The influence of ultrasonic treatment on the properties of oil systems

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Abstract. In this work, we summarize experimental data on the influence of ultrasonic treatment alone and sonication with subsequent introduction of oil with high resin content, on the structural and rheological parameters of highly paraffinic oil. Our results clearly indicate that Ultrasonic treatment of oil stimulates the crystallization of paraffin. This leads to an increase in viscosity, pour point and the amount of paraffin deposited. The introduction of highly resinous oil into the sonicated highly paraffinic oil improves the viscosity-temperature characteristics, reduces the specific energy of degradation of the supramolecular structure, and positively affects the mass and the structure of sediments. Significant inhibition of the process of sedimentation and improvement of the viscosity-temperature properties is observed only when 10 wt.% of resinous oil is added to sonicated paraffinic oil. The results of our work indicate that mixing oils with various compositions in combination with ultrasonic treatment could be used for the transportation of highly paraffinic feedstocks through pipelines at low temperatures.

1. Introduction

Significant parts of the extracted oils are paraffinic. Such hydrocarbons, having a high pour point, are prone to the formation of paraffin deposits on the surface of oil field equipment and the accumulation of sediments in oil storage facilities. The structural and mechanical properties of oils are improved by the resinous components, which are natural viscosity-temperature depressants and precipitation inhibitors.

Traditionally, thermal treatment is used in the extraction and transportation processes of paraffinic oils. In this case, hot water, hot steam and electric furnaces are employed as a heat carrier. The disadvantages of this method are the high energy intensity, the use of high-technological devices, and stringent requirements for the temperature regime.

The most effective way to improve the structural and mechanical parameters of oils and petrochemicals is to use chemical reagents – depressant and inhibitory additives [1]. The chemical method of exposure is quite widespread in the oil industry. It is highly effective, but at the same time expensive and environmentally unsafe. In addition, the researchers note that the effectiveness of the additives substantially depends on the hydrocarbon composition of the feedstocks.

Physical methods (magnetic, ultrasonic, vibrational, etc.) have a positive effect on the physicochemical properties of oils [2-10]. The advantages of ultrasonic treatment (UT) over numerous
ways to improve the structural and mechanical properties of paraffinic oils are its low energy consumption, high efficiency, technical and environmental safety.

In this paper, the effect of exposure to ultrasound alone and sonication with subsequent introduction of oil with high resin content (oil-2) on the properties of highly paraffinic oil (oil-1) is considered.

2. Experimental methods and materials
The initial oil-1 (field in the Tomsk Region) was sonicated using an ultrasonic disintegrator operating at a frequency of 22 kHz. The intensity of the ultrasonic field was 18 W/cm²; the time of UT was varied in the range of 3-10 min. In the followed case, 3 or 10 wt.% oil-2 from the Khanty-Mansiyskiy Autonomous okrug field were added to the treated oil-1. The group composition of oils is shown in table 1.

Table 1. Characterization of oils.

| Sample    | T_p, °C | Oil fraction (paraffin hydrocarbons), wt.% | Resins, wt.% | Asphaltenes, wt.% |
|-----------|---------|------------------------------------------|--------------|-------------------|
| Oil-1     | 0.4     | 98.6 (6.9)                               | 1.4          | absence           |
| Oil-2     | -18.0   | 59.0 (1.1)                               | 31.1         | 9.9               |

The rheological parameters of samples were determined using a Brookfield DV-III Ultra rotational viscometer.

The pour point of oils was determined on an SX-800 Kristall analyzer of low-temperature parameters of petroleum products (Russia).

The sedimentation process was studied using a setup operating on the “cold finger” principle under the following conditions: a rod temperature of 5 °C, a sample temperature of 30 °C, an experiment time of 1 h, and a weighed portion of the sample – 40 g. The weight of the sediment formed on the rod was determined gravimetrically; the obtained values were converted per 100 g of the sample.

The process of changing the structure of sediments was investigated by optical microscopy on an AXIO LAB.A1 Carl Zeiss microscope in transmitted light.

3. Results and Discussion
Exposure of oil-1 to ultrasonic led to an increase in structural and rheological parameters (table 2). After the UT during 10 minutes, the effective viscosity (\( \eta^* \)) increased by 4.4 times, the pour point (\( T_p \)) changed from 0.4 to 4 °C, and the activation energy of the viscous flow (\( E_a \)) rose by 2.3 times compared with the initial system.

Table 2. Influence of exposure time on structural and mechanical parameters of oil-1.

| Sample         | \( \eta^* \), mPa*s | \( T_p \), °C | \( E_a \), J/mol |
|----------------|---------------------|--------------|-----------------|
| Oil-1          | 82                  | 0.4          | 122             |
| Oil-1 + 3 min UT | 140                | 2.2          | 124             |
| Oil-1 + 5 min UT | 150                | 2.9          | 176             |
| Oil-1 + 10 min UT | 363               | 4.0          | 277             |

* Effective viscosity at a shear rate of 3 s⁻¹

After UT of the investigated system, sedimentation stability was changed. Due to the sonication of oil-1 for 3-5 minutes, the mass of sediment, extracted from oil, rose by 1.5 times. An increase in processing time up to 10 minutes contributed to an increase in the mass of sediment by 44% compared with the untreated sample oil-1 (figure 1).

The leveling of the negative effects of ultrasound can be achieved after the introduction of petroleum resins into the treated sample. It was shown [11] that the combined effect of UT and silica gel resins helped to improve the structural, rheological and energy parameters of a model system that simulated oil with a high paraffin content.
The introduction of 3 wt.% of oil-2 into the sonicated sample oil-1, suppressed the negative effect of ultrasound. The dynamic viscosity values reduced over the entire range of shear rates. After adding 10 wt.% of oil-2 into sonicated oil-1 decrease in dynamic viscosity was more significant than for previously case (figure 2).

In addition, in the presence of 3 wt.% of oil-2, T_p decreased by 4.6 °C compared with the sonicated oil-1 sample. The maximum depression of the pour point was 6.7 °C relative to the initial sample and was observed when 10 wt.% of resinous oil-2 is added to sonicated paraffinic oil-1.

**Figure 1.** The effect of processing time on the sediments weight extracted from oil-1.

The specific energy of degradation of the supramolecular structure of the disperse system (ΔW) was calculated from the area of the loop formed by the ascending and descending curves. This parameter characterizes the strength of the structural network of sediment. Rheological curves were taken at a temperature of 9 °C according to the procedure described in [12]. Because of the treatment of oil-1 with ultrasound ΔW significantly increased as well as the values of viscosity and pour point. The addition of 3 wt.% of oil-1 to the treated oil-2 sample led to a 1.8 fold decrease in energy compared to the ΔW value for the system after UT. However, this energy value is still higher than ΔW of the initial sample. The addition of 10 wt.% of oil-2 is sufficient not only to neutralize the negative effect of UT, but also to reduce ΔW to 75 J/m^3, which is 1.6 times lower than ΔW for the initial system (table 3).

As noted above, after the UT, the weight of sediment, isolated from oil-1, significantly increased (figure 1). Adding 3 wt.% of oil-2 slightly reduced the weight of the sediment. More substantial inhibition of the sedimentation process was observed after the addition of 10 wt.% of oil-2 into the sonicated oil-1.

**Table 3.** The influence of processing conditions on the pour point, specific energy of degradation of the supramolecular structure, the weight of sediment.

| Sample                          | T_p, °C | ΔW, J/m^3 | Sediment weight, g / 100 g of petroleum |
|---------------------------------|--------|-----------|----------------------------------------|
| Oil-1                           | 0.4    | 122       | 4.7                                    |
| Oil-1 + 10 min UT               | 4.0    | 277       | 8.4                                    |
| Oil-1 + 10 min UT + 3 wt.% oil-2| -0.6   | 152       | 4.6                                    |
| Oil-1 + 10 min UT + 10 wt.% oil-2| -6.3   | 75        | 4.0                                    |

The deposits structure was studied by optical microscopy. It is evident from the micrograph that fibrillar crystals with a length of 6-60 μm represent the sediment of the original oil-1 (figure 2 a). After exposure of the oil-1 ultrasonic field, dispersion degree of aggregates increases (figure 2 b). The addition of 3 wt.% of oil-2 to the initial oil-1 leads to changes in the structure of the crystallizing paraffin. The structure of the precipitate is no longer an ordered crystalline network, but needle-like crystals are still
present in the sediment (figure 2 c). After adding 10 wt.% of oil-2 the sediment structure becomes amorphous. Needle crystals are absent (figure 2 d).

![Image of sediment structures](image)

**Figure 2.** The crystal structures micrographs of the sediments: а – oil-1; b – 10 min; c – 10 min + 3 wt.% oil-2; d – 10 min + 10 % wt.% oil-2.

### 4. Conclusion

The influence of ultrasonic treatment and oil with high resin content on the structural and mechanical properties of oil with high paraffin content is investigated. Sonication with subsequent introduction of oil with high resin content, leads to a significant improvement in viscosity and pour point of paraffinic oil. Addition of 10 wt.% of resinous oil to sonicated paraffinic oil helps to reduce the specific energy of destruction of the supramolecular structure ($\Delta W$) in 1.6 times in comparison with the values of $\Delta W$ for the initial oil. A decrease in $\Delta W$ indicates a change in the structure formed upon crystallization of paraffin hydrocarbons from highly paraffinic oil after sonication with subsequent addition of resinous oil. This is confirmed by optical microscopy. After the sonication and introduction of oil with high resins content, a less ordered structure is formed in the region of lowered temperatures. This fragile structure is easy to break. Due to this fact, transportation of paraffinic oil is more cost efficient.

The results of our work indicate that mixing oils with various compositions in combination with ultrasonic treatment could be used for the transportation of highly paraffinic feedstocks through pipelines at low temperatures.

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