Research Article

Solutions of Asphaltene Deposition Problems and Their Impacts on Petroleum Production

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Abstract

Asphaltene precipitation, flocculation and deposition are known as one of the major challenges in petroleum industry especially in the area of oil production, transportation and processing facilities. There are many factors that enhance asphaltene precipitation such as changing in the chemical composition of the petroleum fluid, changes in temperature or pressure. Asphaltene precipitation may occur also due to blend the heavy crude oil with other light oil or adding diluents. As a consequence of asphaltene deposition; the reservoir permeability is reduced especially near the well-bore region which may cause formation damage, plug-up well tubing and may lead to operational problems. This could lead to decrease the production efficiency.

In this article, we display a survey on the most important factors that effect on asphaltene precipitation, also the composition, physical and chemical properties of asphaltene. Moreover the laboratory methods that detect the onset point of asphaltene precipitation are discussed. In addition methods used for overcoming Asphaltene deposition related issues are mentioned.

Keywords: Asphaltene, Precipitation onset point, Deposition Problems, Heavy Crude Oil

1. Introduction

Crude oil is a complex blend of hydrocarbons, which can be classified into various molecules; saturates, aromatics, resins, and asphaltenes. Among these molecules, the asphaltene (**Fig. 1**) causes many problems during production and crude oil transportation [1]. During production, the asphaltenes deposition causes significant oil production loss as significantly reduces the productivity of wells and sometimes lead to shut off the production of crude oil, rather than it inhibits the process of crude transportation [2-6].

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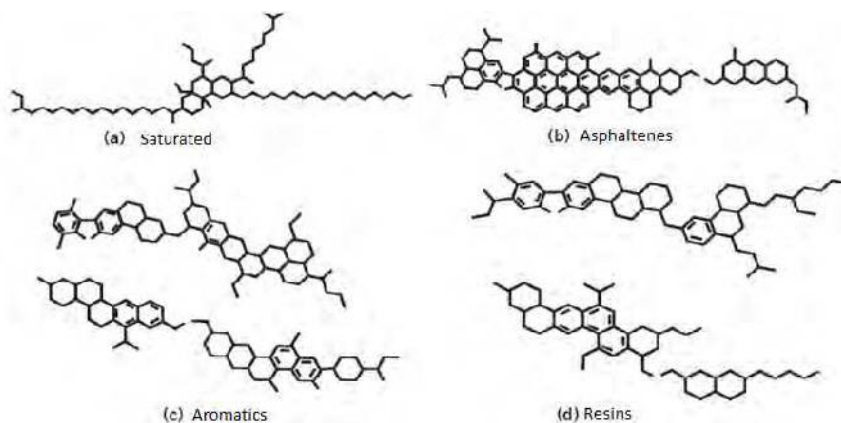
Fig. 1: Structures representing saturated, asphaltenes, aromatics, and resins. Source: Bernucci et al., 2006 [7].

One of the greatest challenges is the handling of heavy crude oil properly to be become economically viable during production and transportation because of the high viscosity and density as well as a relatively high content of heavy component as asphaltenes. Asphaltenes are the most polar and heaviest molecules in crude oils. It is aromatic in nature and contains high ratios of oxygen, sulfur, and nitrogen, and heavy metals, such as Ni, Fe, Cu, and V complexes. Due to its high metallic and sulfur content, the asphaltene fraction is known to poison or inhibit all of the catalytic functions by coking and by deposition of metal sulfides during the reaction in the hydroprocessing process. In addition, asphaltene has been described as a structure of naphthenic and aromatic linkage by aliphatic chains, sulfur bridges and nickel and vanadium structures. The scientist J.B. Boussingault in 1837 [8] was the first who defined the expression "Asphaltene" as the residue of the distillation of bitumen, which soluble in turpentine and insoluble in alcohol [9]. Asphaltenes are defined Nowadays by American Standard Test Methods (ASTM), in terms of its solubility, as the fraction of crude oil that is soluble in aromatic solvents such as benzene and toluene, and insoluble in alkanes, particularly n-pentane (nC5) and n-heptane (nC7) [10].

1.1 Physical properties of asphaltene

Asphaltene is a semi-crystalline solid material with a molecular weight ranges from 1000 to several hundreds of thousands. The boiling point is not clear due to their strong tendency to self-aggregate [11-13]. Various studies have carried out to detect its molecular weight utilizing different logical analytical tests, for example, mass spectrometry and fluorescence depolarization. Tanaka et al. [10] proposed a theoretical asphaltene aggregate hierarchy on the premise of results acquired by means of small-angle X-ray scattering (SAXS), and X-ray diffraction (XRD) and small-angle neutron scattering (SANS). **Fig. 2** shows the hierarchy model for asphaltene aggregation, which can be briefly illustrated as following; (a) – stacking of individual asphaltene molecules to form core aggregates (2 nm), (b) medium aggregates formation (5–50 nm) due to interactions of core aggregates with maltenes, oils, etc., and (c) core aggregates form big size agglomerates (>100 nm) via diffusion- or reaction-limited cluster aggregation (DLCA or RLCA, respectively), which is independent of any media [11].
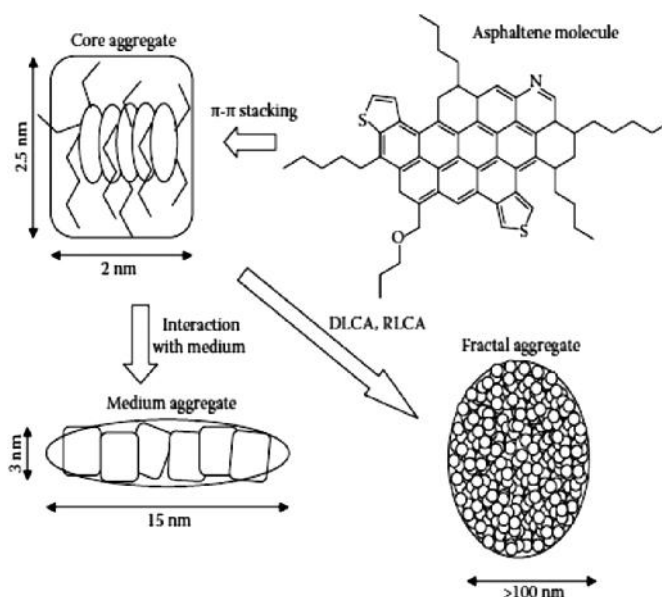
Fig. 2: Hypothetical representation of the hierarchy in asphaltene aggregates based on XRD, SAXS, and SANS data [14].

1.2 Roll of resins

It is generally known that only polar particles such as aromatics and resins have the ability to disperse asphaltene molecules in the oil. In this manner expressing that the asphaltenes are colloidally dispersed in crude oil. The role of resins in stabilizing asphaltenes is well recognized. But the exact mechanism of how the asphaltenes are stabilized in the presence of resins is not well understood.

It was reported that resins adsorb on small aggregates of asphaltene to be peptized with saturates and aromatics in the medium forming a colloidal system. The molecules of the resin fraction are generally considered to be smaller than the asphaltene molecules [11, 15, 16].

It is reported that the asphaltene molecular architecture has been explained by two different proposed models. The first one is called the archipelago model which, Strausz et al. [17] suggested bridging of aromatic moieties via aliphatic compounds. Dickie & Yen [18] reported that the second model is the island model which indicates that asphaltenes molecules are joined to polycyclic aromatic hydrocarbon (PAH) via suspended aliphatic chains. These models were strong and relied upon till few years ago, where new studies using different techniques such as time-resolved fluorescence depolarization (TRFD) [19], mass spectrometry, two-step laser desorption laser ionization mass spectrometry (L2MS) [20], NMR [21] and high-Q ultrasonics [22], appeared to support otherwise. For example; Sedghi & Goual 2010 [23] stated that resin in anhydrous solvent aren't stacked to asphaltene nano-agglomerates which excludes the island-like model and the hypothetical model by Nellensteyn. So it isn't true to say that resin could adsorb on asphaltene surface to form a stable layer model [24]. On the other hand, there will be a great importance for resin on stabilization of asphaltene aggregates when the solvent is mixed with water. It was reported by Magual et al. that resins as well as natural surfactants have the ability to transfer to the water/Solvent interface firstly, and then it may be replaced by asphaltenes [25]. The ratio of resin to asphaltene is the main factor that controls the amount of adsorbed asphaltene on water surface.
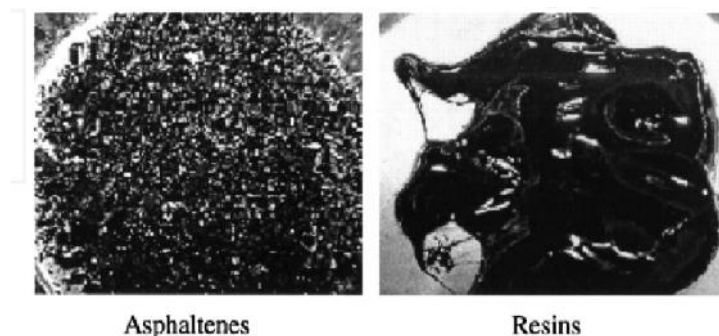
Fig. 3: Separated Asphaltenes and resins from crude oils [26]

1.3 Modified Yen model

The Yen model of asphaltene structure has been used for approximately 40 years. But it has some drawbacks especially in determining the molecular weight and its colloidal structure. Thus there was a need for another approach. Mullins et al conducted a modification for Yen model especially on the asphaltene molecule structure [16]. Schematic diagram of the modified Yen model is shown in Figure 4 in which asphaltene molecule displays both attractive forces comes from interior poly aromatic hydrocarbon and repulsion forces from exterior (outer alkane groups). Due to change in pressure, temperature or chemical composition; asphaltene molecules can attract to each other to form nanoaggregate, and then cluster with higher particle size. Creek et al., 2010 [27] reported that asphaltene aggregates and clusters were precipitated in oil reservoirs due to gravity effects. The size of asphaltene molecules, nanoaggregate and cluster as shown in Fig. 4 were confirmed using different analytical methods.

Fig. 4: Asphaltene structure according to the modified Yen model [16]

2. Asphaltene precipitation and deposition

2.1 Reasons of Asphaltene Precipitation

The instability of asphaltenes in the crude oil inside the oil reservoir is linked to many factors such as the variation in temperature, pressure, and composition of the oil. Such changes can precipitate the asphaltenes aggregates and asphalt. Although a lot of researchers did not differentiate between the two terms, Speight et al. reported that asphalt is the asphaltenes plus resin [28].

In the past decades, a huge amount of conventional oil reserves was depleted, so there was a need to exploit unconventional oil which contains large contents of heavy hydrocarbons with high asphaltene content [29]. Furthermore, most of the old oil fields have lost their natural derived force during production demanding the use of one or more of Enhanced Oil Recovery (EOR) methods. However, the deposition of asphaltenes has noticed from downhole of the reservoir up to surface facilities. Moreover, miscible flooding by carbon dioxide or natural gas as EOR method has a great efficiency in oil recovery, unfortunately, it is considered as one of the most effective reasons for asphaltene deposition due to the alteration of the asphaltene-to-resin ratio of crude oil.

2.2 Determination of Asphaltene instability index

The stability of asphaltenes in crude oil depends on the exact balance between its fraction and the lighter ones of the crude oil. Any change in this balance could prompt asphaltene self-aggregation [29]. The instability index of asphaltene can be determined by Eq. (1) [30]. Decreased concentration of resin enhances the precipitation, flocculation, and deposition of asphaltenes.

Asphaltene instability index = Saturates + Asphaltenes = Resins + Aromatics Eq. (1).

This index can be explained as follows:

If the asphaltene instability index is lower than 0.7; it means dispersed asphaltenes in the oil, while the unstable asphaltenes are found only if the asphaltene instability index was higher than 0.9. A metastable state region asphaltene instability index in the regime of 0.7 – 0.9 indicates medium instability with the considered possibility for asphaltene deposition.

The dissolution effect of crude oil on asphaltene aggregates is affected by the reservoir temperature. Any increase in the temperature is offset by a decrease in oil solvating power of crude oil components [31]. The effect of temperature on asphaltene aggregates still needs more clarifications. Many authors reported that temperature adversely affects the size of asphaltene aggregates [32]. On the other hand, Speight et al. found that the increase in temperature may lead to asphaltene precipitation.

Changing crude oil composition by adding paraffinic components to crude oil increases the chance for asphaltene to precipitate and self-aggregate [33]. Resins re-keep the thermodynamic equilibrium by leaving asphaltenes and solvate in the new additive components which will decrease the crude oil solubility power towards the asphaltenes.

In downstream operations, crude oils blending from different sources may cause asphaltene precipitation and severe asphaltene deposition in processing facilities due to change in the chemical composition of the crude oil [34] which is responsible for various problems, starting from obstruction of production equipment passing through plugging of flow pipelines.

2.3 Asphaltene precipitation related issues

Asphaltene is called as "the bad cholesterol" of oil due to its deposition asphaltene, which is responsible for a lot of serious issues inside the reservoir, during production processes, transportation, and storage of the petroleum fluids (**Fig. 5**). Asphaltene deposition doesn't depend on the asphaltene content of the crude oil as it may deposit in oil even in the presence of a small percentage of asphaltene [29]. As asphaltene solubility in light oil reservoirs is normally low, it contributes to higher destabilization in the crude oil. For example, in Venezuela Boscan oil field, asphaltene doesn't suffer precipitation, although its weight percent reaches 17%. On the other hand, Hassi-Masoud oil field in Algeria with asphaltene content of 0.15 wt. %, the crude oil suffers from a lot of problems during extraction, production storage, and transportation as a result of the precipitation and deposition of asphaltenes [35]. The problem appeared firstly in surface facilities, mainly in oil field separators then along the pipeline. In addition, asphaltene deposited inside tubing at a pressure near the bubble point pressure. During reservoir depletion, asphaltene deposition zone increase and migrate to inside the reservoir. Now today, the transportation of heavy oils and bitumen has become an important issue to the oil industry. It is not easy to be pumped through the pipelines, due to the aggregation and precipitation of asphaltene through the inner wall of the pipeline and formation water in oil emulsion that increases the oil viscosity and the needed high pumping pressure.

Fig. 5: Asphaltenes clogging a pipe [35]

2.4 Formation Damage by Asphaltenes deposiotion

The production system would probably suffer asphaltene deposition anywhere, but the deposition on pore walls of oil formation especially the region near
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wellbore may be the most affected place, which reduces the porosity and permeability in addition, wettability alteration on pore surfaces [36, 37]. This may lead to formation damage.

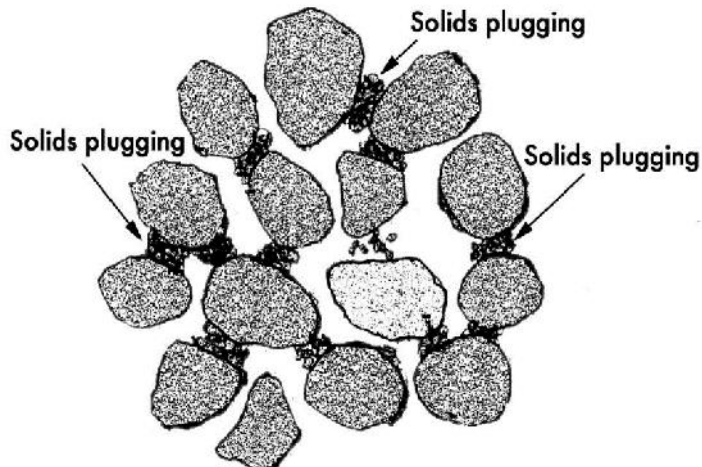**Fig. 6** shows the plugging of the formation-rock pore.

Fig. 6: formation damage caused by solids plugging

3. Determination methods for the onset of asphaltene precipitation

It is critical to identify "when" and "how much" asphaltene will precipitate in finding solutions for asphaltene related issues. Also, precise assurance of the onset of asphaltene precipitation is essential to test existing hypothetical models [38-40]. A few strategies are accessible for determining the onset of asphaltene precipitation and deposition with various degrees of accuracy.

Asphaltene precipitation may start inside the reservoir at pressure higher than the bubble point pressure

during primary recovery of crude oils that are rich in gas content and have low content of asphaltene.

With the decrease in pressure due to reservoir depletion, colloidal asphaltene starts to precipitate then deposit inside the reservoir, tubing and flow lines. Ordinarily, the maximum amount of precipitated asphaltene is at the bubble point pressure.

Gases evolved from the reservoir fluid below bubble point which decrease the amount of saturates and increase the amount of aromatics and resin. This may lead to re solvation of the precipitated asphaltene after remixing the media in good manner [29]. Figure 7 shows the phase diagram of asphaltene inside the reservoir.
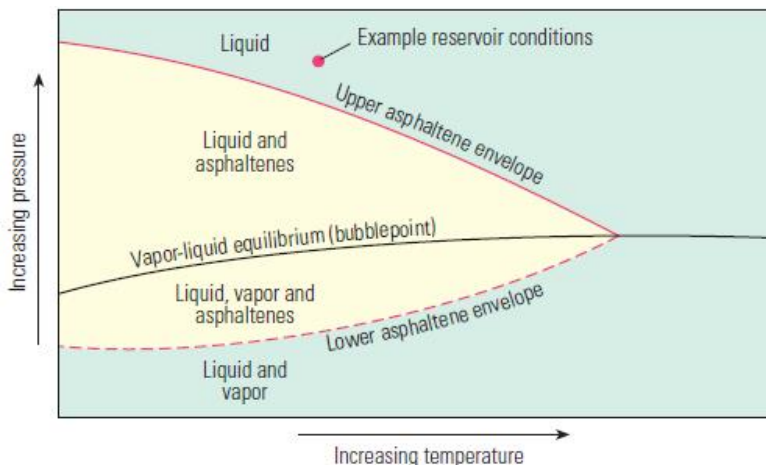

**Fig. 7:** P-T diagram for Asphaltene precipitation onset

There are many methods using PVT cell and high-pressure microscope are used to detect the onset precipitation point inside the reservoir.

3.1 Gravimetric Method

This technique gives information about asphaltene content in the selected sample at different pressure stages while the temperature is constant using a PVT cell. SARA analysis is conducted to portions from the sample at different pressure descending, which shows a decrease in asphaltene content. The accuracy of the results is commitment to the selection of low intervals pressure steps which may consume much more time. Also the onset precipitation point might be missed with large intervals of pressure steps. This is may be one of

most important drawbacks. Another one is the need for high amounts of reservoir fluid.

For example, a live crude oil sample from the Middle East was tested at the reservoir temperature (240°F) using the gravimetric method to detect firstly the onset precipitation point of asphaltene [41]. Then SARA analysis was conducted to determine the content of asphaltene insoluble in n-heptane and asphaltenes insoluble in n-pentane. As shown in **Fig. 8** the asphaltene content is stable with decreasing the pressure till reach a point called upper asphaltene onset at 43 MPa. After that by decreasing the pressure, the asphaltene content decreases till reach the minimum at the bubble point pressure at 22 MPa. Below bubble point pressure there is an obvious increase in asphaltene content.
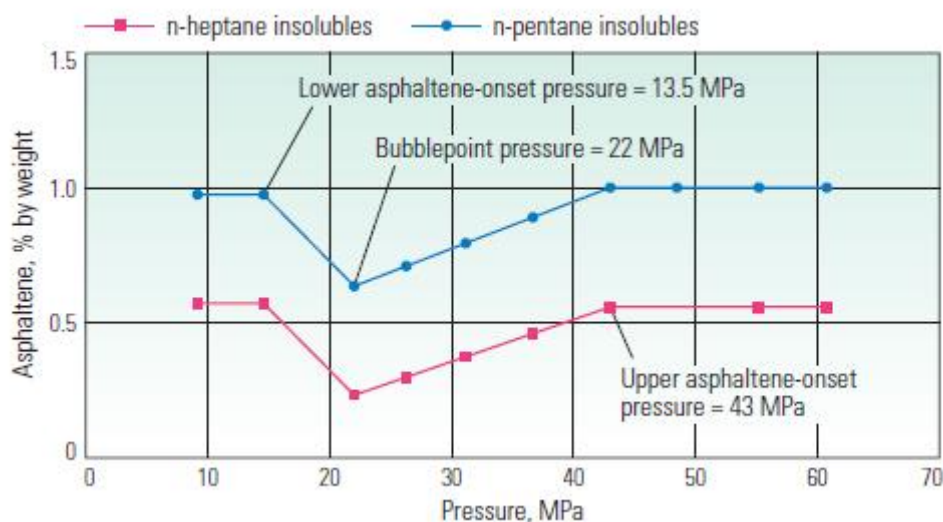
Fig. 8: Gravimetric detection of asphaltene precipitation in Middle East oil [41]

3.2 Filtration

PVT cell with a filter of size 0.22 to 45 micron is used for filtration method to obtain the precipitated asphaltene from the small volume of injected oil. [41-43]. The most important advantage of this technique is that the precipitated asphaltene can be used for further investigation via SARA analysis technique. However, the accuracy of the filtration technique depends on the filter size.

3.3 High-pressure microscopy

PVT cell is used in this method to determine the onset point for the deposition of the asphaltene molecules at different conditions of high pressures up to 15000 psi and temperatures may reach 200 °C, while the roll of high pressure microscope (HPM) is observe the change in size or structure of asphaltenes and the other solid particles versus time, pressure or temperature. [41, 44, 45]. The oil sample is conducted

into the PVT cell at reservoir conditions for mixing and restoration. After that the sample is transferred to the HPM cell under controlled conditions.

3.4 The light-scattering technique (LST)

The light-scattering technique (LST) is also famous for solids-detection system (SDS), in this technique the near-infrared light (NIR) is used to test fluids while asphaltenes may precipitate either isobarically or isothermally. NIR light source is fixed on one side of PVT cell can generate light at wavelength about 800 to 2200 nm. A fiber optical system is fixed on the other side to detect the light transmittance. The light transmittance power is inversely proportional to pressure. By decreasing pressure there will be an increase in light transmitted until reach the onset precipitation point of asphaltene there will be a sharp decrease in transmission power. The advantages of this method are consuming a small volume of the required fluid sample and testing rapidity [41, 43].
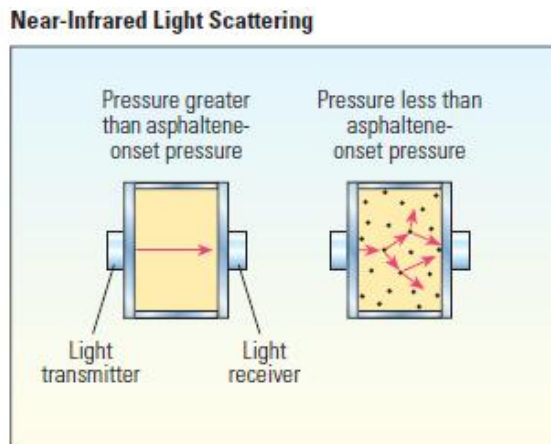
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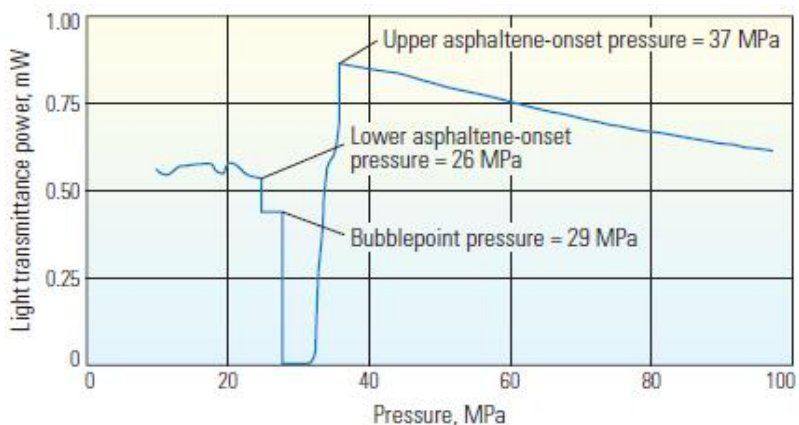**Fig. 9:** simple model for Near-infrared light scattering technique [41]

Fig. 10: Asphaltene precipitation onset via light scattering technique [41]

The onset point of asphaltene precipitation in the pipeline during production can be detected through one of the following methods:

3.5 Spectrometric analysis

Spectrometric analysis is famous for the determination of the onset point for asphaltene precipitation using UV-vis spectrometer at a certain wavelength. The analysis is conducted using either crude oil or asphaltene itself in which asphaltene dissolved in series of heptane/toluene mixture (10-90, 20-80, 30-7 and so on till 90-10 volume percent). The absorbance of the mixtures are determined and plotted against heptane volume percent as shown in **Fig. 11**. The minimum absorbance point is related to the asphaltene onset point of precipitation. The curve can be divided into three segments; the first segment is related to the absorbance of asphaltene which decreased upon the increasing of diluent till reaching a minimum point which is the second segment that corresponds to the onset precipitation of asphaltene molecules. Moreover, the third segment shows abroad absorbance which can be explained as the swelling of the precipitated asphaltenes [46].
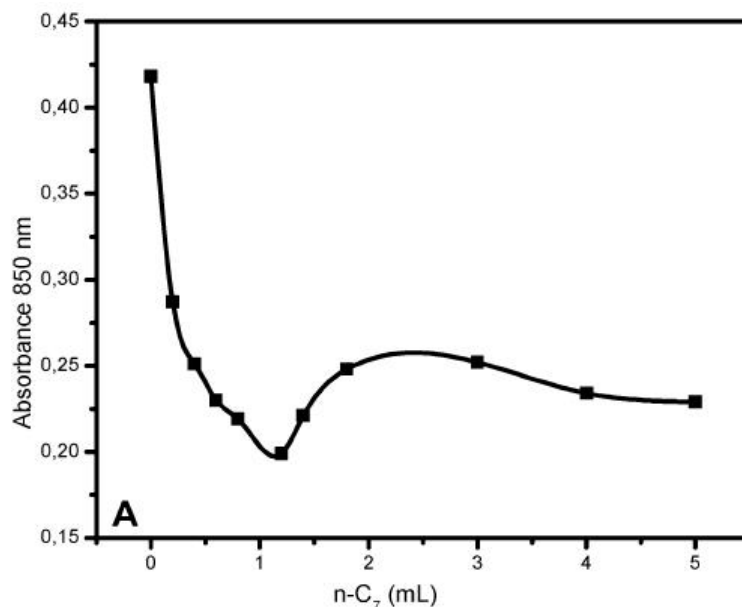
Fig. 11: Onset of precipitation for asphaltene solutions using UV-Vis spectrometer method [46].

3.6 Density

This method is used to detect the onset precipitation point of asphaltenes. It is well known that the addition of n-alkanes to crude oils accelerates aggregation even at concentrations lower than the flocculation threshold. Series of different ratios of n-heptane to toluene mixture is mixed with a certain amount of crude oil then measured with density-meter apparatus. The break of the Plotted curve of oil density versus the added n-heptane volume reflects the onset of asphaltene precipitation [47]. This method could be generalized to dead and live oil.

3.7 Viscometric method

The viscometric method was used to study the threshold of asphaltene precipitation. In this method, the onset point was determined by titration with n-heptane as an asphaltene precipitant.

Fig. 12 shows a general reduction in kinematic viscosity with the increment in the n-heptane to oil ratios. The curve shows a flat area of a kinematic viscosity value, which indicates the asphaltene precipitation onset point, while the decrease of viscosity after the threshold point is due to the dilution of the solvent [38].
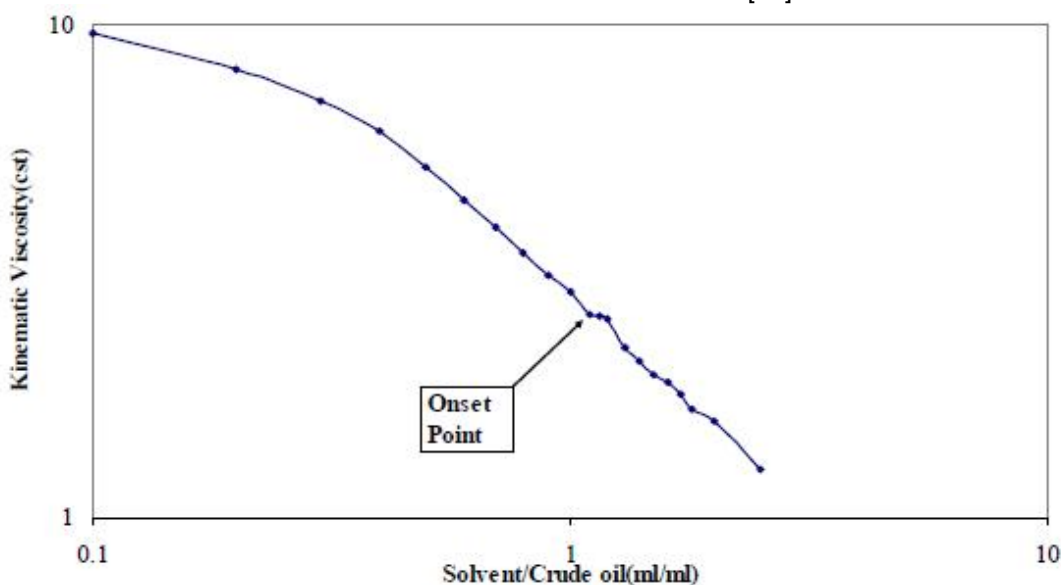

Fig. 12: Kinematic viscosity vs. solvent/ crude oil ratio [38]

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4. Solutions for issues related to asphaltenic crude oil transportation

There are several options to overcome the asphaltene related issues during transportation via pipeline such as;

4.1 Mechanical treatment

It includes manual stripping, mechanical vibrations, pigging, etc. manual stripping is the oldest method known for the removal of deposited asphaltene or deposited heavy hydrocarbon generally. It is done by mechanically scraping the tubing. Pigging technology is well established, but it is most suitable for foams and wax deposit removal. Although this method may be effective for cleaning the tubing and lines to some extent, it is not effective in removing the heavy organic deposits at the formation. Also, mechanical removal of deposits may need operation shut off the disposal of the deposits sometimes causes difficulties.

4.2 Dilution

In this method, the crude oil is being blended with the diluents such as xylene or blended with lighter crude oil. These blends may be efficient to some extent and bring down the viscosities of heavy oils, but it consumes much money.

4.3 Heating

This technique can be used either inside the reservoir as an Enhanced Oil Recovery technique or along with the pipeline. Heating consumes a lot of energy, so it is usually used only for short distance pipeline transportation. Partially upgrading on the production site needs a large capital investment to build cookers or hydro-processors with high operating cost, while In-situ upgrading is still in the research phase.

4.4 Chemical treatment

There are different possible ways to reduce the frictional pressure loss in the transportation of oils via adding a drag reducing polymer, transporting the oil as an oil-in-water emulsion, or adding asphaltene dispersants. There is a promising pipeline technique is the transportation of viscous crudes as concentrated oil-in-water (O/W) emulsions. The technical viability of this method was demonstrated in an Indonesia pipeline and in California. In this method, with the aid of suitable chemicals (asphaltene dispersant and water-soluble surfactant), the oil phase becomes dispersed in the water phase and stable oil-in-water emulsions are formed. The formation of such emulsion causes a significant reduction in the emulsion viscosity [48, 49].

Several asphaltene dispersants with different physical and chemical properties have been assessed. **Fig. 13** shows the chemical structure and the polarity of the compounds.
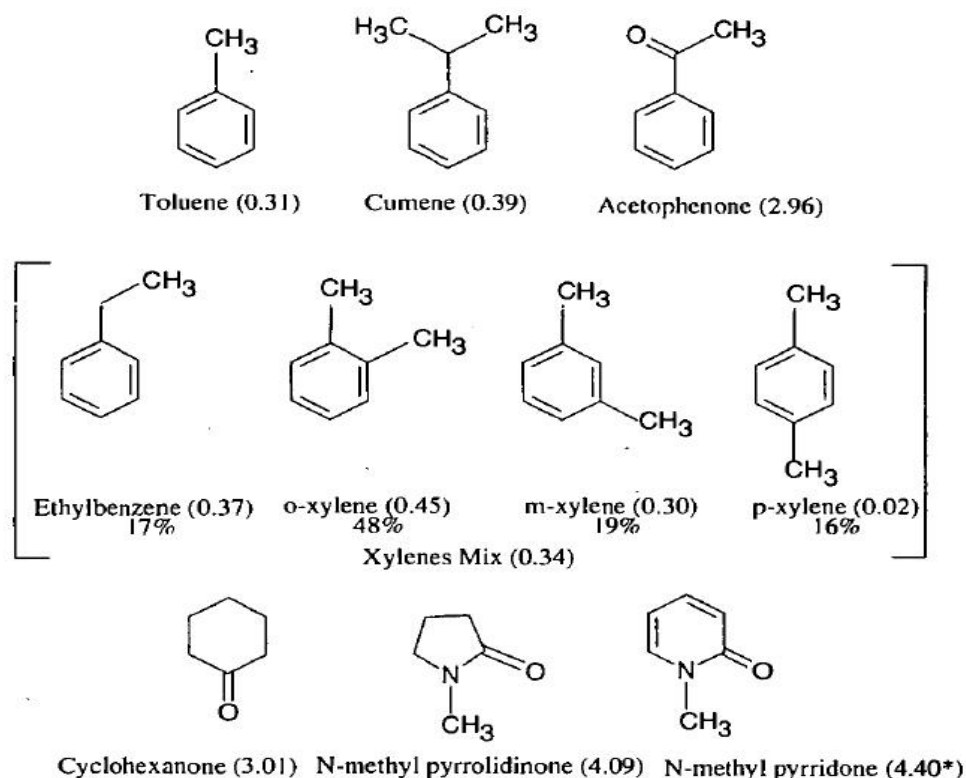
Fig. 13: Chemical structures and polarities (in Debye units) of the additives used [50].

The compounds were chosen for their ring type structures. The presence of electrons in the ring plays a role in the interaction between the compounds added and the electrons in the polyaromatic core of the asphaltene agglomerates. The compound characteristics must have at least one benzene ring that can do -complexation with asphaltene moieties to easily penetrate into asphaltene agglomerates and detached some asphaltene compounds from each other.

Based on the previous literature, phenol formaldehyde resins and alkyl benzene derivatives are the most proper dispersants according to their structures. It is, therefore, worthwhile to look at chemical ways for asphaltene dispersion and supplementing the role of asphaltene in the emulsion formation to change the high viscosity water in oil (w/o) to low viscosity oil in water (o/w) emulsions. In this context, some new compounds will be prepared with specific characteristics that have the ability to disperse the agglomerated asphaltenes that play a key role in the formation of w/o emulsion.

5. Conclusion

Asphaltene is the polar part in crude oil, which is dispersed in the form of colloidal clusters. There are many reasons for asphaltene precipitation during oil production processes such as the change in crude oil composition, pressure or temperature as a result of gas injection, phase separation, addition of solvents or mixing of fluid streams. Due to deposited asphaltene is responsible for a lot of serious issues inside the reservoir, during production processes, transportation and storage of the petroleum fluids, It is important to know and determine the onset point for asphaltene precipitation. This helps on solving the asphaltene precipitation related issues. Several different methods have been proposed to determine the onset of asphaltene precipitation such as: Gravimetric Method, viscosity measurement, density measurement, microscopic measurement, filtration techniques, heating transfer-based method, electrical conduction technique, light scattering method, spectrophotometric and UV method.

Since each technique has its special definition for onset, which may be the onset of precipitation, flocculation or deposition; it is important to recognize the differences according to the physical mechanism for each technique. These have been widely used to explain crucial fundamental properties.

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15