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EXPERIMENTAL STUDY OF TEMPERATURE EFFECT ON ONSET PRESSURE OF ASPHALTENE IN LIVE OIL

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Abstract

The phenomena of asphaltene deposition have become a severe problem to almost all petroleum production, processing and transportation facilities. Asphaltenes, the heaviest fraction in crude oil, are either in dissolved state or in colloidal dispersion form in crude oil. Temperature has a significant role in dissolving the asphaltenes in continuous phase of crude oil. However, there are differing views on the effect of temperature on solubility and precipitation of asphaltenes. In this work, an investigation was carried out on the effect of temperature on onset pressure of asphaltenes for an Iranian live crude oil sample in the temperature range of 46-135°C and pressure range of 34246-46464 kPa, by performing a series of pressure depletion tests using the mercury-free, variable volume, fully visual PVT system with laser light scattering. The P- T phase envelope and the Asphaltene Deposition Envelope (ADE) were developed. The experimental data show that solubility of asphaltenes increased with increase in temperature. The Colloidal Instability Index (CII) was established for this crude oil and found to be greater than one indicating definite asphaltenes instability.

Keywords: Asphaltenes; Precipitation; Onset pressure; PVT; Temperature.

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1. Introduction

Asphaltenes are the heaviest and most complex molecules in crude oil and are defined by its solubility class as the constituents of oil which are soluble in toluene but insoluble in n-heptane. Asphaltene was defined by Srivastava *et al.* [1], as the polar poly-aromatic and high molecular weight hydrocarbon fraction of crude oil that are generally characterized as insoluble in n-heptane or in n-pentane. They are believed to exist either dissolved in oil or as a finely dispersed colloidal suspension in oil stabilized by resins adsorbed on their surface. The nature and behavior of asphaltenes in crude oils are complicated. Asphaltenes are complex organic materials that are thought to be arranged in stacked, multi-ring structures. They consist primarily of carbon, hydrogen, and a minor proportion of hetero-elements such as oxygen, sulfur and nitrogen.

There are different methods to determine asphaltene precipitation conditions. These methods include: gravimetric, light transmission, light scattering, refractive index, straight observation, heat transfer measurement, electric convection measurement, viscosity measurement, IFT measurement and dynamic method. Presence of asphaltenes in crude oil has been linked to several problems in petroleum industry. Much of the research has been driven by the tendency of asphaltenes to aggregate, precipitate and deposit onto surfaces [2-5]. The presence of asphaltenes on heat transfer surfaces further favors fouling of equipment because asphaltenes are more prone to attach to already coked surfaces than a clean metallic alloy surface [6]. In order to mitigate problems caused by asphaltenes, a thorough understanding of the process of asphaltenes precipitation, flocculation and deposition and the factors affecting them is necessary [7]. The precipitation of asphaltene is caused by a number of factors including changes in pressure, temperature, chemical composition of the crude oil, mixing the oil with diluents or other oils, and during acid stimulation [8].

Whether a change in temperature dissolves asphaltenes in oil or it favors precipitation of asphaltenes from oil; and whether the asphaltenes exist in crude oil in dispersed state forming a colloidal suspension of oil or they exist in dissolved state in oil like a true solution, are still debatable. There are different schools of thoughts on relationship between phase behavior of asphaltenes and change in temperature. Some studies show that a part of asphaltenes in oil is dissolved and the rest of asphaltenes is in colloidal dispersed form [9-11]. Asphaltenes can either precipitate or dissolve in crude oil on changing thermodynamic conditions such as temperature. According to Mansoori [13], asphaltenes appears in crude oil both as soluble phase and as well as colloidal one and asphaltenes deposition from petroleum fluids is partly due to solubility effect and partly due to colloidal phenomenon. The asphaltenes colloids are considered as molecules in a true solution and are also reported to be thermodynamically a liquid phase at higher temperature, forming liquid-liquid equilibrium with oil phase [12-13].

Mehranfar *et al.* [14] used atomic force microscopy to observe the structural changes in asphaltene nano-aggregates as a function of temperature (25-80°C), demonstrating the transition of asphaltenes to liquid phase with increase in temperature above 70°C [14]. Maqbool *et al.* [5] used optical microscopy to evaluate the effect of temperature on asphaltenes precipitation kinetics. They presented a hypothesis that destabilized asphaltenes aggregate more at 50°C than at 20°C but precipitation rate is lower due to lesser number of particle collisions because of the higher aggregate size [5].

Hu and Guo [15] studied the effect of temperature and molecular weight of n-alkanes on asphaltenes precipitation using flocculation onset titration method along with light scattering technique, and their data show that amount of asphaltenes precipitation was higher at 20°C than at 65°C [15]. Andersen and Stenby [16] precipitated and then redissolved asphaltenes in n-heptane-toluene solution to study thermodynamics of asphaltenes precipitation in the temperature range of 24 to 80°C and observed that asphaltenes solubility increased with the increase in temperature and increase in concentration of toluene in n-heptane-toluene solution [16]. According to a study by Storm *et al.* [17], dependence of asphaltenes solubility on temperature was observed, they established conclusions in their rheological and small-angle x-ray scattering study on asphaltenes flocculation that asphalttenes flocculate at 150-200°C and the flocculation is purely a physical phenomenon not a chemical one [17]. As production continues, the reservoir fluids understandably go through composition changes with time, and also, variation with depth. Obviously in a later stage, the reservoir will be poorer of lighter-ends, and as a consequence, GOR will start to diminish after a certain production period and the density of reservoir fluids will increase. When oil looses its lighter-ends, more of the asphaltene content would go into solution with the oil. Therefore, intuitively we would expect lesser problem of asphaltene precipitation in older producing reservoirs.

Data from SARA analysis are used to obtain cross-plots of two ratios, namely, saturate/aromatic and asphaltene/resin. The saturate/aromatic ratio is used as an indication of the solvent power for asphaltenes; for example, higher the aromatics, stronger the asphaltene solvency resulting in more stable asphaltene in the reservoir oil. The asphaltene/resin ratio on other hand indicates the colloidal state of asphaltenes in the oil. As indicated earlier, resins stabilize asphaltene in the oil. Therefore, a low asphaltene to resin ratio ensures a better colloidal stabilization. It is obvious that between the two ratios, the asphaltene/resin ratio has had a greater impact on the asphaltene stability [18]. In order to understand the effect of temperature on onset pressure and precipitation of asphalttenes, it would be rational to use the actual crude oil so that results can be used to mitigate the real asphaltenes precipitation and deposition problems in the field. In conjunction with it, the details of the experimental equipment and procedure are described in the experimental section followed by results and discussion section.

2. Experimental tests

One major limitation of most laboratory studies pertaining to asphaltenes is that they are often conducted using either dead oil or with recombined live-oil. The goal of using recombined oil in tests is to make it as representative of the reservoir oil as possible. However, in spite of our best efforts, a recombined oil sample would not be able to fully represent the oil in its reservoir state because the conventional sampling procedures would require the reservoir oil to go through the biphasic state during its collection. Thus, its asphaltene content would not be retained in its native reservoir state during laboratory tests. Although it is more expensive, single phase bottom-hole sampling is highly recommended to obtain reservoir fluid samples for asphaltene studies. The details of the experimental equipment and procedure are described in the following experimental sections.

2.1. Solid detection system (SDS)

A Solid Detection System (SDS) was used in this study. It consists of a mercury-free, fully visual, PVT cell equipped with fiber optics light transmission probes (source and detector) to measure the onset of organic solids precipitation (due to temperature, pressure, and compositional changes) concurrently with fluid volumetric data. The SDS is designed to operate up to pressures of 69000 kPa and temperatures up to 180°C. The incident laser is mounted on the front of the PVT cell such that its beam passes through the high-pressure sample chamber before reaching the light detector probe. Thus, any changes in the opacity of the crude oil resulting from a density change and/or suspended solids will be registered at the detector. A magnetically coupled stirrer is used to rapidly (1400 rpm) mix the fluid in order to keep any solids suspended and achieve equilibrium conditions following a compositions, temperature or pressure changes. The schematic diagram of the SDS system is illustrated in figure 1.

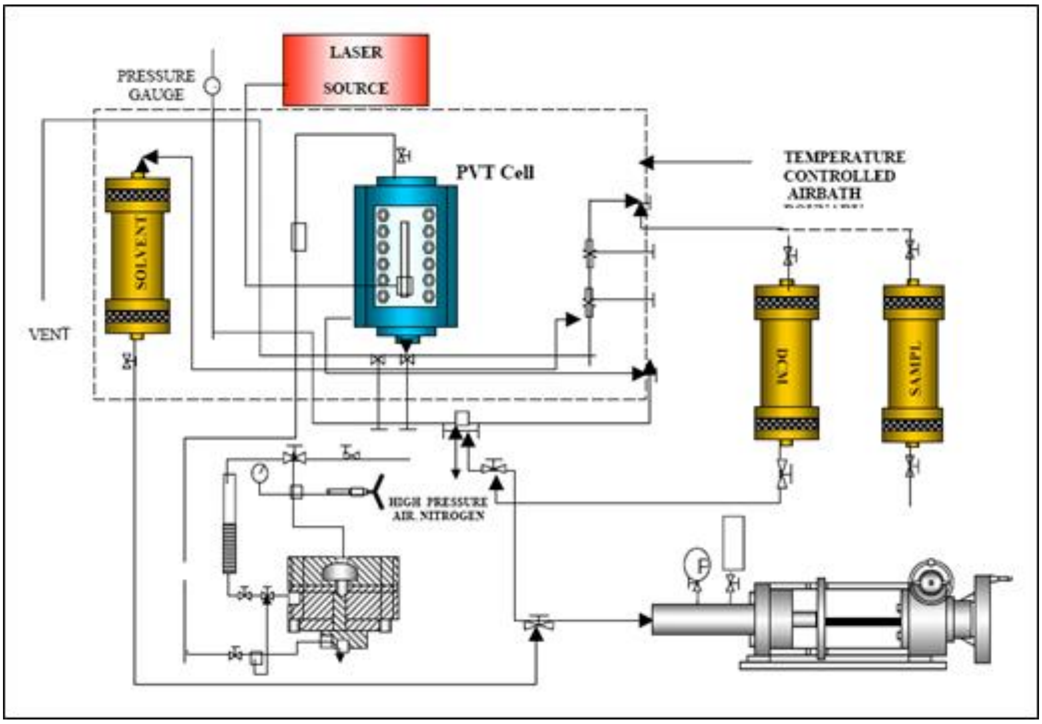

Figure 1 Solid Detection System

2.2. Properties of crude oils

In this work Bottom-hole and Stock-Tank oil (STO) samples from one of Iranian reservoir were used in this study. The crude oil has an API gravity of 34, asphaltene content of 0.3 wt% and GOR value of 1455 SCF/BBL. Table 1 shows the composition of the reservoir fluids. SARA data are shown in figure2.

Table 1 The composition of the reservoir fluid

Components	H_2S	N_2	CO_2	C_1	C_2	C_3	iC_4	nC_4	iC_5	nC_5	C_6
Mol %	0.42	0.08	2.02	48.91	9.14	6.19	1.22	3.22	1.02	1.05	3.23
Components	C_7	C_8	C_9+								
Mol %	2.83	2.79	17.85								

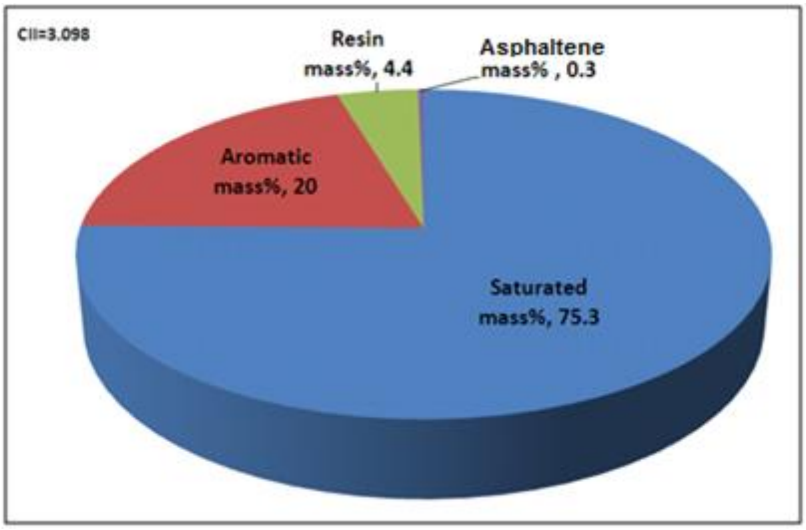

Figure 2 SARA analysis

The stability of asphaltenes in petroleum-crude oils is of utmost concern to oil producers and it varies from crude to crude. Not all crude oils deposit asphaltenes and neither the asphaltene content nor the API gravity of a crude oil is indicative of its propensity to precipitate asphaltenes. The Colloidal Instability Index (CII) is one accurate test for measurement of stability of asphaltenes in crude oils. It considers the crude oil as a colloidal solution made up of the pseudo components: Saturates, aromatics, resins and asphaltenes and expresses the stability of asphaltenes in terms of these components. CII is defined as the sum of the asphaltenes and its flocculants (saturates) to the sum of asphaltene peptizers (resins and aromatics) in crude oil. Empirical evidence has shown that values of 0.9 and more indicate an oil with unstable asphaltene, while values below 0.7 indicate stable asphaltenes. Between 0.7 and 0.9, the stability of the asphaltenes is uncertain [19].

$$CII = \frac{Asphaltene + Saturate}{Aromatic + Resin} \quad (1)$$

In this study CII is equal to 3.098 which is shown an unstable asphaltene in this Iranian reservoir oil and it shows that production from this reservoir encountered to sever asphalttene problems with disasters consequences.

2.3. Sample preparation

It is important for any PVT and asphaltene studies that the Bottom Hole Samples (BHS) is restored at reservoir temperature and pressure and agitated vigorously for some time. The exact period for this process is not known and it depends on the nature of the sample and amount of asphaltene in the sample. According to our experiences from previous studies for Iranian reservoirs, it was concluded that the sample should be restored for at least ten days, before starting any asphaltene studies.

2.4. Procedure of operation

The reservoir fluid was tested for its propensity to precipitate asphaltenes during isothermal pressure depletion at five different temperatures followed by the standard Constant composition expansion (CCE) experiment to measure the bubble point pressure. Initially, around 50cc of BHS were charged into the PVT cell isobarically and isothermally at reservoir temperature and above reservoir pressure (to avoid any asphaltene deposition inside the PVT cell and the pipe lines during charging process). The sample was mixed in the PVT cell for some time to achieve equilibrium. Asphaltene Onset Pressure (AOP) and bubble point pressure (Psat) were measured using SDS (Solid Detection System) by laser spectroscopy. A pressure depletion test was performed isothermally at reservoir temperature from 55160 kPa by 345 kPa (pressure step) and mixed vigorously continuously till equilibrium conditions were achieved. At each equilibrium condition, the final pressure, temperature, laser transmission, volume and time were recorded automatically through a data acquisition system. This process is repeated continuously till the final set pressure (3400 kPa) was reached. After completion of the above test the sample in the cell was re-pressurized to 55160 kPa and mixed vigorously for a 12hrs period and the AOP test was repeated as per above technique. During pressure depletion a decreasing trend of power versus pressure has been established which is called asphaltene onset pressure (AOP). This procedure carried out for five different temperatures and five onset pressures have been detected.

3. Results and discussion

Figure 3 shows the depletion tests for the BHS at reservoir temperature. As shown in this figure the power of transmitted light (PTL) signal increases linearly as the pressure decreases from 55000 to 25000 kPa at five different temperatures. This is due to the decrease in the fluid density with decreasing pressure within this range. The point of departure of the PTL curve from the linear behavior (the maximum PTL value) is interpreted as the onset of asphaltene precipitation. The observed break in the curve is the net effect of two competing processes. The effect of fluid density decreases with decreasing pressure causing an increase in PTL, and the simultaneous increase in size and amount of precipitated asphaltenes tends to decrease the PTL reading.

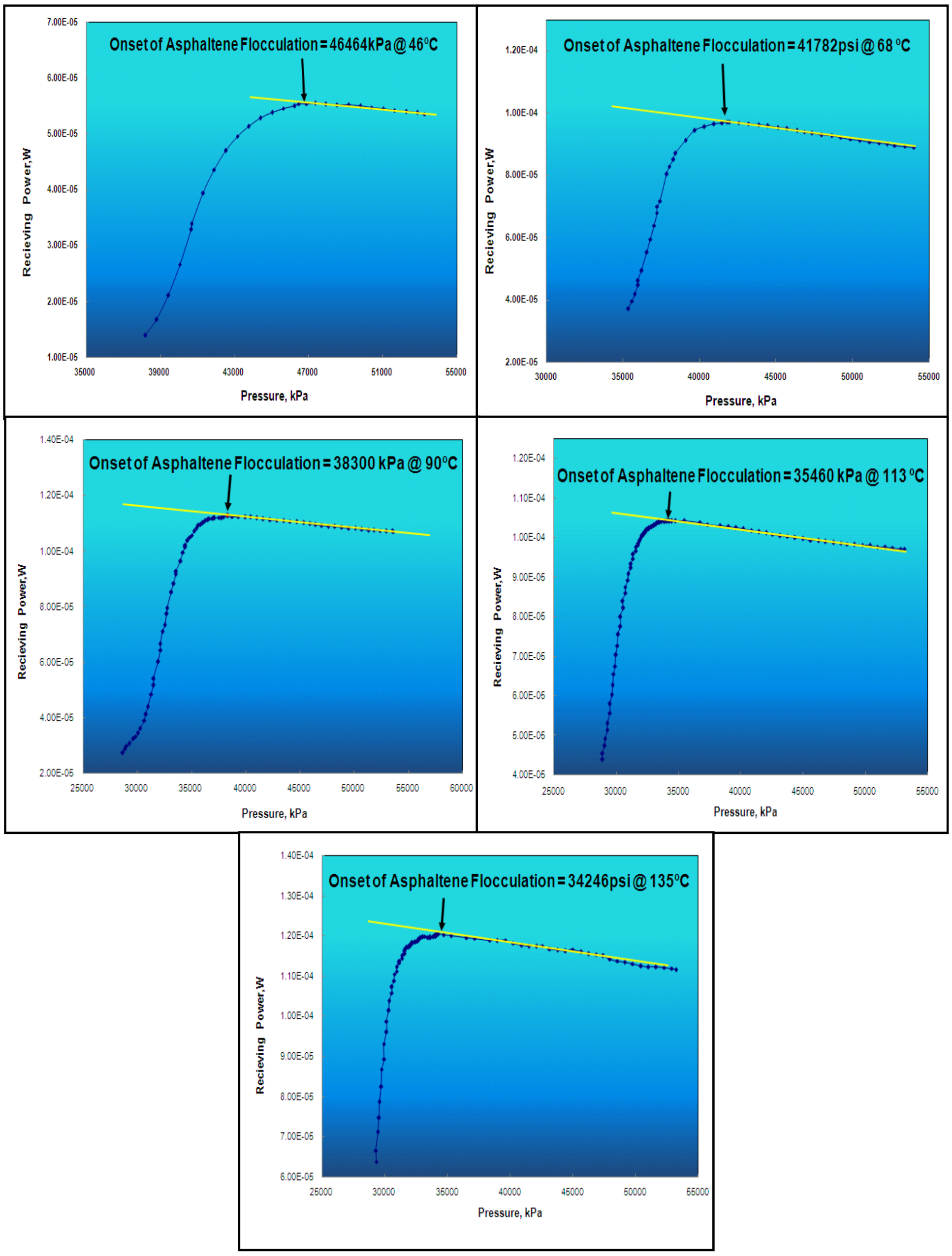

Figure 3 Asphaltene onset pressure (AOP) for five different temperatures

Precipitated, suspended and dissolved asphaltenes in oil is illustrated by the schematic diagram as shown in figure 4. In the figure, precipitated asphaltenes at low temperature are shown in (a), the fully dispersed asphaltenes in oil making a stable colloidal suspension at low temperature is illustrated in part (b) of the figure, partially dissolved and partially dispersed asphaltenes with increase in temperature are represented in the part (c), and the (d) represents a solution of oil and asphaltenes at high temperature. So, it can be assumed that the oils contain more dissolved asphaltenes and less colloidal asphaltenes, at higher temperature.

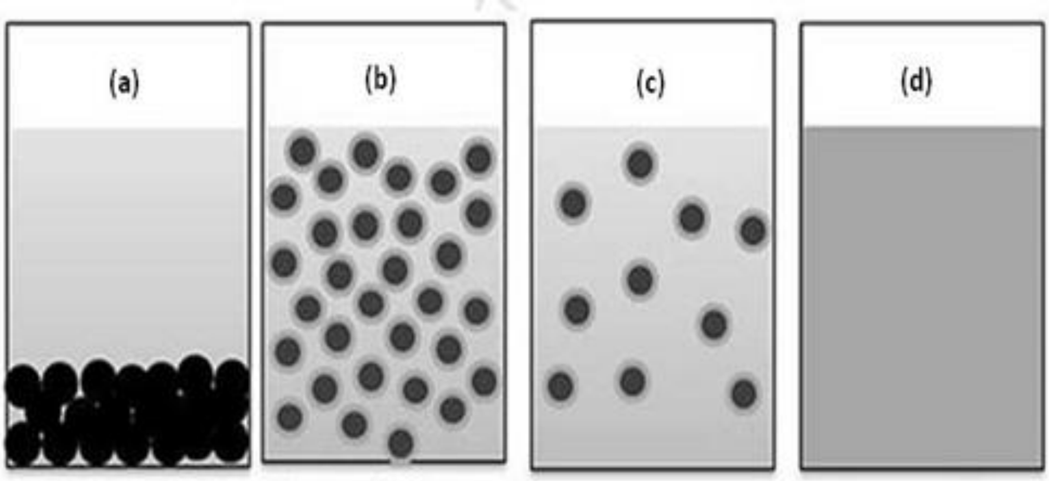

Figure 4 Precipitated, suspended and dissolved asphaltenes in oil

Table 2 P-T and ADE data

Temperature, ºC	Onset Pressure, kPa	Saturation Pressure, kPa
135	34246	25649
113	35460	24709
90	38300	23533
68	41782	22225
46	46464	20736

Asphaltene deposition envelope (ADE) and P_T diagram were developed by drawing onset pressure and saturation pressure values versus temperature respectively, As seen in table 2, as the temperature decreases, the AOP increases, and the bubble point increases.

4. Conclusions

1. A number of AOP tests and PVT analyses were performed on an Iranian bottom-hole sample (BHS) at reservoir pressure and five temperatures.
2. The Colloidal Instability Index (CII) was established for this crude oil and found to be greater than one indicating definite asphaltenes instability and it shows that production from this reservoir encountered to sever asphaltene problems.
3. AOP and CCE tests were performed at reservoir condition. The P- T phase envelope and the Asphaltene Deposition Envelope (ADE) were identified. As the temperature decreases, the AOP increases, and the bubble point increases
4. The observed break in the curve of power versus pressure is the net effect of two competing processes. The effect of fluid density decreases with decreasing pressure causing an increase in PTL, and the simultaneous increase in size and amount of precipitated asphaltenes tends to decrease the PTL reading.
5. It can be conclude that the oils contain more dissolved asphaltenes and less colloidal asphaltenes, at higher temperature.

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