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On the evaluation of the performance of asphaltene dispersants

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ABSTRACT

Asphaltene precipitation and subsequent deposition is a potential flow assurance problem for the oil industry nowadays. Moreover, because oil production is moving to more difficult production environments – e.g. deeper waters – or is focusing on extracting residual oil using enhanced oil recovery techniques, the significant changes of pressure, temperature and/or composition can aggravate the asphaltene deposition problems. One of the most common strategies to prevent or at least reduce asphaltene deposition is the utilization of chemical additives. However, there are still several unresolved challenges associated to the utilization of these chemicals: First, the experimental conditions and results obtained in the lab are not always consistent with the field observations. Also, in some cases these chemical additives seem to worsen the deposition problem in the field. Therefore, there is a clear need to revisit the commercial techniques that are used to test the performance of asphaltene inhibitors and to provide a better interpretation of the results obtained. In this work, a technique based on NIR spectroscopy is presented to evaluate the performance of three commercial asphaltene dispersants. The method presented in this work is faster and more reproducible compared to the available methods such as the Asphaltene Dispersion Test (ADT) and the Solid Detection System (SDS). Also, unlike the ADT test, our proposed method can evaluate the performance of the dispersants in a wide range of temperatures and compositions. The experimental evidence shows that the asphaltene dispersants neither shift the actual onset of asphaltene precipitation nor reduce the amount of asphaltene precipitated. We believe that some results that have been reported that suggest that asphaltene dispersants can actually shift the onset of asphaltene precipitation are an unfortunate combination of insufficient sensitivity of the commercial instruments used and the slowing down of the asphaltene aggregation process by the effect of the added dispersants. The chemical additive dosage, aging time and temperature effect on the asphaltene aggregation process are also discussed in this manuscript.

With this work we aim to contribute to a better understanding of the variables that affect the performance of asphaltene dispersants, and the effect that these chemicals have on the complex multi-step mechanism of asphaltene precipitation and aggregation.

1. Introduction

Asphaltenes are defined as a poly-disperse distribution of the heaviest and most polarizable fraction of the crude oil. Asphaltene characterization [1–4], chemical structure and physicochemical properties are still under investigation [5–8]. Precipitation and deposition of asphaltenes are phenomena induced by changes in pressure, temperature and composition [9,10]. During pressure depletion at low enough pressures, the asphaltene precipitation onset is reached and asphaltenes begin to precipitate [9]. At these conditions the oil expands and becomes a poor asphaltene solvent. Once asphaltenes precipitate, a multistep process begins, which involves aggregation, diffusion, advection and finally deposition of the asphaltene aggregates [9]. Oil production from deeper waters [11] and enhance oil recovery operations such as carbon dioxide injection [12], tend to worsen asphaltene deposition. Potential solutions for asphaltene deposition include physical deposits removal [10], solvent washes [10,13] and chemical treatment with appropriate additives [14–16].

Asphaltene deposition in reservoirs, wells, and facilities severely impacts the oil production economics [17]. It can cause formation damage and wellbore plugging, which require expensive treatment and clean-up procedures [14], even in some extreme cases a wellbore can be completely plugged [9]. For the Gulf of

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Mexico oil fields the economic impact associated with this problematic has been estimated in USD $70 M per well (wet tree) when well shut in for ring interventions is required [18]. If the deposition occurs in the surface controlled subsurface safety valve (SCSSV) the cost increases to USD $100 M per well. Downtime losses based on a 10,000 BBL per day production and oil price of USD $60 per barrel, can reach up to USD $600,000 a day. Replacing a lost well with a side track raises the cost to around USD $150 M [18]. Chemical additive injection for typical Gulf of Mexico production of 10,000 BBL/day, represents costs estimated in a range between USD $330,000 and USD $390,000 per well per year [18]. For Middle Eastern fields chemical additive injection represents costs in a range between USD $31,000 and USD $46,000 per well per year [19].

The cost of installing and maintaining asphaltene mitigation equipment and chemicals is in the millions of dollars per year [11]. Differentiation between cases with substantially impaired production requiring well intervention from those with minimal or no wellbore deposition could save the expense of installing unnecessary equipment and injecting chemical inhibitors when they are not needed as well as helping in the development of improved chemicals for prevention of wellbore deposition problems [11].

Extensive research has been already conducted to elucidate the variables that affect additives performance [15,17,20–23]. It has been reported that asphaltene characteristics [21,24,25], solvent condition [15,23,26,27], additive structure [20,21,27], and additive amount adsorbed on asphaltenes [2,23,26] influence additive performance. In the case of dispersant additives it is accepted that dispersant interaction with asphaltenes decreases the aggregates size of precipitated asphaltene and/or hinders possible subsequent aggregation [28]. However, in other cases the dispersants seem to promote the aggregation [23]. The study of asphaltene dispersant additives has shown that additives can have different performance, acting as stabilizers, enhance aggregation or they can have no effect [14]. Chemical additives efficiency is typically measured in terms of a delay in the detection of asphaltene precipitation [15,29,30]. At this point it is important to alert the reader that asphaltene precipitation is a necessary but not sufficient condition for asphaltene deposition [9,31].

Some methodologies such as microscopy [10,32], polarized light microscopy [33], solid detection system [15], filtration [22], filter drop spreading method [29,34] and spectroscopy [35] have been used to evaluate the performance of chemicals intended to reduce or prevent asphaltene deposition problems. One of the most common and widely used commercial techniques is the Asphaltene Dispersion Test (ADT) [12]. To evaluate the tendency of asphaltenes to precipitate and the efficiency of chemical additives, the ADT uses normal gravimetric sedimentation measured over a period of time after diluting the oil with an asphaltene precipitant such as n-heptane [12].

The Solid Detection System (SDS) is another technique that is used by service laboratories to evaluate the stability of asphaltenes. Unlike the ADT test, the SDS can analyze live oil samples at high pressure and high temperature (HPHT) to determine the asphaltene onset pressure (AOP) with and without the addition of asphaltene dispersants.

In this work, a technique based on NIR spectroscopy is presented to evaluate the performance of three commercial asphaltene dispersants at ambient pressure. This technique is faster and more reproducible compared to the available tests such as the Asphaltene Dispersion Test (ADT) and the Solid Detection System (SDS). Furthermore, we have been able to reproduce the effect of inhibitors on the shift of the onset of asphaltene precipitation that is obtained by the Solid Detection System (SDS) at high pressure and temperature, using dead-oil samples at ambient pressure. The experimental evidence shows that the asphaltene dispersants neither shift the actual onset of asphaltene precipitation nor reduce the amount of precipitated asphaltene. We believe that the results obtained by the SDS that suggest that asphaltene dispersants can actually shift the onset of asphaltene precipitation are an unfortunate combination of insufficient sensitivity of the instrument and the slowing down of the asphaltene aggregation process by the effect of the added dispersants. The chemical additive dosage, aging time and temperature effect on the asphaltene aggregation process are also studied in this work.

2. Experimental section

2.1. Materials

Experiments were conducted with crude oil S and crude oil A from the Middle East. The crude oil S was decanted and centrifuged to remove aqueous phase and suspended particles. The properties for this crude oil have been reported previously [36], and are listed in Table 1 along with the properties of the crude Oil A. The commercial asphaltene dispersants 8, 9 and 15 were used to treat the crude oil samples. All the reagents used for the experiments were a high performance liquid chromatography (HPLC)-grade and were procured from Sigma–Aldrich.

2.2. Asphaltene dispersant test (ADT)

The crude oil S was treated with dispersants 8, 9 and 15. Different chemical dosages were tested. For dispersant 8, 9 and 15, 70 and 500 ppm were prepared and analyzed. All the solutions were prepared by diluting a concentrated solution, e.g. 3000 ppm, of the corresponding dispersant in crude oil. The homogenization of the sample was achieved in a closed beaker for a period of one hour using a magnetic stirrer at 700 rpm. 250 μL of the corresponding crude oil sample were placed in graduated centrifuge tubes and mixed with 9.75 mL of n-heptane. A sample of crude oil with no dispersant was used as a control.

Finally, the samples were left undisturbed for a specific period of time (also known as aging time) and the amount of sediment obtained was recorded in mL at the end of the experiment. The aging times used were 1 h, 24 h and 1 week. When no sediment was observed the data entry was recorded as "clear" and when precipitation was observed but it was not measurable the data entry was recorded as "trace" [12]. The criterion for evaluation of the performance of dispersants using the Asphaltene Dispersion Test (ADT) consists in comparing the amount of sediment obtained in mL for the different chemicals and dosages with respect to the control or untreated oil, which was the mixture of crude oil and n-heptane without the addition of the dispersant.

2.3. Solid detection system

This instrument measures the transmittance of light at a fixed wavelength in the near infrared (NIR) region it is usually combined

Table 1
Crude oil A properties at 15 °C and 1 atm and crude oil S properties at 20 °C and 1 atm.

Property	Crude oil S value	Crude oil A value
Density (g/cm^3)	0.843	0.763
Molecular weight (g/mol)	193	177
Viscosity (cP)	9.5	1.057
Saturate (wt%)	66.26	68.9
Aromatic (wt%)	25.59	21.8
Resin (wt%)	5.35	7.1
n-C_5 Asphaltene (wt%)	2.8	0.5