and tedious work. The experimental work, but often cannot select a performance of the best paraffin remover suitable for certain crude oil. Most researchers have not fully investigated the matching relationship between hydrocarbon carbon chain distribution and paraffin removal agents in crude oil, and the basic physical properties of crude oil are the most important factors in screening the basic formula of paraffin removal agents for crude oil [1]. The methods for determining the basic physical properties of crude oil mainly include chemical method for measuring wax content of crude oil, rotary privatimeter method for measuring the viscosity-temperature curve of crude oil, differential scanning calorimetry (DSC) method for measuring the thermal characteristics of wax evolution of crude oil, etc. [2]. Among them, the chemical method uses toxic reagents such as phenylacetone in the process of testing, and the analysis speed is slow. The crude oil sample of the rotating viscometer method consumes a large number of samples. At the same time, with the change of crude oil temperature, the change of its viscosity takes a certain time, so the measured viscosity-temperature curve has a certain lag. In addition, the instrument used in the analysis is also cleaned with much trouble. DSC method is a method to measure the thermal characteristic parameters
of wax precipitation in crude oil by changing the enthalpy of wax precipitation with the precipitation of wax crystals during the cooling process of crude oil samples. This method can not only test crude oil samples quickly and accurately, but also measure many parameters, such as wax precipitation point, wax precipitation amount, wax precipitation hot melting at different temperatures and specific heat of crude oil, without using toxic reagents [3]. It has a large amount of information and a relatively small amount of work. It can preliminarily analyze the distribution and branching of hydrocarbon carbon chain length in crude oil. The results provide a reference for the rapid screening of the basic formula of crude oil paraffin remover and inhibitor [4]. In this study, the parametric changes of wax precipitation of 8 crude oil samples before and after adding additives were compared and analyzed by DSC method, and the application of DSC in optimizing the selection of basic formula of crude oil paraffin remover was studied.

2. Experimental
In this investigation, all of the crude oil samples are collected from oilfield in northwest China without any pretreatment. All the DSC experiments were performed on a Mettler-Toledo DSC 822e equipped with an intercooler and sample robot. Each oil sample was heated in a sealed container prior to sampling and the purge gas for all experiments was nitrogen at a flow rate of 70 ml/min from 80℃ to -30℃ with heating rate of 20℃/min and cooling rate of 8℃/min. The wax content of oil sample was calculated by the proportion of wax precipitation heat at dt and the average crystallization heat of crude oil.

Wax removing test was carried out as follow: about 0.4ml crude oil was put in a cylindrical mold, and the weight of formed wax mass was assigned to \( m_1 \). Then the wax mass and 15mL wax remover was placed in a glass bottle at 40℃. After 2h, the remaining wax mass was weighted and its weight was assigned to \( m_2 \). The wax removing rate \( f \) was calculated as the following:

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f = \frac{m_2 - m_1}{m_1} \times 100\%
\]

3. Results and discussion

3.1. Determination of wax precipitation
Commonly, the average crystallization heat is an essential parameter to determine the wax precipitation by thermal method. As suggested before, the carbon number and branch degree have close relationship with the average crystallization heat of wax in crude oil [7]. Previous studies reported that the average crystallization heat of crude oil is distributed in the range from 200 to 230J/g [5], while others suggested that the average crystallization heat of wax sample with wax precipitation point of -20℃can be treated as standard average exothermal value [6]. In this study, the effect of average crystallization heat on the wax precipitation quality was investigated over eight crude oil samples using different calculation method. For comparison, standard alumina method was included in Table 1. From the results, it can be found that the wax precipitation of waxy crude oil calculated by reported average crystallization heat has some deviation from the result of standard alumina method. For the wax sample with same structure the crystallization temperature is increase with the carbon number contributed to the easy formation of net space. Conversely, decrease of average crystallization heat can be found if more branch chain hydrocarbons were contained. Considering both of the carbon number and branch degree in our test samples, the 210J/g was selected as average crystallization heat in our follow experiment.
Table 1. Effect of average crystallization heat on the wax precipitation

| Average crystallization heat (J/g) | Wax precipitation wt% |
|-----------------------------------|-----------------------|
|                                   | 1        | 2       | 3       | 4       | 5       | 6       | 7       | 8       |
| 200\(^a\)                         | 8.79     | 10.41   | 7.97    | 10.23   | 9.98    | 12.91   | 5.84    | 6.14    |
| 230\(^a\)                         | 7.64     | 9.05    | 6.93    | 8.89    | 8.68    | 11.22   | 5.08    | 5.33    |
| 225\(^b\)                         | 7.81     | 9.25    | 7.08    | 9.09    | 8.87    | 11.47   | 5.19    | 5.46    |
| 210\(^b\)                         | 8.43     | 9.98    | 7.65    | 9.81    | 9.57    | 12.38   | 5.60    | 5.88    |
| Alumina method/wt%                | 8.59     | 9.69    | 8.01    | 9.43    | 9.40    | 12.20   | 5.68    | 6.17    |

\(^a\): The average heat of crystallization of crude oil is 200–230J/g [5].
\(^b\): As the standard of pure wax, the average heat of crystallization of crude oil was equal to the wax crystallization enthalpy integration from wax precipitation point of crude oil to -20℃ [6].

3.2. Influence of wax remover in wax crude DSC behavior

As suggested before the crystallization of wax in crude oil happens with hydrocarbon atom ranged from 21 to 36, and the process is divided into two steps: the first exothermic change is contributed to the phase transformation from liquid to crystallization and the next exothermic signal is the released thermal during the transversion from \(\alpha\) phase to \(\beta\) phase, a more stable phase, during the cooling process. The temperature range between two exothermic steps will be narrow if the carbon number in wax hydrocarbon increase [8]. The DSC experiments were carried out on waxy crudes (4\# and 7\#) before and after adding wax remover and the corresponding DSC curves were showed in Fig 1.

\(a\): 4\# crude oil; \(b\): 7\# crude oil; \(c\): 4\# crude oil + wax remover; \(d\): 7\# crude oil + wax remover

Figure 1. DSC curves of 4\# and 7\# before and after adding paraffin remover

For 4\# crude oil, there are two relative sharp thermal events at 38.89℃ and 36.56℃, which indicated that the content of low carbon number wax hydrocarbons is relatively high. Furthermore, the exothermic signal of wax precipitation appeared at low temperature compared with normal wax hydrocarbons. Thus, the carbon number of alkanes in 4\# crude oil may be ranged from 16 to 25. The exothermal signal corresponding to crystallization of liquid wax dispersed and the thermal signal in phase transform is
relatively weak compared with 4# crude oil after adding wax remover, which indicates the wax crystallization is inhibited effectively.

From the results, it can be found that the thermal properties of 7# crude oil including WAT, temperature of wax precipitation apex and wax precipitation enthalpy have been changed to a low value as wax remover was added, which proves great potential to prevent the wax precipitation. The WAT of 7# crude oil decreased from 22.72°C to 21.92°C, and the first exothermic peak assigned to the phase transformation disappeared after adding wax remover, which gives a good agreement with the high wax removal rate of this wax remover.

In the following work, the DSC curves of waxy crude sample 1# crude oil to 8# crude oil have been investigated, which showed that the waxy crude oils concentrated mainly normal wax hydrocarbons. The wax hydrocarbon in 5# crude oil and 6# crude oil are mainly between C_{20} and C_{30} with high branch degree, while 7# crude oil and 8# crude oil, the wax hydrocarbons focus in C_{25}.

3.3. Optimization of wax remover
According to composition and properties of waxy crudes tested by thermal analyze, surfactant was chosen as wax remover for its high wax hydrocarbon number from C_{20} to C_{35}, and more branched-chain hydrocarbons [10]. For comparison, the wax remover rate of deferent common oil-based wax remover such as sulfonate, fatty alcohol polyoxyethylene ether (JFC), SP169, SP80, mahogany sulfonate calcium and mixed alcohol etc., were tested separately on 7# crude oil.

From the tested results (Table 2), it can be seen that JFC, SP169, calcium petroleum sulfonate and mixed alcohol display better wax removal performance than other tested agents. Due to the wax characteristics of waxy crudes are complex for the high wax content and large carbon number distribution sample, high wax removal efficiency would be obtained as the combined wax remover is used [10, 11].

| No. | Agent                          | Dosage /% | m_1 /g | m_2 /g | Wax removal rate /%h^{-1} |
|-----|--------------------------------|-----------|--------|--------|--------------------------|
| 1   | Sodium petroleum sulfonate     | 0.2       | 0.28652| 0.07059| 38.02                    |
| 2   | JFC                            | 0.2       | 0.25185| 0.05070| 39.97                    |
| 3   | SP169                          | 0.2       | 0.22825| 0.03224| 43.40                    |
| 4   | SP 80                          | 0.2       | 0.29455| 0.07130| 37.91                    |
| 5   | Calcium petroleum sulfonate    | 0.2       | 0.23547| 0.04440| 40.76                    |
| 6   | Mixed alcohol                  | 0.2       | 0.22186| 0.02109| 43.54                    |

M_1, M_2: the quality of wax before and after treatment

Different wax removers were combined with proportion of 1: 1 or 1: 1: 1 and the wax precipitation inhibition was analyzed by DSC, then their wax removing rate at 40°C were tested. Table 3 illustrated the results of wax removal rate of combined wax remover. The results shown that with the dosage of 150mg/L, No.9 wax remover displays the most efficient ability with the removing rate is 457 mg / L·h^{-1}, which is coincide with the result measured by DSC. And in fact, the efficiency is much higher than that of the commercial one using locally, the compositional wax remover can be used in oilfield to remove the wax deposition effectively.
Table 3. Wax removal rate of combined wax remover

| No. | Wax remover                                      | Dosage / % | Wax \(m_1\)/g | Wax \(m_2\)/g | Wax removing rate%/h⁻¹ |
|-----|--------------------------------------------------|------------|----------------|----------------|------------------------|
| 1   | JFC+SP169                                        | 0.21       | 0.20777        | 0.07315        | 32.70                  |
| 2   | JFC+ Calcium petroleum sulfonate                 | 0.27       | 0.24184        | 0.03983        | 31.75                  |
| 3   | JFC+ Mixed alcohol                               | 0.48       | 0.23887        | 0.08581        | 32.40                  |
| 4   | SP169+ Calcium petroleum sulfonate               | 0.22       | 0.22342        | 0.03509        | 42.15                  |
| 5   | SP169+ Mixed alcohol                             | 0.25       | 0.25100        | 0.11141        | 28.45                  |
| 6   | Calcium petroleum sulfonate + Mixed alcohol      | 0.31       | 0.31275        | 0.10707        | 32.88                  |
| 7   | JFC+SP169+ Calcium Petroleum Sulfonate           | 0.24       | 0.22512        | 0.06374        | 42.48                  |
| 8   | JFC+SP169+ Mixed alcohol                         | 0.23       | 0.22507        | 0.06374        | 35.56                  |
| 9   | JFC+ Calcium petroleum sulfonate + Mixed alcohol | 0.22       | 0.22068        | 0.02855        | 45.56                  |
| 10  | SP169+ Calcium petroleum sulfonate + Mixed alcohol | 0.33     | 0.32851        | 0.06589        | 40.47                  |
| 11  | JFC+SP169+ Calcium petroleum sulfonate + Mixed alcohol | 0.23 | 0.23071        | 0.07431        | 33.88                  |

\*\(m_1\), \(m_2\): the calculated quality of wax before and after treatment of wax remover by DSC.

4. Conclusion

The wax precipitates before and after adding wax remover measured by DSC provide exact reference for the selecting of wax remover composition. According to the thermal property of 7# crude oil, several surfactants were screened and combined as oil-based wax remover. With 150mg/L surfactants combination (JFC + calcium petroleum sulfonate + mixed alcohol), the wax removing rate is 457mg/L·h⁻¹ (40°C).

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