Characterization of compositions in crude oil and the effect of inhibitor on the crystallization of paraffin

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Abstract. Flowability is one of the important characters of a crude oil in pipelines. The viscosity of one crude oil is affected by many factors (e.g., temperature, water cut, composition distribution, paraffin deposition, etc.). In this study, IR, thermogravimetry analysis (TGA) and UV measurement are employed to characterize the composition of the crude oil (HN-1) provided by Henan Oilfield. The paraffin morphology analysis is employed to rate the property of a mixture of paraffin inhibitors and analysis the mechanism of the paraffin inhibition.

1. Introduction
Paraffin in crude oil is the mixtures of hydrocarbon molecules with hydrocarbon numbers ranging from 20 to 40. The paraffin crystals formation starts as the temperature decreases lower than the pour point of the crude oil [1]. The formation and aggregate of the paraffin crystal will lead to the formation of the three-dimensional crystal network. The network of the paraffin crystal can block the flow the production liquids in the pipelines. The crystallization and the growth of the paraffin crystal can be affected by many factors such as the composition of the crude oil, temperature and chemicals applied during the hydrocarbon extraction. Therefore, it is very important to analysis the composition of the crude oil to rate the risk of pipeline blockage caused by paraffin formation and deposition.

Several options can be applied to mitigate the paraffin risk in the pipelines such as stream heating, blending with lighter hydrocarbons, mechanical scraping and the addition of chemicals in the crude oil [2-4]. Addition of chemicals (paraffin inhibitors) is considered to be a promising method to reduce the paraffin deposition risk because of its simplicity and cost-effective. Paraffin inhibitors can alter the morphology of the paraffin crystals and retard the growth of the crystals [5]. The paraffin inhibitor molecules contain the hydrocarbon chains that can co-crystallize with paraffin and the polar groups can disturb the degree of co-crystallization and prevent the formation of large paraffin crystals [6]. Besides, the resins and asphaltenes are natural surfactants that can be adsorbed on the surface of paraffin crystals to disturb the growth of wax crystals.

In this paper, the column chromatography separation method is applied to separate and evaluate the SARA fractions of the crude oil sample. The FTIR, TGA and UV measurements are employed to
characterize the composition the HN-1 crude oil sample. The performance of a 1:4 mixture of Hexane trimethylammonium chloride and methanol, which is used as the paraffin inhibitors, is investigated by analyzing the morphology of the paraffin crystals in the presence of the inhibitors in the crude oil.

2. Experimental

2.1. Materials
Petroleum ether, toluene, chloroform, dichloromethane, hexane trimethylammonium chloride and methanol are purchased from Aladdin Bio-Chem without further purification. Three crude oil samples are provided by Henan Oilfields.

2.2. Thermogravimetric analysis
The TGA (Thermogravimetric Analysis, TGA/SDTA851) measurement was employed to monitor the mass the sample over the desired temperature range from 35 °C to 600 °C at a heating rate of 20 °C/min. The experiment is conducted at a nitrogen atmosphere (with a flow rate of 10 mL/min). In each TGA test, 3 to 6 mg sample is placed into an alumina pan and placed into the furnace. The mass of the sample is automatically recorded by a precise balance placed inside the TGA equipment.

2.3. Separation of crude oil components
The crude oil sample is separated by the column chromatography separation method [7,8]. In each test, 50 mg dehydrated oil sample is dissolved into petroleum ether (boil point: 30-60 °C) and filtered with filter paper to remove the asphaltene groups. Then the oil sample without asphaltene is obtained through drying and weighted with a precise balance. The oil sample without asphaltene is then loaded into the layer consists of neutral silica particles forming oil coated solid phase. The solid layer is then flushed with 50 mL petroleum ether (boil point: 30-60 °C), a 1:2 mixture of CH₂Cl₂ and petroleum ether and a 1:1 mixture of chloroform and methanol successively, and correspondingly, the saturate, aromatic and resin fractions subsequently elute off the column. The eluted fractions are collected by evaporating the solvents with a rotary evaporator. The components’ names and their contents were shown in Table 1. As presents in Table 1, the content of saturate in HN-1 is found to be 64.46%.

| Table 1. The physical parameters of HN-1 crude oil sample. |
|-----------------------------------------------------------|
| Pour point (°C) | ρ¹⁰⁰⁰(g·cm⁻³) | Saturate | Aromatic | Resin | Asphaltene |
|-----------------|----------------|----------|----------|-------|------------|
| 30.5            | 0.86           | 30.13%   | 36.76%   | 25.31%| 7.55%      |

2.4. IR analysis
After the separation of the crude oil by the column chromatography, each SARA fraction of the crude oil is characterized by FTIR (Bruker Tensor with the wavelength range of 400-4,000 cm⁻¹). The silica particles which may contain residual oil components are also tested by FTIR.

2.5. UV analysis of the crude oil components
Each of the separated SARA fractions is dissolved in trichloromethane at a concentration of 10 mg/L. The SARA fraction is then characterized by a UV spectrophotometer (UV-2600).

2.6. Optical microscopy analysis
The saturated hydrocarbon component was separated from the crude oil using the standard 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. A small amount of wax crystal was loaded onto the glass slide inside a copper stage with a central window. During the measurement, the temperature of the copper stage was controlled at 10 °C in a circulating bath.
3. Results and discussion

3.1. IR analysis

The IR results of silica gel containing residual oil is displayed in Figure 1. The IR curve plotted in Figure 1 shows that a certain amount of oil remains in the silica particles after the column chromatography separation.

The adsorption peaks appear at 3600-3350 cm\(^{-1}\), 1630 cm\(^{-1}\) and 1100 cm\(^{-1}\). The wide and strong peak at 3600-3350 cm\(^{-1}\) may be due to the stretching vibration of amino and hydroxyl groups of residual oil in the residual oil. The adsorption peak at 1630 cm\(^{-1}\) may be attributed to the delocalized π bond of the aromatic ring, the stretching vibration of C=O bond in the heterocyclic ring or bending vibration of N-N bond in nitrogen-containing heterocyclic structure. The peak at 1100 cm\(^{-1}\) may be caused by the presence of C-O-C groups in the residual oil in silica particles. The presence of peaks plotted in the curve in Figure 1 confirm that a certain amount of residual oil with high polarity (e.g., resins and asphaltenes) is contained in the silica particles after the chromatography separation.

![Figure 1. The IR spectrum of the residual oil in the silica particles after the column separation.](image)

3.2. TGA measurement

The TGA measurement is employed to analysis the component of the oil sample. The TGA curve of the HN-1 oil sample is plotted in Figure 2. As can be seen in Figure 2, the mass loss occurs at the beginning of the test. The mass loss of the oil sample is found to be 18.87% as the temperature heated up to 150 °C, the mass loss is mainly caused by the evaporation of the light components in the oil sample. As the temperature of the sample is increased from 150 °C to 350 °C, the mass loss of the sample is found to be 41.83%, which may be due to the evaporation of the residual hydrocarbons with carbon numbers less than 25. The mass loss of the sample in the temperature range of 350-450 °C turns out to be 17.34%, which corresponds to the decomposition of heavy hydrocarbons with carbon numbers ranging from 25 to 35. As the temperature is further increased from 450 °C to 500 °C, a mass loss of 10.75% is observed. The mass loss occurred in the temperature range of 450-500 °C may be attributed to the loss or decomposition of the paraffin, resin and asphaltene (with carbon numbers higher than 35) in the residual oil. When the temperature is higher than 500 °C, the content of residuals is observed to be 0.85%.
3.3. **UV measurements**

UV spectroscopy is an effective method to characterize the polycyclic aromatic hydrocarbons in crude oil. Based on the theory of the UV spectrum, the maximum absorption wavelength ($\lambda_{\text{max}}$) appears at a longer wavelength as the number of the aromatic molecules gradually increases. The saturate, aromatic and resin fractions from the oil sample are analyzed by UV spectroscopy and displayed in Figure 3. The asphaltenes and resins have the maximum absorption near 270nm, which implies that the number of aromatic rings in the resins and asphaltenes is about 3 to 4 [12]. The absorption peak appeared in the range of 220-230 nm corresponds to the adsorption peak of a typical non-conjugated saturate compounds. As can be seen from Figure 3, the absorption peak wavelength increases as the polarity of the component increases.
3.4. Effect of paraffin inhibitor on wax morphology

As the temperature decreases below the pour point, the paraffin crystals will deposit and may block the pipelines. Paraffin inhibitors will prevent the formation of paraffin crystals caused by the orientation of the saturate hydrocarbons with high molecule weights. Paraffin inhibitors will also lower the growth rate of the paraffin crystals. Moreover, the paraffin inhibitor also has the ability to modify the size and shape of the crystals and prevent the formation of regular paraffin crystal lattices. In this study, a 1:4 mixture of Hexane trimethylammonium chloride and methanol dissolved in butyl alcohol is employed as the paraffin inhibitor and is introduced into the HN-1 crude oil at a dosage of 500 ppm. The morphology of paraffin crystals without and with the presence of paraffin inhibitor is present in Figure 4 (a) and Figure 4 (b) (using a BX41-POLYMPUS polarized microscope), respectively. In Figure 4 (a), paraffin crystals with large sizes are observed. The paraffin crystals aggregate together and form a three-dimensional crystalline net, which can increase the volume of the solid phase (paraffin phase) and prevent the mobility of the crude oil. The paraffin crystals formed in the presence of inhibitor is present in Figure 4 (b). As can be seen in Figure 4 (b), the amount of paraffin crystals can be significantly reduced. No big aggregates of paraffin crystals are observed in the oil phase. A little amount of paraffin crystals are randomly dispersed in the crude oil. The morphology of paraffin crystals in the presence of the inhibitor indicates the effective inhibition of paraffin crystal formation and growth. The inhibitor molecules may absorb on the micro-nucleus through the interaction between the hydrocarbon tails of the inhibitors and the hydrocarbon molecules that can form paraffin crystals. After the adsorption of inhibitor molecules on the micro-nucleus, the other polar groups on the inhibitors will disturb and block the further growth of the paraffin crystals, and herein, the formation of a three-dimensional network is inhibited [9-12].

![Figure 4. Morphology of paraffin crystal without (a) and with (b) paraffin inhibitor.](image)

4. Conclusion

In this study, column chromatography separation, FTIR, TGA measurement and UV measurement are employed to characterize the composition the HN-1 crude oil sample. With the column chromatography separation method, the nature of high saturate content in the oil sample is confirmed. The FTIR, TGA and UV measurement give further information on the composition of the HN-1 crude oil sample. The
A 1:4 mixture of Hexane trimethylammonium chloride and methanol introduced into the crude oil gives high performance in paraffin crystallization.

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