Study on the Effect of Crude Oil Composition on Waxing Characteristics of Waxy Crude Oil

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Abstract. The waxing deposition characteristics of crude oil is of great significance to the exploitation and transportation of high waxy crude oil. Therefore, three series of simulated crude oils were prepared on the basis of composition analysis and composition remixing of crude oil. The carbon distribution of oil samples and their corresponding wax components were analyzed by high temperature gas chromatography. The variation of waxing point, peak temperature and average exothermic enthalpy of these simulated crude oils were measured by Differential Scanning Calorimetry (DSC). The results showed that the increase of resin and asphaltene content had little effect on the waxing apprearance temperature (WAT) and Wax precipitation peak temperature (WAPT). The increase of aromatics content significantly decreased them, while some asphaltene may precipitate. The increase of wax content will greatly increase these two temperature, which is detrimental to the wax removal by heating method.

1. Introduction

The wax deposition makes the pipeline transportation capacity to decline, or even block the formation during lifting, gathering and long-distance transportation of crude oil, therefore the following wax removal and control operations are very indispensable, hence, the accurate prediction of the waxing characteristics are of great significance for grasping the timing of wax removal and control [1]. It is very difficult to predict the waxing characteristics accurately due to the complexity of crude oil composition. Yu [2] et al. applied the wax deposition dynamic model to consider the influence of resin and asphaltene on the deposition mechanism of paraffin in crude oil. Li [3] et al. applied the rotary dynamic waxing device to explore the influence of different crude oil composition on the wax deposition of crude oil pipelines. Riazi [4] et al. divided crude oil into normal paraffins (P), isomeric and naphthenic (N) and aromatic hydrocarbons (A), and established a series of thermodynamic relationships for PNA components in crude oil.Based on this model Zuo [5] et al. introduced Poynting vector to enlarge pressure range of the model.Leonataritis [6] proposed a state equation model that took into account the effects of resin (R) and asphaltene (B) components. Wang [7] investigated the wax deposition process of the high-condensate crude oil in the pipeline transportation process, and investigated the deposition law of the wax affected by the temperature, hence it can seen that aromatic hydrocarbons, resin and asphaltene all play an important role on the prediction of wax deposition. In this paper, wax, aromatic hydrocarbon, resin and asphaltene were prepared by different methods. The differential scanning calorimetry (DSC) method was used to analyze the waxing point of crude oil of a certain area in north china Oilfield in order to study the effect of crude oil composition on the waxing point of crude oil [8].

2. Experimental Materials and Methods

2.1. Experimental Materials

Dehydrated crude oil, North china Oilfield; Xylene, Analytical pure, Tianjin Jin Dong Tianzheng Fine Chemical Reagent Factory; 58# crude wax, north china Oilfield; acetone, analytical pure, Tianjin East Tian Zheng Fine Chemical Reagent Factory; methanol, analytical purity, Tianjin Feng Chuan Chemical Reagent Technology Company.

2.2. Four-component separation of crude oil

The separation of four components was separated by using liquid-solid adsorption chromatography in the instrument Analysis Center of China University of Petroleum (Beijing) to separate crude oil.

2.3. High-temperature gas chromatography of crude oil

Some crude oil was fully cooled in a beaker at 0°C, and a wax sample taken from the wall surface. High temperature gas chromatography with agilent simulated distillation (SimDis) and 6890N chromatograph was then used to detect wax components at 430°C with helium shielding gas.

2.4. Preparation of simulated oil

(1) Simulated crude oil with different wax content. According to the results of the four-component analysis of crude oil, a certain amount of 58# crude paraffin was added into five parts of crude oil to get simulated oil with wax content of 19.78%, 25%, 30%, 35% and 40% respectively. Then they were heated in a water bath at 70°C and stirred to make it dissolve uniformly.

(2) Simulated crude oil with different aromatics. Xylene was added in the crude oil to get simulated oil with aromatics content 17.42%, 25%, 30%, 35% and 40% respectively. Then, the simulated crude oil was dissolved in a water bath at 40°C.

(3) Simulated crude oil with different resin and asphaltene. Resin and asphaltene were extracted from crude oil according to literature (Rex 1990) [9] and dried in a vacuum oven. Then, added into crude oil to get simulated oil with content 24.18%, 25%, 30%, 35%, 40% and 45% respectively. The mixture was heated to 60°C and emulsified by a homogenizer at 5000 r/min for 5 min.

2.5. WAT

WAT was detected by DQ20 Differential Scanning Calorimeter of TA Company. The sample was cooled from 80°C to -20°C at a cooling rate, 1°C/min, in argon atmosphere.

3. Results and discussion

3.1. Quadratic Analysis of crude Oil

The four-component analysis of crude oil was shown in Table 1. The crude-oil yield was 85.45%. The total content of resin and asphaltene is 24.18% and they were used as a single component of crude oil in the following experiments.

Table 1. Contents of four components of crude oil.

Component name	Saturated hydrocarbon /%	Aromatic hydrocarbons /%	Resin%	Asphaltene /%
Crude oil	58.40	17.42	22.87	1.31

3.2. The result of high temperature gas chromatography

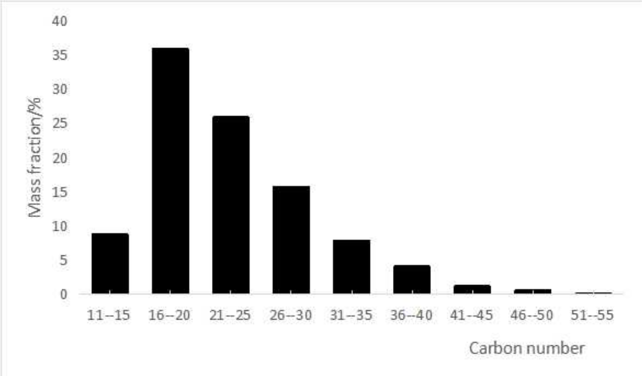

Figure 1. Relationship between carbon number and mass fraction of wax precipitated in crude oil.

The crude oil components analyzed by high temperature gas chromatography were shown in Figure 1. From Figure 1, it can be seen that the main component of wax precipitation is the hydrocarbon of C_{16}~C_{25}, about 60% of the total wax content. The content of C_{26}~C_{40} is about 30%, and hydrocarbons with higher carbon number than 40 only account for 2% of the total wax content. The composition of C_{11}~C_{15} is 8%, and the alkanes or cycloalkanes in this carbon number range are mostly liquid in the standard state, and they may be adsorbed in the network of precipitated wax [10].

3.3. Effect of resin and asphaltene on WAT

The effect of resin and asphaltene on wax evolution of crude oil is shown in Figure 2.

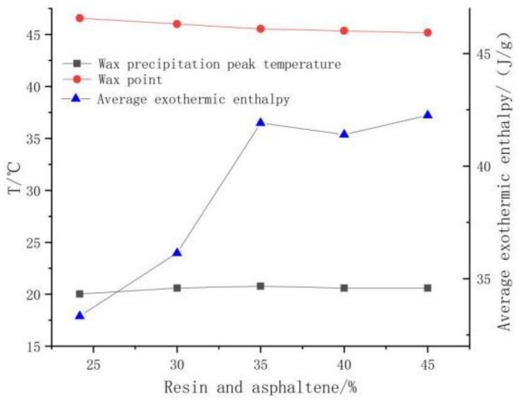

Figure 2. Effect of resin and asphaltene contents on WAT.

Figure 2 shows that with the increase of resin and asphaltene content, WAT decreases slowly from 46.6℃to 45.5℃, WAPT increases from 20.1℃ to 20.6℃, and the average exothermic enthalpy increase to a certain extent. Resin and asphaltene are fused aromatic hydrocarbon compounds, usually dispersed in crude oil in colloidal state. They are apt to adsorb high carbon alkanes, which make the WAT decrease slowly, but this decrease is limited. WAPT also changed within 1℃ in this experiment, which indicates that the increase of resin and asphaltene had little effect on the crystallization of C_{16}~C_{25}. The average exothermic enthalpy increases rapidly at first and then changes little when the content of resin and asphaltene is 35%, which indicates that the adsorption of resin and asphaltene on the waxy crystal surface gradually reaches saturation. Obviously, when resin and asphaltene account for more than 25% in crude oil, they have little effect on the WAT and WAPT. Therefore, the effect of resin and asphaltene on prediction of WAT need not be considered in the thermodynamic method, but also they may affect the wax deposition amount to some extent.

3.4. Effect of aromatic hydrocarbons on WAT

The effect of aromatics content on WAT is shown in Figure 3.

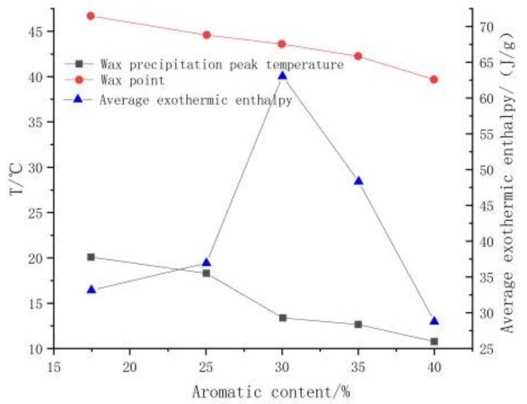

Figure 3. Effect of aromatic hydrocarbons on WAT.

From Figure 3, with the increase of aromatics content, WAT decreases from 46.6℃ to 39.6 ℃, WAPT decreases from 20.1℃ to 10.8℃ and the average exothermic enthalpy increases first and then decreases. The increase of aromatics effectively improves the solubility of high carbon alkanes and makes it difficult to precipitate. The high temperature liquid chromatography is not sensitive to the detection of aromatic hydrocarbonse when the thermodynamic method only considering paraffin and cycloalkane will get a greater WAT than its true value [11]. The increase of aromatics also effectively prevented the precipitation of C_{16}~C_{25} in crude oil. Aromatics can increase resin solubility in crude oil and thus decreases resin adsorption on asphaltene surface. This phenomenon promotes asphaltene to precipitate easily with the wax crystal until it was completely precipated at 35%. Therefore, appropriate measures should be taken to avoid co-crystallization of asphaltene and wax when using aromatics as the wax remover.

3.5. Effect of wax content on WAT

The effects of different wax content on WAT is shown in Figure 4.

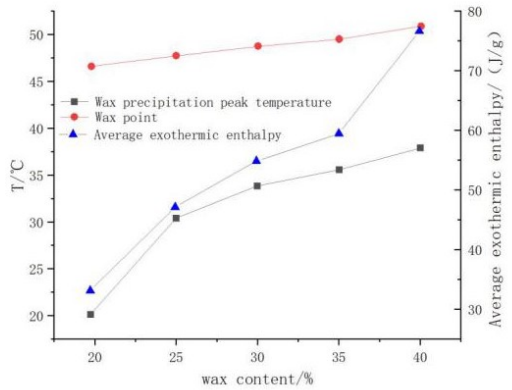

Figure 4. Effect of wax content on WAT.

From Figure 4, with the wax content increasing, WAT increased from 46.5℃ to 50.7℃, while WAPT increased from 20.1℃ to 37.7℃. The main components of 58# crude wax are alkanes with carbon numbers greater than 25. After it was adding into crude oil, the alkane of higher carbon number in crude oil increased, so these two temperatures increased significantly and the exothermic enthalpy rise greatly. The average exothermic enthalpy of wax can be estimated to be 216.5 J/g, which is close to 210 J/g of pure wax in literature [12]. For the development of waxy crude oil, after oil wells have been invaded by cold fluids in the operations, the wax with high carbon number crystallizes near the well and blocks the oil passage. When the wax blockage is removed by hot washing, the crude oil from the far end of the well dissolves the wax crystalline. Both WAT and WAPT will rise greatly, so it is necessary to raise the bottom hole temperature and prolong the washing time.

4. Conclusion

Here, based on well-designed preparation of simulated oil, the effects of components in crude oil on WAT and WAPT are analyzed by using DSC, and the following conclusions are obtained:

(1) Resin and asphaltene with weight content more than 25% in crude oil has little effect on WAT and WAPT;

(2) With the increase of aromatics, WAT and WAPT decreased significantly, but the asphaltene may be precipitated, which is detrimental to wax removal using by aromatics;

(3) With wax content increasing, WAT and WAPT increased significantly, which indicates that the operation temperature or time of heat washing of heat washing should be properly raised or prolonged.

Acknowledgments

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