Characteristics of a crude oil and the interaction between the compositions

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Abstract. In this paper, the characteristics of a crude oil from DY reservoir of JD Oilfield and the interaction between the compositions were researched. The components were separated using silica gel column chromatography, and the characteristics of each component and their influence on wax crystallization were studied. It was found that the separated fractions have an inhibitory effect on the wax crystallization of the crude oil, and the effect of the inhibition is remarkable. Therefore, it can be concluded that the components can affect on the waxing process by changing the amount of wax precipitation or the morphology of the wax.

Keywords: Crude oil; Component; Saturated hydrocarbon; Waxing inhibition.

1. Introduction
In the study of the composition of crude oil, the viewpoint that saturated hydrocarbons, aromatic hydrocarbons, resins and asphaltenes are the main components of crude oil has been shared by the petroleum industry and researchers. In addition, waxes are an organic mixture, which are usually classified as the saturated hydrocarbon component for including paraffin hydrocarbons with a small amount of naphthenic and aromatic hydrocarbons [1]. The components could affect rheological properties of crude oil at different temperature ranges. For instance, waxes in crude oil will precipitate as crystals at lower temperature, while other liquid hydrocarbons will be wrapped by a network structure formed by wax crystals, resulting in deterioration of the fluidity of crude oil [2]. Besides, the strong hydrogen bonds formed by the resin and asphaltene molecules cause the heteroaromatic fused ring overlap into aggregates, which further aggravates the high viscosity of crude oil [3]. Noticeably, resins and asphaltenes are the larger and more polar components, which exist as aggregates by the strong hydrogen bonding and π-bonding[4, 5]. Moreover, resins and asphaltenes also can be adsorbed on the wax crystals to decrease the surface energy of wax crystals, hindering the aggregation of wax crystals [6].
The study of the relationship between the components is conducive to controlling the fluidity of crude oil and improving the efficiency of crude oil extraction and transportation. Though the interactions between components of crude oil are relative complex, it is particularly significant to regulate them reasonably. In this paper, column chromatography was used to separate several components in crude oil, and the main structures of samples were characterized by UV and IR spectrophotometry. Furthermore, the process of wax precipitation and the effect of components on wax morphology were analyzed by differential scanning calorimetry and polarized light microscopy.

2. Materials and methods

2.1. Basic parameter of the crude oil
The crude oil used in the experiment was from DY reservoir of JD Oilfield. The main physical properties of the crude oil are shown in Table 1, which of the determination method referred to national and other petroleum industry standards, the crude oil fractions were determined by silica gel column chromatography, and the content of asphaltenes was determined by the n-heptane method [7, 8].

| μ30 / (mPa·s) | Pour point t/℃ | ρ20 / (g·cm⁻³) | Resins W/% | Asphaltenes W/% | Aromatic hydrocarbons W/% | Saturated hydrocarbons W/% |
|----------------|----------------|-----------------|------------|----------------|--------------------------|--------------------------|
| 3600           | 18.5           | 0.886           | 22.1       | 6.8            | 35.2                     | 35.9                     |

2.2. Experimental

2.2.1. Thermogravimetric analysis conditions. The TGA/SDTA851 instrument was used to determine the weight loss rate of the sample over the temperature range of 35–550 ℃, nitrogen flow rate of 20 mL/min. After the baseline was stabilized, 3–8 mg of the sample was put into the SiO2 sample cell. The program automatically heated up from 35 ℃ to 550 ℃, and the heating rate was 10 ℃/min.

2.2.2. Separation of oil sample. The chromatography column was used to separate the components of crude oil. The oil sample was dissolved in chloroform, fully adsorbed on the 100 to 150 mesh silica gel and dried at room temperature. The prepared sample was loaded into the middle layer of the chromatography column filled with uniform and dense silica gel. Then a certain amount of silica gel was added over the layer of sample, and a piece of cotton wool was filled at the top of the chromatography column. Subsequently, the oil sample was successively eluted with different solvents. After the solvents in eluates were evaporated, the corresponding fractions were obtained. The name of each component and its content are shown in Table 2.

2.2.3. IR analysis. For sediments deposited on silica gel which are difficult to elute, a small amount of vacuum dried deposits were taken and analyzed by using Fourier transform infrared spectroscopy. Fourier transform infrared spectra were recorded using the Bruker Tensor 37 spectrometer with a 4 cm⁻¹ resolution. The sample was evenly applied to the internal mirror and compressed into transparent sheets. Then it was placed on the sample rack for full-wavelength scanning (400–4,000 cm⁻¹).

2.2.4. UV analysis. The UV spectrums were recorded using UV-2600 spectrophotometer in the range 200–400 nm. The separated constituents were solve in chloroform respectively at a concentration of 10 mg/L, and the chloroform solvent as reference solution.
2.2.5. *Optical microscopy analysis.* The saturated hydrocarbon component was separated from the oil sample using the chromatography column method for the optical study. Wax crystal morphologies were observed using a BX41-P OLYMPUS polarizing microscope. Samples were initially heated to 50 °C and then cooled to 10 °C for 5 min.

| Eluant                          | Labels | w/% |
|---------------------------------|--------|-----|
| Petroleum ether                 | Y1     | 31.20 |
|                                 | Y2     | 6.60  |
|                                 | Y3     | 4.55  |
|                                 | Y4     | 7.65  |
| Petroleum ether: Ethyl acetate (30:1) | Y5     | 13.62 |
|                                 | Y6     | 7.21  |
| Petroleum ether: Ethyl acetate (10:1) | Y7     | 5.33  |
| Petroleum ether: Ethyl acetate (3:1) | Y8     | 2.26  |
|                                 | Y9     | 1.38  |
|                                 | Y10    | 3.20  |
| Petroleum ether: Ethyl acetate (1:1) | Y11    | 3.25  |
|                                 | Y12    | 1.90  |
| Methanol: Trichloromethane (30:1) | Y13    | 2.80  |
| Methanol: Trichloromethane (10:1) | Y14    | 2.88  |
| Methanol                        | Y15    | 2.30  |

3. Results and discussion

3.1. *Thermogravimetric analysis*

The thermogravimetric analysis was carried out to measure the content of the crude oil. The results were shown in the Figure 1. The oil sample is continuously evaporated at the whole temperature range, it almost becomes a horizontal line from 450 °C to 500 °C. When the temperature increases from 50 °C to 350 °C, the weight loss rate reaches 79.30%, indicating that the light content of the crude oil is more. While at the range from 350 °C to 450 °C, the rate is only 15.62 %, which manifested that the sample in the carbon number range of 25 to 35 in the range of compounds less. At 450 °C, the loss rate reached 94.92%, which manifested that the volatile compounds in the sample with a carbon number greater than 35 are very low [9].
3.2. IR analysis

Resins and asphaltenes are strong polar compounds that are easily adsorbed on the column chromatography silica gel and difficult to elute, which were characterized by infrared spectroscopy (IR). As it can be seen in Figure 2, the relative strong and wide absorption peak at 3600~3400 cm\(^{-1}\) is observed, which may correspond to the absorption of amino or associative hydroxyl stretching vibration. And the two peaks at 2600 and 2550 cm\(^{-1}\) could be ascribed to the stretching vibration absorption peaks of the mercapto groups. While the absorption peaks at 1630 cm\(^{-1}\) was detected, which could be ascribed to the delocalized \(\pi\) bond of the aromatic ring. In addition, it may be the stretching vibration absorption peak of the C=O bond in the heterocyclic ring and amide or bending vibration absorption peak of N-N bond in nitrogen heterocyclic structure [10]. As discussed above, it can be inferred that the sediment contains N, O, S and other heteroatoms, which belongs to the strong polar compounds. Furthermore, the sediment adsorbed on the chromatography column might be strong polar components such as resins or asphaltenes [11].
3.3. UV analysis
UV spectroscopy is a powerful tool for the study of polycyclic aromatic hydrocarbons in crude oil. According to the theory of electric spectrum, with the increase of the number of rings in the aromatic condensation structure, the maximum absorption wavelength ($\lambda_{\text{max}}$) moves to the long wave. The oil samples were analyzed by UV spectroscopy. The UV spectrum of the separated constituents is shown in Fig 3. The number of aromatic rings in the resins and asphaltenes is mostly 3 to 4 rings [12]. Asphaltenes and resins have the maximum absorption near 270nm. With the increase of wavelength, the UV absorption intensity gradually decreases. As can be seen from Fig. 3, the absorption peaks appear in the range of 220 nm to 230 nm, and the absorption peak wavelength becomes larger as the polarity of the component increases, which is the absorption peak of a typical nonconjugated saturated compound. Moreover, Y5, Y6 and Y7 have absorption peaks not only at about 225 nm, but also at about 270 nm. Similar peak and similar resins’ and asphaltenes’ aromatic chromophores manifest that these three fractions contain both resins and asphaltenes. The intensity order and the wavelength of the absorption peak are Y5 < Y6 < Y7 at 270nm from Fig. 3, which indicates that the number of aromatic rings in these three fractions increases in turn [13].

![Figure 3. The UV spectrum of the separated constituents](image)

3.4. Effect of components on wax morphology
In the crude oil precipitation of small particles play the role of seed, so that wax crystals quickly grow up, and gather each other in crude oil. The aggregates formed by the accumulation of wax crystals increase the viscosity of crude oil and have a great influence on the flow of crude oil [14,15]. When the crude oil mobile phase is completely surrounded by the formation of waxy network structure, the crude oil can not continue to flow. And wax crystals are generally adsorbed on the surface of the oil, which increases the volume of dispersed particles. In Fig. 3 b, c and d are the waxy crystal forms of Y5, Y6 and Y8 added to Y1, respectively.
It can be seen from Figure 4 a that the precipitated wax crystals are flaky and needle-like, and the volume of the wax crystals is larger, irregular arrangement, low dispersion, and the wax crystals are clustered to form a network structure for only the fraction of Y1. Figure 4 b, c, d relative to a, the size of wax crystals was significantly reduced, the particles increased, the shape close to the spherical, which makes the wax crystals more dispersed and the growth of wax crystals inhibited. At present, there are two main explanations for suppressing the growth of precipitated wax in crude oil: (1) Since the other fractions inhibit the normal aggregation of wax crystals, that is, when the micro-nuclei are produced in the oil, other fractions adsorbed on the nucleus, occupy the highest surface of the location, and reduce the surface energy of the crystal, so that the crystal nucleus and the crystal ions are separated, thus preventing the growth of grain; (2) Since it is not possible to arrange in accordance with the normal lattice, it is difficult to form a dense network structure [16-18].

4. Conclusion
The number of rings in the aromatic condensation structure is gradually increased with the polarity of the crude oil component gradually strengthens. The addition of Y5, Y6 and Y7 components can increase the number of wax crystals when the saturated hydrocarbon components are crystallized, the size decreases, the dispersion increases, and the shape changes from needle to sheet. And the three components contain a small amount of resin, asphaltene. The addition of Y5, Y6, and Y7 components can increase the number of wax crystals when the saturated hydrocarbon component crystallizes, but reduces the size of the crystal, increases the dispersion of the crystal, and makes the shape of the crystal from the needle and the sheet into a similar spherical shape.

Acknowledgments
The work was supported financially by National Science Foundation of China (50874092) and The Youth Innovation Team of Shaanxi Universities. And we thank the work of Modern Analysis and Testing Center of Xi’an Shiyou University.
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