

An Investigation of the Asphaltene Effect on Wax Precipitation of Iran Asmari Reservoir Dead Crude Oil

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ABSTRACT: Wax and asphaltene precipitations cause many problems and high costs in the petroleum industry; therefore, the significance of studying these depositions' behavior is considerable. Evaluating the asphaltene effect on wax precipitation can help find the behavioral trends of waxes and prevent them from precipitating. In this paper, Iran Asmari reservoir Dead Crude oil (IADC) and asphaltene from this oil were used for the experiments. The extracted asphaltene was analyzed by FT-IR analysis. The pour point and wax precipitation content were determined according to the ASTM-D97 Standard test and modified UOP 46-64 method, respectively, and Wax Appearance Temperature (WAT) was measured via differential scanning calorimetry (DSC). At low asphaltene concentrations (0 and 0.057 wt %), adding asphaltene decreased the pour point and wax precipitation content. At asphaltene concentrations of 0.057 wt %, the least wax precipitation content and pour point were measured. A rise in pour point and wax precipitation content was observed at more asphaltene concentrations (0.057-20 wt %). The wax appearance temperature of IADC (36.5 °C) has been decreased in asphaltene-free IADC (25.1 °C). By changing the asphaltene concentration from 0 to 0.1 wt %, the behavior of wax precipitation changed intensely, and this behavior varied gently by increasing the asphaltene concentration from 0.1 to 20 wt %.

KEYWORDS: Wax precipitation; WAT; Asphaltene; Pour point; Iran reservoir dead crude oil.

INTRODUCTION

Several major problems occur because of heavy organic compounds deposition from petroleum fluid [1]. Nowadays, the solid depositions formation of wax and asphaltene leads to myriad problems in the petroleum industry. Prevention

methods, control, and elimination are considerably expensive, complicated, and time-consuming [2-8]. Wax precipitations, also known as paraffin precipitations, form crystals by decreasing at a specific temperature of crude oil,

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which is the wax temperature appearance. After this process, the wax precipitations settle at the bottom of the crude oil. Normal paraffin (normal alkanes) is considered the significant constituent of wax precipitations, and as a result of deposition, they form large crystals called microcrystals [9-11]. The length of macrocrystal chains is C_{20} - C_{50} . Isoparaffins and naphthenes (C_{30} - C_{60}), which exist in small amounts in wax precipitations, form crystals that are generally small and called microcrystals [9, 10, 12]. The primary quantity typically measured for wax precipitation is Wax Appearance Temperature (WAT). The wax appearance temperature is the lowest temperature at which the first wax crystals appear. The wax appearance temperature represents the ability of the crude oil fluid to make wax precipitations. Increasing the temperature raises paraffin's solubility and decreases the amount of wax precipitation [13, 14]. The crude oil pour point is another quantity measured concerning wax. The pour point of a crude oil sample is the lowest temperature at which the sample can move [15]. Other factors, such as composition, pressure, and flow regime of crude oil can affect wax precipitating [16]. There are different mechanisms proposed regarding wax precipitation formation [6]. Singh et al. proved that molecular diffusion is the ascendant and original mechanism in forming wax precipitations [17]. In the seabed pipeline, where the temperature reaches the wax appearance temperature, there is a temperature change in radial, and crystallization of wax occurs in the colder zones closer to the wall. Therefore, solid wax crystals become unbalanced by temperature change. Due to the wax solubility reduction with temperature, a concentration change resulting from the temperature change is created inside the pipeline with colder zones close to the pipe wall, and it has the lowest wax concentration in the phase of liquid. This process conducts the molecular diffusion of wax from the fluid into the pipeline walls [6]. One of the wax inhibition methods is pigging, in which waxes come out in large quantities from the pipelines and can be seen well [18].

Asphaltene is a mixture of hydrocarbons with polyaromatic rings with complex structures and short side chains around aromatic rings in heavy oils and bitumen [19]. Stabilization of asphaltene enhances by light components of crude oil. Thus, asphaltene deposition occurs in most oil reservoirs [20]. Asphaltenes are insoluble in normal heptane but soluble in toluene [21]. Asphaltene deposition has nearly an unequal distribution form in the wellbore because of velocity increase and

pressure drop [20]. Different molecular weights of asphaltenes exist. Asphaltenes in crude oil are like colloidal solutions and could be stable by resins [1]. The molecular structure of asphaltene is divided into two models: the continental and archipelago models [22]. In these models, asphaltenes contain a small or large aromatic zone center attached to naphthenic rings and alkyl branches and atoms such as nitrogen, oxygen, and sulfur in their structure [23-26]. Asphaltene can interact with wax molecules, meddle in wax precipitation formation, and cause changes in the structure [27, 28]. Asphaltenes are dark brown to black powders [29].

Many studies have examined the effect of asphaltene on wax precipitation formation. Philp et al. concluded quantifying the wax precipitation and crude oil asphaltene could play a prominent role in eliminating or minimizing production problems caused by wax and asphaltene depositions [30]. Garcia has observed that adding asphaltene (0.21 wt %) to the crude oil sample elevated the wax appearance temperature since they acted as nucleation sites for wax crystals [31]. Garcia and Carbognani have realized that adding asphaltene made the crude oil samples' pour point rise [32]. Scott Fogler et al. found adding asphaltene (up to 0.2 wt %) lowered wax gel formation temperature. They have also found that increasing the amount of asphaltene reduced the yield stress of the wax gel. By examining the asphaltenes' polarity, they observed that the more aliphatic the added asphaltene, the lower the wax gel formation temperature compared to the more aromatic state. In the microscopic images, they found that wax crystals were taller, thinner, and rod-shaped in the absence of asphaltenes compared to the condition that asphaltenes exist. In the presence of asphaltenes (0.1 wt %), wax crystals became spherical or amorphous [33]. Chuanxian Li et al. indicated that decreasing the asphaltene polarity increased wax content, WAT, wax aging rate, and declined wax deposition rate [34]. Andersen and Kriz observed that WAT increased by ten degrees centigrades at low asphaltene concentrations (0.01 wt %). The increase of asphaltene (0.02 and 0.05 wt %) made WAT decrease by 8.5 °C, and again by increasing the asphaltene concentration (by 0.1, 0.2, and 0.5 wt %), WAT elevated by two degrees centigrades [3]. Jack Tinsley et al. have proved that WAT tended to reduce by 1.6 °C at low concentrations of asphaltene (0-0.2 wt %) while it rose by 5.4 °C at high concentrations (3 wt %) [35]. Vara and Gonzalez have indicated that WAT decreased at concentrations of asphaltenes of 0.01 and 0.31 wt % [36]. Gonzalez et al. have realized that WAT reduced by 1-2 °C at the asphaltene

Table 1: Iran Asmari reservoir dead crude oil (IADC) properties

Property	Amount
Molecular weight (g/mol)	218.35
Density (g/cm ³ @ 26 °C)	0.894
API gravity	26.8

concentrations of zero and 0.05 wt %, and they also observed a reduction in the pour point of the crude oil sample. Besides, they have observed that the more aliphatic the asphaltene, the lower the pour point. It is important that the less aliphatic and more aromatic core of asphaltene inhibited wax crystals' growth [37]. *Jaber Taheri-Shakib et al.* have revealed that increasing aromatic compounds compared to aliphatic in crude oil made the shape of the crystals of waxes spherical and uniform.

Moreover, they have observed polar compounds, such as aromatics, strengthened the wax structure, and raised the WAT. They found that if the wax components were microcrystalline, the wax and asphaltene interaction would increase, and the wax particles would become spherical. On the other hand, if the wax contained cyclic and paraffin compounds, the wax crystals would become plate-shaped in the presence of asphaltene. Finally, if the wax compounds of crude oil were macrocrystalline, the wax crystals would be smaller, interwoven, and honeycomb-shaped [38]. *Jinjun Zhang et al.* realized that asphaltenes with a specific concentration (0.2 wt %) had prevented wax formation, and WAT has gradually elevated (at concentrations of 0.01, 0.05, 0.1, and 0.2 wt % of asphaltene). They also observed that the wax system crystals' size changed by adding asphaltene, and their shape turned from the rod to spherical [39].

However, most early studies used commercial asphaltene or asphaltene of other crude oil not studied in their works. Besides, most used oil samples were made as a combination of several solvents with wax and asphaltene. The actual oil sample corresponded to the same wax, and asphaltene was not employed. The behavior of asphaltenes and waxes in samples made with several solvents might differ from their behavioral reality in actual crude oil samples. In many studies, the asphaltene effect on wax precipitation was analyzed only at low asphaltene concentrations (up to 7 wt %)[3, 31-33, 35, 36, 39, 40]. In this work wide range of asphaltene concentrations was considered (zero to 20 wt %). In this study, the wax precipitations behavior in the actual crude oil sample

of one of the Iranian reservoirs has been studied. The extracted asphaltene of this actual oil sample has been employed to test and prepare samples. This article's capital purpose is to investigate the asphaltene effect on wax precipitation formation by determining the oil samples' pour point, wax precipitation content, and the wax appearance temperature and to offer a specific trend for wax precipitation. The National Iranian South Oil Company and Sahand Oil and Gas Research Institute assisted us in this paper.

EXPERIMENTAL SECTION

Materials and samples

In experiments, dead crude oil from the Iran Asmari reservoir was used. Table 1 shows the properties of crude oil with the American Petroleum Institute (API) gravity 26.8. In this study, required asphaltene depositions were extracted from IADC by ASTM–D6560 Standard test method [41].

Methods

Preparation of asphaltene-free crude oil and pure asphaltene

During the ASTM–D6560 Standard test method, asphaltene-free crude oil was prepared by adding some steps. After filtration, initial asphaltene-free crude oil remained in the vacuum flask in the third step of this standard method, consisting of a normal heptane solvent. The vacuum flask blend was poured into a beaker and placed under the hood to evaporate the normal heptane solvent. On the other hand, some waxes might precipitate alongside asphaltene deposition, and some crude oil components (resins and aromatics) could remain on filter paper. These substances were washed in the Soxhlet extractor with normal heptane solvent and were collected in the Soxhlet flask. After extracting, the blend of the Soxhlet flask was added to the initial asphaltene-free crude oil. It was mixed entirely to prepare crude oil so that only the asphaltenes were separated and not other components. The resulting solution was then placed under the hood to completely evaporate the normal heptane solvent and remain only asphaltene-free crude oil in the beaker. What remained at the bottom of the beaker after four days was asphaltene-free IADC. Fig. 1 shows the ASTM–D6560 Standard test method and asphaltene-free oil preparation method in the form of a schematic diagram.

Table 2: Properties of prepared IADC samples with different asphaltene concentrations

Sample	1	2	3	4	5	6	7	8	9	10	11	12
Asphaltene-free crude oil (g)	7	7	7	7	7	7	7	7	7	7	7	7
Asphaltene deposition content (g)	0	0.004	0.007	0.021	0.035	0.05	0.071	0.101	0.143	0.37	0.78	1.75
Asphaltene (wt %)	0	0.057	0.1	0.3	0.5	0.71	1	1.43	2	5	10	20

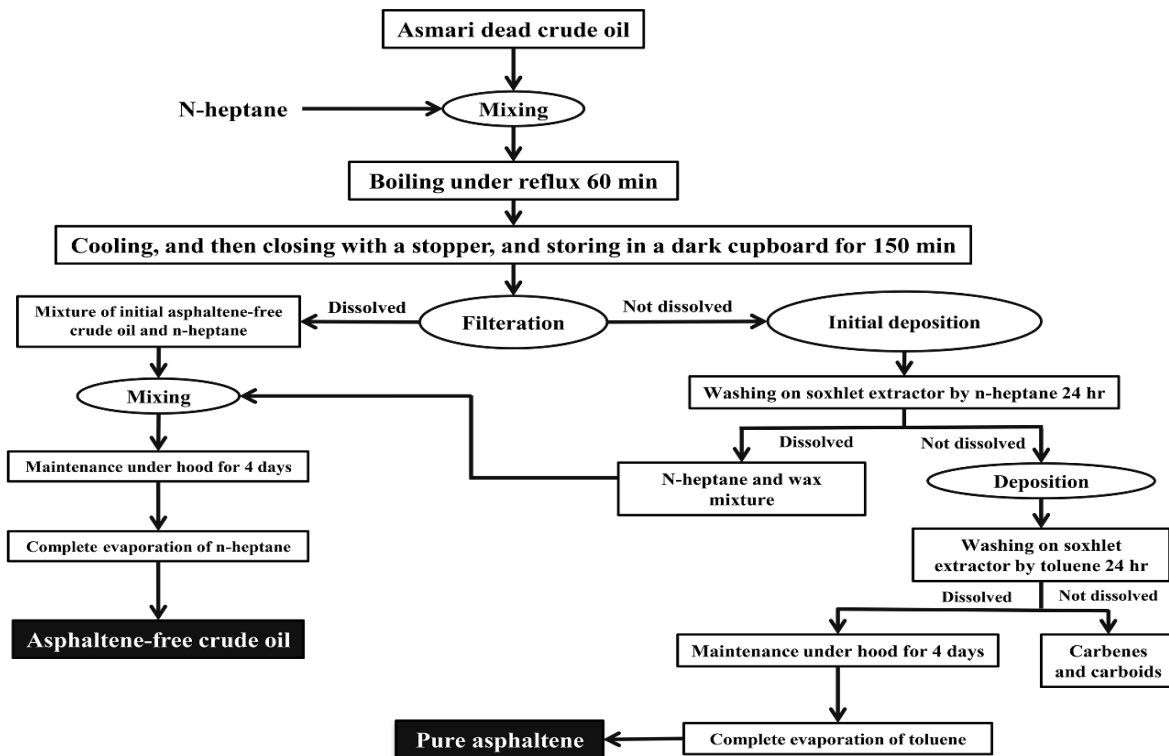


Fig. 1: Diagram of pure asphaltene and asphaltene-free crude oil preparation methods

Preparation of crude oil samples with different asphaltene concentrations

A toluene solvent was used to thoroughly dissolve asphaltene in asphaltene-free crude oil to prepare samples with a specific asphaltene concentration. The solution was placed under the hood until the toluene solvent evaporated, and then the crude oil sample with a particular concentration had left. In this article, 12 samples with diverse asphaltene concentrations were arranged. Table 2 shows the properties of the samples.

Pour point of crude oil measurement method

An experimental setup was designed and employed to determine the pour point of samples according to the ASTM–D97 Standard test [15]. Fig. 2 displays the experimental apparatus. This apparatus consists of the following parts:

1. Ethylene glycol bath
2. Compressor
3. Heater
4. Temperature controller
5. Pump

The ethylene glycol bath could be heated to 60 °C and cooled to – 48 °C (by heater and compressor, respectively). A pump was used to equalize the temperature in all bath parts. Whereas reading the registered temperature of the mercury thermometer that should be used in the ASTM–D97 Standard test could have a human mistake. Hence, two temperature sensors (Sunward thermometer reference temperature sensor) and the bath temperature sensor with a key were connected to the Sunward temperature controller. In this case, the temperature of samples could be measured precisely without human mistake and with an accuracy of ± 0.1 °C. Samples and bath temperature could be observed simultaneously only by changing the key.

Table 3: Properties of Whatman and GVS filters

Filter	GVS	Whatman
Type	Glass Microfiber	Glass Microfiber Grade 934-H
Efficiency (%)	99	98
Diameter (millimeter(mm))	90	90
Thickness (mm)	0.26	0.43
Particle retention (micrometer (μm))	1.6	1.5



Fig. 2: Pour point measuring experimental setup

Wax precipitation content measurement

In this study, the modified UOP 46–64 method [42] was used to determine wax precipitation content. In order to obtain pure wax precipitation, three steps were added to this method (steps 7, 8, and 9) which are the following steps:

1. 5 grams(g) of crude oil was weighed as a sample and poured into a beaker.
2. 35 milliliters (ml) of petroleum ether solvent was added to the sample and stirred utterly.
3. 110 ml of acetone was increased to the mixture and mixed up thoroughly.
4. The resulting mixture was put in the refrigerator for 2 to 3 hours to reach a temperature of -20°C .
5. Some other instruments were precooled to -20°C : Büchner funnel, vacuum flask, Whatman fiberglass filter paper, a mixture of acetone in three parts, and petroleum ether in one part.
6. The Whatman filter was placed in the Büchner funnel before filtering the cooled sample, and it became wet with an acetone/petroleum ether mixture. The filtration was done by turning on the vacuum pump and gently pouring the sample into the funnel. After filtration, some precipitations were left at the bottom of the sample beaker and some on the filter. The left precipitations at the bottom of the sample beaker were washed with toluene and poured

into the small beaker-1. The beaker-1 was left under the hood for four days to evaporate toluene entirely. Then, it was put in the oven and desiccator after evaporating toluene.

7. The small beaker-1 and filter were washed on the Soxhlet extractor with normal heptane solvent for one day.
8. After one day, the mixture of pure waxes and normal heptane solvent was collected in the Soxhlet flask. This mixture was poured into beaker-2 to evaporate the normal heptane solvent. After evaporating, pure wax precipitations of crude oil sample were at the bottom of the beaker-2.

Of course, in this work, GVS fiberglass filter paper was used instead of Whatman filter paper. The properties of both filter papers are shown in Table 3.

Analysis

Fourier Transform InfraRed (FT-IR) spectroscopy analysis

In this research, this analysis has been employed to analyze the components of the obtained asphaltene depositions like other works[38, 43-45]. The device used in this research is UNICAM 4600 with the Mattson 1000 model.

Differential Scanning Calorimetry Analysis (DSC)

DSC analysis has been employed to determine the wax appearance temperature (WAT) in IADC and asphaltene-free IADC samples. The DSC device measures the samples' heat based on temperature during heating and cooling and gives the diagram defining the relationship between heat flow and temperature. When the first wax crystals are formed in the crude oil sample during cooling, the formation of these crystals releases heat, which is considered an exothermic peak in its DSC diagram. This exothermic peak's starting point will be the oil sample's wax appearance temperature or WAT point. The temperature program employed to find the WAT point is as follows:

Table 4: ASTM–D6560 standard test results of IADC

Test number	1	2	3	4	5	6	7	8	9	10
Asphaltene (wt %)	1.41	1.40	1.48	1.40	1.42	1.41	1.46	1.36	1.37	1.43
Test number	11	12	13	14	15	16	17	18	19	20
Asphaltene (wt %)	1.47	1.39	1.45	1.48	1.40	1.44	1.49	1.43	1.38	1.45

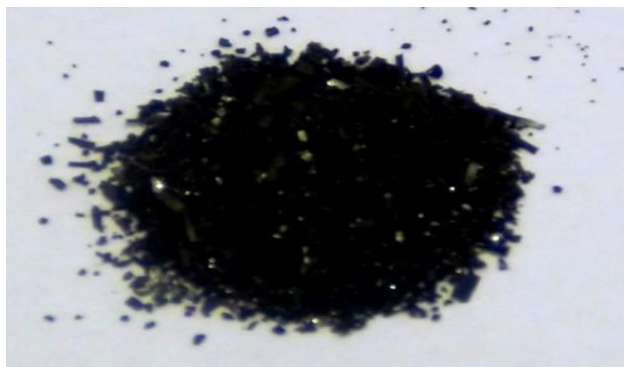


Fig. 3: Pure extracted asphaltene of IADC

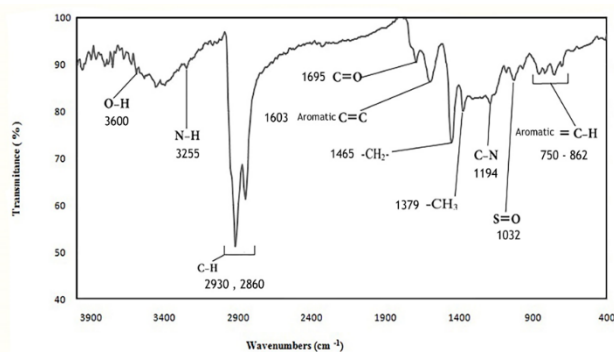


Fig. 4: FT-IR analysis of extracted asphaltene from IADC

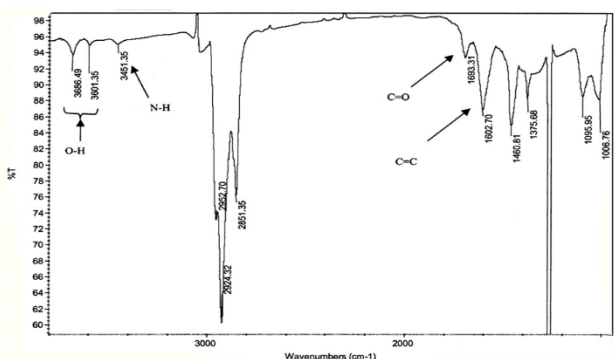


Fig. 5: FT-IR analysis of extracted asphaltene of Fulmar crude oil [43]

- 1) Heating the sample from ambient temperature to 100 °C at 5 °C per minute and staying at 100 °C for 5 minutes.
- 2) Cooling the sample from 100 °C to -30 °C at the rate of 5 °C per minute.

In this research, the DSC device is Netzsch with DSC 200 F3 Maia model made in Germany.

RESULTS AND DISCUSSION

In this article, all the experiments were performed at ambient temperature and pressure.

Pure extracted asphaltene precipitation and asphaltene-free IADC

Pure asphaltene precipitation was extracted for preparing crude oil samples with different asphaltene concentrations by performing the ASTM–D6560 Standard test twenty times with 30 g crude oil at any time. Table 4 illustrates the results of these twenty tests.

Based on the results of ASTM–D6560 Standard tests asphaltene content of IADC was 1.43 wt %. By performing the ASTM–D6560 Standard test, 8 g pure asphaltene deposition and 500 g asphaltene-free IADC was extracted. With this content of asphaltene and asphaltene-free crude oil, three series of samples with different asphaltene concentrations (0, 0.057, 0.1, 0.3, 0.5, 0.71, 1, 1.43, 2, 5, 10, 20 wt %) were set up that 7 g of asphaltene-free crude oil was used to prepare every sample.

Fig. 3 displays pure extracted asphaltene from IADC that were like black powder. FT-IR analysis was performed to analyze asphaltene components. Fig. 4 represents the FT-IR analysis of asphaltene of IADC.

Comparing FT-IR spectra of asphaltene of IADC (Fig. 4), asphaltene of Fulmar crude oil (Fig. 5) [43], and the FT-IR spectra of other asphaltene samples (Fig. 6)[38] reveals that they are consistent with each other, so this consistency confirms that the resulting materials are asphaltene.

Fig. 4, like Figs 5 and 6, shows that the absorption peaks at 2860 centimeters⁻¹ (cm⁻¹) and 2930 cm⁻¹ are related to the C – H normal alkane functional group[45, 46]. As explained in this article, asphaltene has aliphatic components around the aromatic core at the center of their structure. The small peaks located at 3600 cm⁻¹ – 3650 cm⁻¹ are

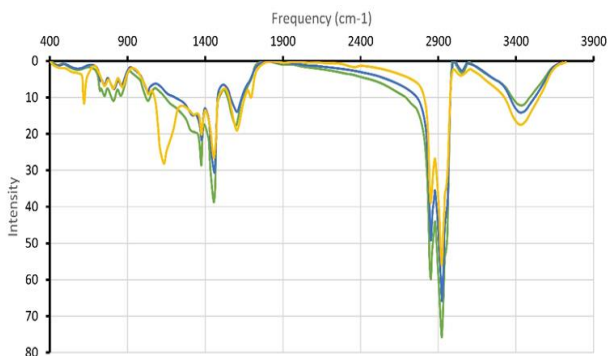


Fig. 6: FT-IR spectra of asphaltene samples of southwestern Iranian crude oil fields[38]

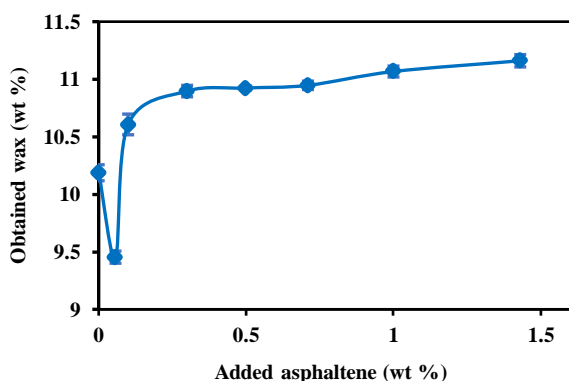


Fig. 7: Wax precipitation contents of IADC vs. added asphaltene at low concentrations

related to the phenol with oxygen[46] corresponding to the asphaltene. The peak of absorption was observed at 1695 cm^{-1} corresponds to the $\text{C}=\text{O}$ carboxyl functional group [46] that shows asphaltene oxygen, as asphaltenes are considered organic materials, including aromatic and naphthene rings components with oxygen, nitrogen, and sulfur molecules contain heavy metals[47-49]. $\text{C}=\text{C}$ of the aromatic ring was observed at 1603 cm^{-1} frequency peak, and also, the peaks located at 750 cm^{-1} to 862 cm^{-1} are related to the bond $\text{C}-\text{H}$ of the aromatic ring[45, 46]. The 1194 cm^{-1} and 3255 cm^{-1} absorption peaks correspond to the bond $\text{C}-\text{N}$ and $\text{N}-\text{H}$ of the amine functional group[46]. As has been shed light on asphaltenes before in this paper, asphaltenes have nitrogen atoms in their structure. The peaks that 1379 cm^{-1} and 1465 cm^{-1} are related to methyl ($-\text{CH}_3$) and methylene ($-\text{CH}_2-$) functional groups [45, 46], respectively, are aliphatic components around the aromatic core of asphaltene. The sulfur element shows itself at 1032 cm^{-1} frequency[46]. As a result, all of these peaks were observed in the study of Xiaoli Yang and Peter

Kilpatrick [43] and Jaber Taheri-Shakib[38], so FT-IR analysis indicates that extracted asphaltene based on ASTM-D6560 Standard test is actual asphaltene.

Asphaltene content effect on wax precipitation content, pour point, and WAT

Intending to investigate the asphaltene effect on wax precipitation, the quantities: wax deposition content, pour point of crude oil, and wax appearance temperature were measured.

Wax precipitation content

The wax precipitation content of samples with different asphaltene concentrations was measured through the modified UOP 46-64 method. This method was repeated three times for each asphaltene concentration (0, 0.057, 0.1, 0.3, 0.5, 0.71, 1, 1.43, 2, 5, 10, and 20 wt %). Figs 7 and 8 represent the results of wax precipitation contents at low and high concentrations.

Fig. 7 shows that extracting whole asphaltenes from IADC has decreased wax precipitation content. This reduction was observed in the study of Huiyuan Li *et al.*, too [50], which could be because of reducing asphaltene contents as nucleation sites for wax growth. The resulting data of wax precipitation content could be explained that at low asphaltene concentrations (0 and 0.057 wt %), asphaltenes dispersed as well as possible in crude oil, and the more asphaltene dispersion, the lower nucleation sites for wax crystals growth. Also, aliphatic components of asphaltenes could form weak bonds with wax components, so prevent wax crystals from connecting strongly to each other, and therefore wax crystals network became loose. As a result, wax precipitation content at low asphaltene concentrations of 0 - 0.057 wt % decreased, and Vara and Gonzalez observed this result in their study, too [36]. These two inhibitor effects led to the minimum wax precipitation content achieved at an asphaltene concentration of 0.057 wt % in IADC. This asphaltene critical concentration (0.057 wt %) is consistent with the study of Gonzalez *et al.* [37]. The more asphaltene concentration, more than 0.057 wt %, the more wax precipitation content. The increasing slope at asphaltene concentrations 0.057 to 0.1 wt % was steep ($26.74 \frac{\text{wax content wt \%}}{\text{asphaltene wt \%}}$) and gentle ($0.42 \frac{\text{wax content wt \%}}{\text{asphaltene wt \%}}$) at concentrations 0.1 to 1.43 wt %. Steep and gentle slopes could be explained that at low asphaltene

Table 5: Pour points of IADC samples with different asphaltene concentrations

Asphaltene (wt %)	0	0.057	0.1	0.3	0.5	0.71	1	1.43	2	5	10	8
Pour point (°C) (first test)	3	3	6	6	6	9	6	9	12	15	15	18
Pour point (°C) (second test)	6	6	6	9	9	9	9	9	12	15	15	18
Pour point (°C) (third test)	6	3	6	6	6	6	9	9	12	15	15	18
Pour point (°C) (fourth test)	6	3	-	6	6	9	9	-	-	-	-	-
Pour point (°C) (recorded)	6	3	6	6	6	9	9	9	12	15	15	18

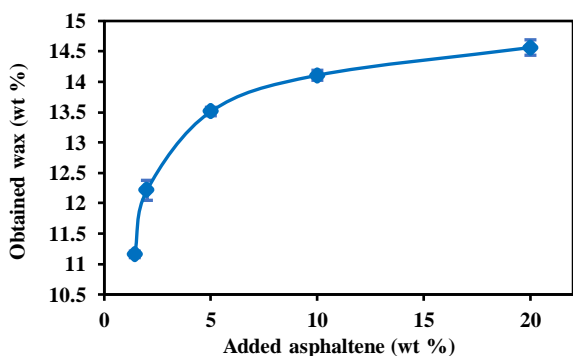


Fig. 8: Wax precipitation content of IADC vs. added asphaltene at high concentrations

concentrations (0 and 0.057 wt %), asphaltenes were dispersed in the crude oil and acted as an inhibitor of wax crystals network formation. By increasing asphaltene concentration (0.057 and 0.1 wt %), asphaltenes have reached an amount that had been able to fluctuate, and they have caused wax precipitation content to soar suddenly with a steep slope. When the asphaltene concentration was raised again (0.1 to 1.43 wt %), a proportion of asphaltenes caused increased nucleation sites for wax crystals growth, and the other proportion was dispersed out of asphaltenes flocculations in crude oil and prevented wax crystals network formation. Consequently, a competitive state between enhancer and inhibitor effects of asphaltenes for wax crystals growth was created. The enhancer effect overcame the other impact and was the cause of a slight rise in wax precipitation content. Also, as shown in Fig. 7, adding asphaltenes at concentrations of more than 0.1 wt % leads to a change in wax precipitation content slightly (0.5 to 1 wt %) that is consistent with the work of Jinjun Zhang et al. on WAT and wax structure [39]. At asphaltene concentrations of 1.43 – 5 wt %, sharp changes in wax precipitation content ($0.48 \frac{\text{wax content wt \%}}{\text{asphaltene wt \%}}$) compared with the changes at asphaltene concentrations of 5 - 20 wt % ($0.07 \frac{\text{wax content wt \%}}{\text{asphaltene wt \%}}$). When asphaltene concentration

raised more than 1.43 wt % (2, 5, 10, and 20 wt %), as shown in Fig. 8, asphaltenes could not scatter quietly due to their high amount in crude oil and connected quickly. Consequently, they were flocculated and elevated as nucleation spots for the formation of wax crystals, and then the wax precipitation content increased.

Pour point of crude oil samples

Table 5 shows the resulting poor points of crude oil samples at different asphaltene concentrations. The test for measuring the pour point was performed three or four times for each sample, and the most repeated temperature was recorded as the pour point of the sample.

The asphaltene effect on the pour point at different asphaltene concentrations is shown in Figs 9 and 10. It corresponded to the results of wax precipitation contents. The least pour point of IADC was measured at an asphaltene concentration of 0.057 wt %, which was the minimum wax precipitation content consistent with wax precipitation content changes. Also, slight increasing changes of pour point at asphaltene concentration 0.1 – 5 wt % ($1.83 \frac{^{\circ}\text{C}}{\text{asphaltene wt \%}}$), and sharp increase at asphaltene concentration 0.057 – 0.1 wt % ($69.77 \frac{^{\circ}\text{C}}{\text{asphaltene wt \%}}$), and also a minor rise at asphaltene concentration of more than 5 wt % ($0.2 \frac{^{\circ}\text{C}}{\text{asphaltene wt \%}}$) were observed as changes in wax precipitation content. Therefore, this consistency could verify the results and discussions and obtain a trend for wax behavior with the presence of asphaltene.

Wax Appearance Temperature (WAT)

WAT was measured for IADC and asphaltene-free IADC samples. Figs 11 and 12 represent the DSC analysis of IADC and asphaltene-free IADC. The phase change of liquid to solid is an exothermic reaction, so the formation of the first wax crystals releases heat, and the radiated heat

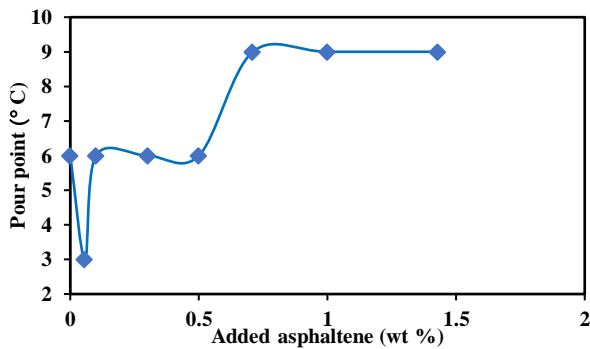


Fig. 9: IADC pour point at asphaltene low concentrations

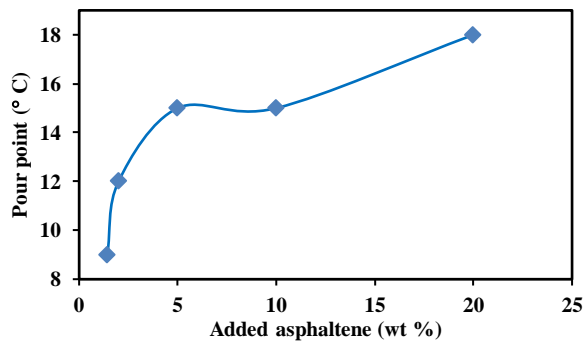


Fig. 10: IADC pour point at asphaltene high concentrations

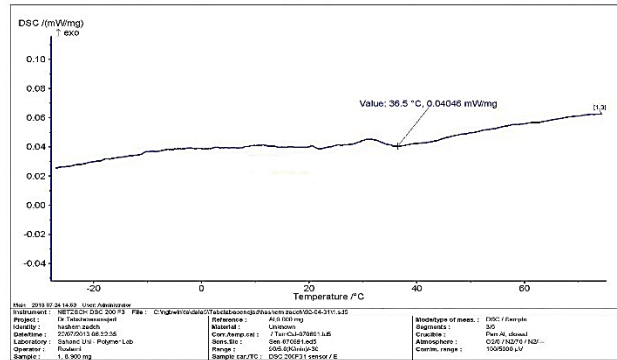


Fig. 11: DSC analysis of IADC

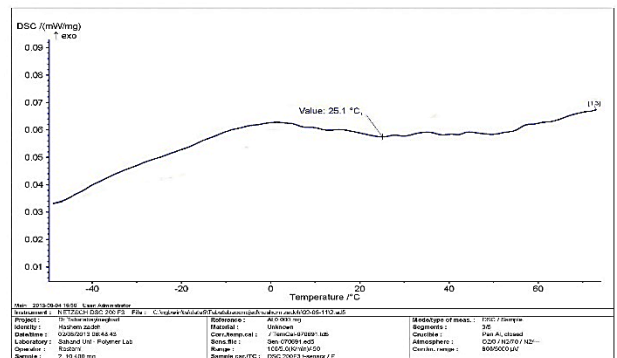


Fig. 12: DSC analysis of asphaltene-free IADC

causes a peak in the DSC diagram. The start point of the exothermic peak is the WAT point. The WAT point of IADC was 36.5 °C (fig. 11), and the WAT point of asphaltene-free IADC was 25.1 °C (fig. 12). Based on these results, the more asphaltene concentration, the more wax appearance temperature. Garcia [31] and Vara and Gonzalez [36] observed this result in their study. The WAT results agree with the behavior of wax precipitation content and pour point of crude oil at different asphaltene concentrations in this study. According to all outcomes, the presence of asphaltene could be an influential enhancer factor in forming wax precipitations by creating nucleation sites for wax crystals' growth. The behavioral trend of wax precipitation with asphaltene presented in this study is consistent with most previous studies.

CONCLUSIONS

In this document, we have seen that the presence of asphaltenes in Iran Asmari dead crude oil enhanced the pour point, wax appearance temperature, and wax precipitation content. Increasing asphaltene content at low concentrations (0 and 0.057 wt %) diminished the pour

point and wax precipitation content. This research paper has clearly shown that the minimum pour point and wax presentation content of IADC at asphaltene concentration 0.057 wt % has appeared. In this study, we discovered that the more the asphaltene concentration (more than 0.057 wt %) was increased, the more the pour point and wax precipitation content were raised. The increasing change of pour point and wax precipitation content by adding asphaltenes is sharp at asphaltene concentrations 0.057 to 0.1 wt % and gentle at asphaltene concentrations 0.1 to 5 wt %, and very slightly rising at asphaltene concentrations more than 5 wt % (5 – 20 wt %). The presence of asphaltenes in IADC raises wax appearance temperature (WAT) from 25.1 °C to 36.5 °C. Providing a trend for wax precipitation was the aim of this paper which has now been achieved. The discussion in this article had given a trend for wax precipitation in IADC that had shown when wax precipitation was at the minimum concentration and by asphaltene concentration changing, wax precipitation behavior varied sharply at low asphaltene concentration (0 – 0.1 wt %), and gradually this behavior became gentle by increasing asphaltene concentration (0.1 – 20 wt %).

Nomenclatures

IADC	Iran Asmari dead crude oil
WAT	wax appearance temperature
API	The American Petroleum Institute

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