EFFECT OF ASPHALTENES ON STRUCTURE OF PARAFFIN PARTICLES IN CRUDE OIL

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During the transportation and storage of crude oil at low temperatures, asphaltenes and paraffin compounds leave deposits that can cause problems and are expensive to remove. We investigated the effect of an increased amount of asphaltenes on the content and the size distribution of paraffin particles in samples of crude oil. Two sets of Azeri Light crude oil samples were used: the one set contained the standard asphaltene content of 0.035 wt.%; the other set was enriched with asphaltenes in propane asphalt form until the final asphaltene content was 0.35 wt.%. Both sets were thermally treated in an autoclave at different temperatures (40, 60, 80, 100 °C) for one hour to eradicate their thermal history. Afterwards, the samples were cooled down to 10 °C, and polarized light microscopy was used to record image data about paraffinic particles present in the samples. Image analysis confirmed our theory that the samples with a tenfold higher asphaltene content had significantly reduced amounts of paraffin particles, which were also smaller in size. The effect of asphaltene concentration on the paraffin particles was dependent on the applied temperature. Our results suggest that the asphaltene addition could affect the deposit formation in crude oil, as well as improving its low-temperature properties.

Key words: paraffin particles, asphaltenes, polarized light microscopy, propane asphalt

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1. Introduction

Mining, transportation, and storage of crude oil are accompanied by the formation of deposits. High molecular weight paraffins in the form of crystals concentrate in these deposits when the temperature of crude oil reaches its cloud point. Asphaltenes are also presented in crude oil and their secretion is associated with a loss of crude oils colloidal stability. Sufficient quantities of both substances can lead to their mutual interactions.

Generally, the crude oil may arise two types of paraffin deposits. The first type is formed on pipeline walls due to a temperature gradient between the wall and crude oil. The second type of deposits is formed in storage tanks, due to the paraffin particles sedimentation. Besides the deposits, paraffin particles may also form a gel structure because of crude oil cooling under static conditions causing e.g., difficulties with restart of pipeline during outages at low temperatures [1].

Crude oil deposits are complicated mixtures of high molecular hydrocarbons – paraffin (n-alkanes, i-alkanes, cycloalkanes and alkylaromates with long alkyl chains) with carbon number higher than 35, asphaltenes, resins, oils and inorganic compounds. Depending on the crude oil type and the content of dominant substances, crude oil deposits can be divided into paraffin and asphaltene. Properties and behavior of crude oil deposits not only depend on total content of paraffins and asphaltenes, but also on their mutual interactions. The role of asphaltenes during paraffin particles formation was studied for example in [2]. It was proven that asphaltenes play an important role during paraffin crystallization. Also, it has been found that the paraffin crystallization is more affected by the level of dispersion or flocculation of asphaltenes than their type or origin.

Asphaltenes are well dispersed or even dissolved at low concentrations. They become easily accessible for interactions with paraffins and may be fully integrated into their crystalline structure. When the asphaltenes concentration reaches a critical levels, or when the character (polarity) of the environment changes, thereby the balance is broken and asphaltenes begin to precipitate (flocculate) out of the solution or dispersion in which they are dispersed. Flocculation will reduce the number of potential sites for interacting with paraffins. Flocculated asphaltenes may interact with paraffins (part is still accessible), but cannot be fully integrated into their crystalline structure. This flocculation leads to formation of large condensed particles or layers, and for paraffins it is difficult to create a compact network. All this leads to a reduction of crude oil yield stress and wax appearance temperature (WAT). Dynamic viscosity increases due to the larger amount of solids in the system at this temperature [2].

There are a number of studies that published results regarding the effect on the asphaltene precipitation of paraffin particles and the formation of paraffinic gel [1, 3, 4, 5]. Rheology is significantly affected by the concentration and chemical nature of asphaltenes. Addition of asphaltenes in to the crude oil (in concentration up to 0.1 wt. %) slowed down a gelation process and improved flow properties of paraffin crude oil. Flow curves indicate that viscosity was positively affected by the most aromatic asphaltenes [3]. Asphaltenes with aliphatic groups promote better result of an asphaltenes-paraffins interaction and better incorporation of asphaltenes into the crystal structure of alkanes. Also, the aromatic rings of asphaltenes cause steric interference at paraffin molecules that inhibits and disrupts the normal growth of paraffin crystals and promote the formation of weak and less stable gel structure.

In study [6] the asphaltenes were removed from crude oil. It was found that the removal leads to the creation of larger, more compact agglomerates of paraffinic particles. At the same time, the tendency was strongly reduced for particles sedimentation.

An appropriate way to observe the particles in the paraffin crude oil is the use of polarized light microscopy. It enables to observe paraffin particles and their aggregates as bright, light spots on a dark background. This technique was also used to determine WAT [7, 8].

Polarized light microscopy was used to study the influence of temperature on the structure of paraffin particles in crude oils [7]. Results showed that when the sample is cooled and re-warmed to the original temperature, there is a return to similar properties of paraffin particles. On the contrary, heating of the sample and its subsequent cooling leads to irreversible changes. These results indicated the possibilities of solving the problems with thermal history of samples simply by cooling between their sampling and laboratory evaluation.

The aim of this study was the use of polarized light microscopy to study the influence of increased asphaltenes content on paraffin particle size distribution depending on the thermal history of the samples. The work continues in the effort paid in [8], where the influence of asphaltene removal from crude oil was examined.

2. Experimental setup

2.1. Samples

We used a mixture of paraffin crude oils Azeri Light (Supsa) and CPC (Caspian Pipeline Consortium) 74:26 vol. % in all experiments. Crude oil was obtained from the IKL pipeline.

Asphaltenes were added to the crude oil in the form of propane asphalt (PA) with asphaltene content of 4.5 wt. %; obtained from Paramo, Pardubice. The lower content of asphaltenes (than generally present in the PA) had no effect on experiments. The main reason for use of PA was the presence of polar substances, such as resins, which should facilitate dissolution due to peptization of the asphaltenes present in crude oil and reduce the possibility of precipitation and phase separation. PA was added as a concentrate of asphaltenes.

2.2. Preparation of a mixture of crude oil – propane asphalt

PA was weighed into a boiling flask and the amount of crude oil was added to produce 1.8 wt. % of asphaltenes concentrate. Boiling flask was hermetically closed after the stirrer was inserted, then the heating and stirring was started. Stirring was set up at 300 RPM, heating at 140 °C for thirty minutes.

After subsequent cooling, this concentrate was mixed with crude oil to a final asphaltenes content of 0.35 wt. %.

2.3. Thermal sample treatment

Thermal treatment of the samples was done in a pressure vessel which was stirred with a magnetic coupling stirrer at 300 RPM.

The temperature program consisted of the following steps:

1. heating to the desired temperature (40 °C, 60 °C, 80 °C or 100 ° C).
2. maintaining the desired temperature for 1 h.
3. cooling at a rate of 1.66 °C/hour to sedimentation temperature 10 °C.

2.4. Polarized light microscopy

Polarized light microscope Jenapol (Carl Zeiss) located in a cooling incubator, to ensure a constant temperature of 10 °C, was used for observation and photographing paraffin particles in crude oil. The photos were taken with a Canon 1000D camera attached to the microscope. The sample shift on the microscope stage was operated remotely in order to maintain the set temperature. For easy orientation during shooting, there was a 1x1 mm grid on microscope slide. A coverslip was modified so that the resulting thickness of the observed liquid sample was 30 μm. The images were recorded in raw (uncompressed) CR2 format. Each sample was scanned in six rows, each row containing 18 frames.

In this paper all displayed images are negatives.

2.5. Image analysis

Image pre-editing was done in the following steps:

1. transfer images from CR2 to TIFF format
2. crop photos to 1986x1986 pixel format
3. joining individual images into rows

The image analysis was done in ImageJ 1.41 image processing software. Images were adjusted to the color depth of 8 bits (256 levels of gray). The background brightness has been consolidated to the same level because of differences of backlight intensity throughout the area of the images. Based on a threshold, boundaries of observed paraffin particles were found automatically by the software. After that, areas inside individual particle boundaries were evaluated. The output was a list of particles with associated areas. The particle frequency is further expressed not by their number, but by the volumetric representation of particles in a specific size range in the sample. For calculating the volume of individual particles, it was necessary to include some simplifications, since the actual shape of the particles is not known, but the projected shape to the image plane can be only observed. Since the distance between the slide and the coverslip was only 30 μm, particles having a diameter larger than that value are deformed between the slides. 30 μm distance decreased their thickness and increased their observed section. To calculate the particle volume it was therefore necessary to proceed with three simplifications:

1. each particle diameter of less than 30 μm was considered as spherical.
2. if the diameter of a hypothetical spherical particles exceeded 30 μm, its volume was calculated as the volume of spherical layer 30 μm high.
3. from the volume of deformed particles (spherical layer) were re-calculated diameters of the original hypothetical spherical particles, from which the deformed particles were formed.

3. Results and discussion

Photomicrographs of the original crude oil and crude oil with asphaltene addition, after temperature program with different initial heating temperatures, are compared in Figs. 1 – 4. All images cover the area of 1x1 mm. The images reveal the change in size, shape, and frequency of paraffins. Crude oil without the asphaltene addition contain more of larger particles than the crude oil with asphaltene addition and simultaneously form more compact aggregates.

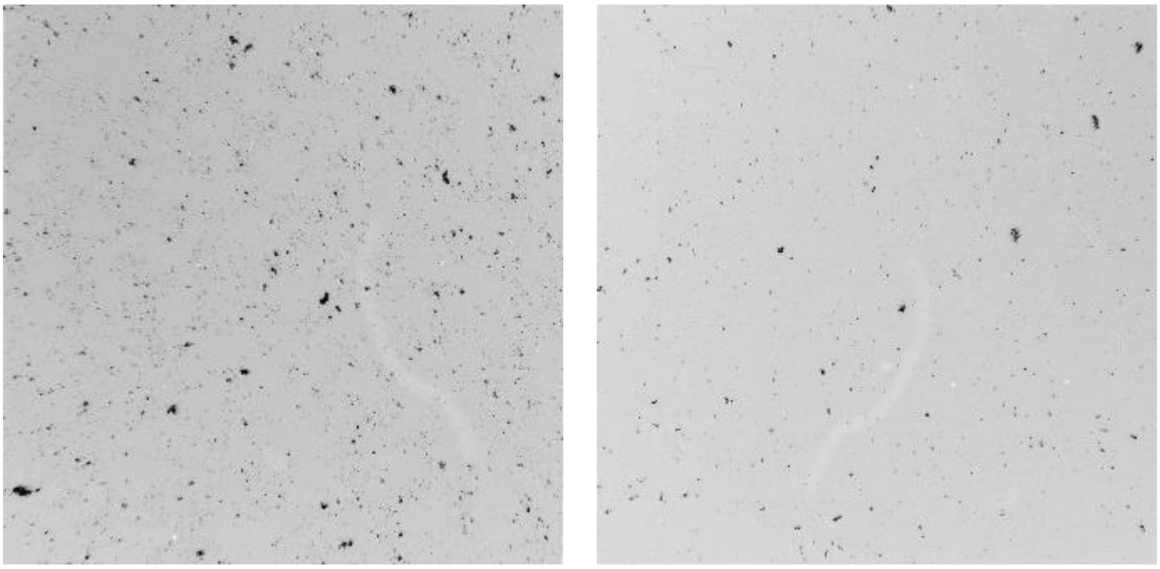

Fig. 1 Neat crude oil (left) and crude oil with addition of asphaltenes, both after pretreatment with maximum temperature of 40 °C

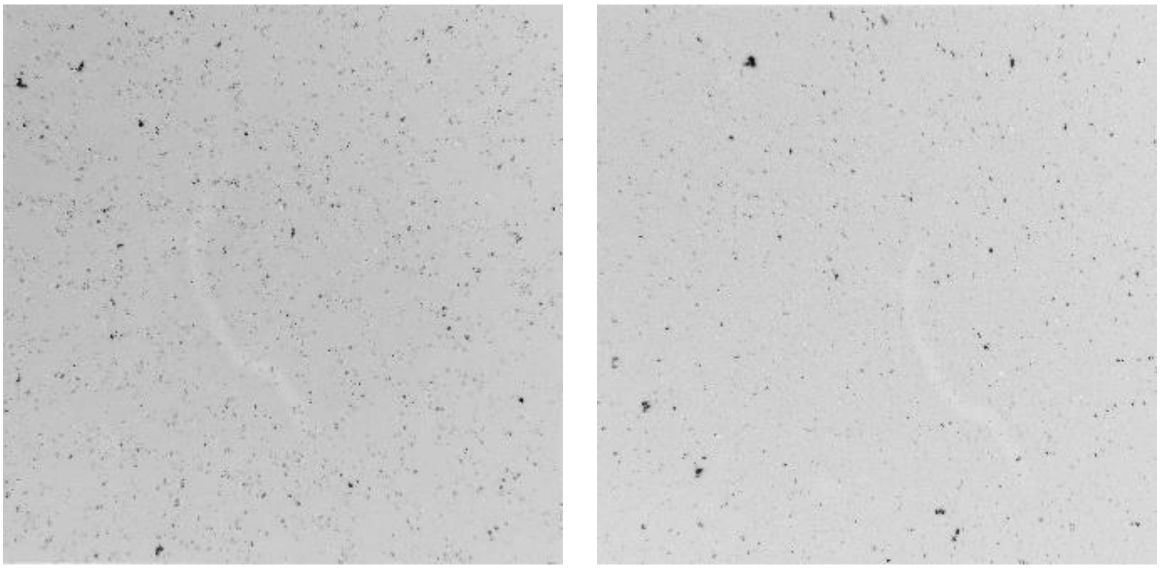

Fig. 2 Neat crude oil (left) and crude oil with addition of asphaltenes, both after pretreatment with maximum temperature of 60 °C

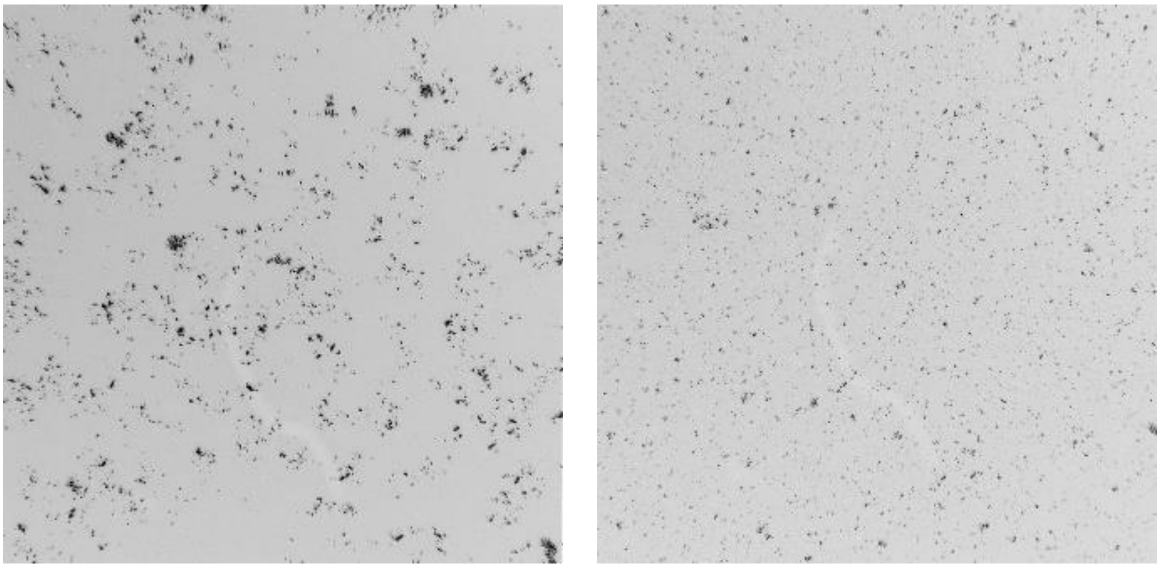

Fig. 3 Neat crude oil (left) and crude oil with addition of asphaltenes, both after pretreatment with maximum temperature of 80 °C

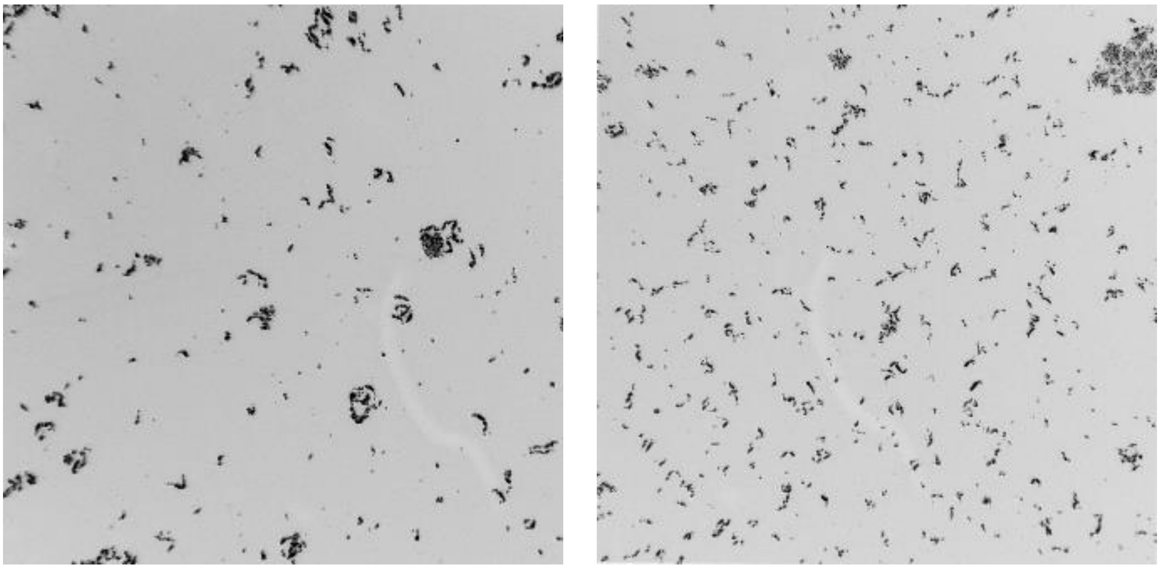

Fig. 4 Neat crude oil (left) and crude oil with addition of asphaltenes, both after pretreatment with maximum temperature of 100 °C

Figs. 5 - 8 show the results of image analysis of the micrographs. The graphs in the figures show the volume fraction of paraffin particles in samples of crude oil according to the particle diameter. Each graph compares the sample of crude oil without asphaltenes addition and the sample with asphaltenes addition over the same temperature program. As can be seen in nearly all graphs, there is a noticeable decline in total paraffin particle content after the addition of propane asphalt. Moreover, the absence of larger particles is evident. Reducing the volume proportion of all observed particles in crude oil is shown in Fig. 9. There was the opposite effect than that was observed when the asphaltenes were from the crude oil samples removed. This resulted in the formation of larger paraffin particles with higher tendency to sedimentation and the formation of paraffin deposits [6].

The explanation may involve a larger number of crystallization centers in the samples with asphaltene addition, but also in disturbing growth of paraffin crystals, which is an effect ascribed to pour point depressants. The effect of the resins and aromatic compounds present in PA cannot be ignored, due to the form in which the asphaltenes were added to the samples.

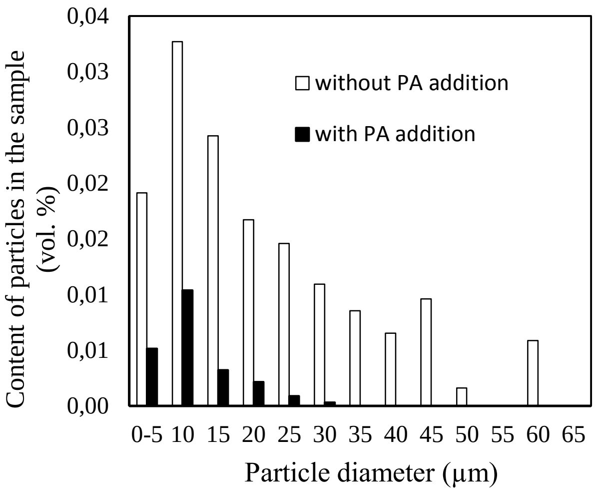

Fig. 5 Volume portion of paraffin particles vs. particle diameter after crude oil pretreatment with max. 40 °C

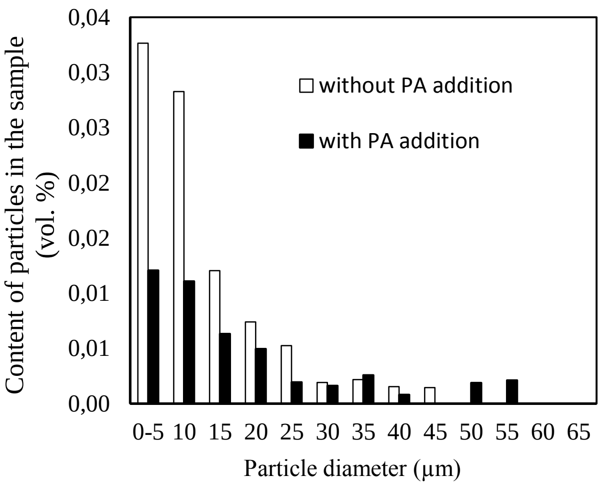

Fig. 6 Volume portion of paraffin particles vs. particle diameter after crude oil pretreatment with max. 60 °C

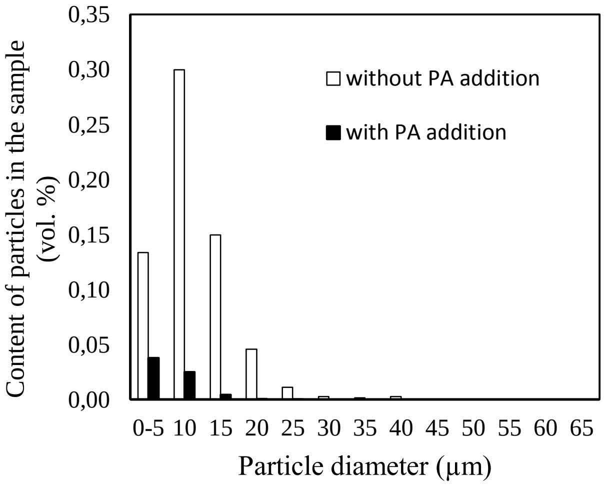

Fig. 7 Volume portion of paraffin particles vs. particle diameter after crude oil pretreatment with max. 80 °C

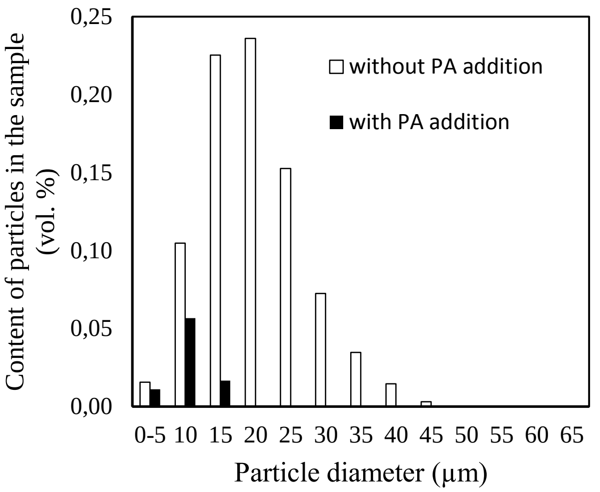

Fig. 8 Volume portion of paraffin particles vs. particle diameter after crude oil pretreatment with max. 100 °C

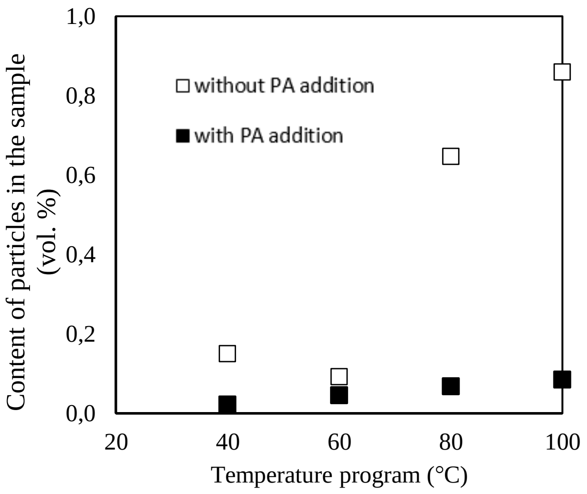

Fig. 9 Volume concentration of paraffin particles vs. sample pretreatment temperature

The effect of pre-treatment, temperature program with variable maximum preheat temperature, is also interesting. In the original sample of crude oil without the PA addition , preheating significantly increased the proportion of precipitated paraffin particles and their size. However, this effect was significantly lesser in extent in samples with PA addition. The minimum difference between the results found for samples with and without the addition of PA using temperature program comprising preheating to 60 °C and subsequent significant increase above this temperature is difficult to explain. Temperature 60 °C is significantly higher than cloud point above which should be all the paraffin particles completely dissolved. Therefore, above the said temperature changes in the interactions of other groups of compounds must take place.

4. Conclusions

Microscopic evaluation of crude oil samples showed that the addition of a propane asphalt with a high content of asphaltenes significantly influenced precipitation of paraffin particles from crude oils. This result can be explained by increasing the number of crystallization centers for the initial growth of paraffin crystals, but also disrupting further crystallization due to the incorporation of molecules or asphaltenes agglomerates in these crystals.

Propane asphalt was added to the used samples instead of pure asphaltenes, because it contains other groups of substances, such as resins, which enhance the colloidal stability of mixtures with crude oil and prevent precipitation of asphaltenes from these mixtures. However, it is probable that these groups of substances also participate in the influence of the precipitation of paraffin particles in crude oil.

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5. References

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