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How much do you know about the methods for determining onset of asphaltene precipitation?

Mohammad Mahdi Shadman, Amir Hossein Saeedi Dehaghani*, Mohammad Hasan Badizad

Faculty of Chemical Engineering, Tarbiat Modares University, P.O. Box: 14155-4838, Tehran, Iran

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ABSTRACT

One of the major problems in all area of petroleum industry, including production, operation, storage and transportation, is formation of heavy organic compounds, e.g., asphaltene and wax, and their consequent deposition in equipment and pipelines. Change in crude oil composition, temperature and pressure leads to asphaltene precipitation. Thus, it is of vital importance to determine onset of asphaltene precipitation during oil production. In this regard, various techniques have been suggested in literature, each with its own pros and cons. However, from practical point of view, one needs to decide which method serves to be proper one. To this end, present study gives a comprehensive critical review for different techniques serve to determine onset of asphaltene precipitation along with comparing their advantages and disadvantages. Since each method presents its own definition for onset, such as onset of precipitation, clustering and deposition; it is necessary to distinguish their difference based on underlying physical mechanisms. It was concluded that mechanism of asphaltene precipitation for determining onset of asphaltene precipitation plays a substantial role.

1. Introduction

1.1. Significance of asphaltene precipitation

The asphaltene deposition during natural production and hydrocarbons processing is a cumbersome facing petroleum industry [1]. The asphaltene deposition has been observed from oil reservoir up to processing equipment [2]. By depletion of conventional reserves, oil industry tends to exploit deeper reservoirs containing heavy hydrocarbons with high asphaltene content [3]. In addition, most old fields have lost their natural energy demanding Improved Oil Recovery (IOR) methods [4]. Applying such methods aggravates asphaltene deposition to be a major issue of current status of oil industry [5]. To tackle this issue, one primarily should characterize asphaltene deposition phenomenon [6]. It has been well understood that any change in crude oil thermodynamic conditions such as composition, temperature and pressure, disturbs equilibrium state of its heavy organic components, e.g., asphaltene and wax. Consequently, these components would deposit while passing through porous media and pipelines. Removing asphaltene deposition often requires costly remediation operations [7].

Identifying operating conditions at which asphaltene deposition occurs, have a significant contribution to maintain economic stability and success of long-term production [8]. Therefore, developing a robust thermodynamic model to predict phase behavior of asphaltene is of crucial importance in order to choosing suitable solvents and inhibitors to delay asphaltene precipitation in oil reservoirs [9].

1.2. Mechanism of asphaltene flocculation and deposition

Generally, asphaltene represents a fraction of crude oil compounds, which tends to form a solid-like phase once adding light

* Corresponding author.
E-mail address: asaeedi@modares.ac.ir (A.H. Saeedi Dehaghani).
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hydrocarbons, normally n-heptane, into the crude [10,11]. It is believed that asphaltene particles are partially dissolved in oil as colloidal or micellar form due to mean polarity of crude oil and presence of stabilizing compounds, e.g., resin [12,13]. In recent years, precipitation, flocculation and deposition of these molecules have been identified and analyzed [14]. As an important point, one should distinguish physical implication of these words; ***precipitation***, ***flocculation*** and ***deposition***.

Precipitation denotes formation of semi-solid phase by aggregation of solid particles [15]. After beginning the precipitation process, particles with sizes of about 1 micrometers are formed through clustering process, which is called flocculation stage [16]. In other words, formation of large aggregates from smaller ones is called flocculation [17]. At the end, during deposition, asphaltene particles are formed on a surface, e.g., pipe wall or rock [18]. Precipitation does not necessarily result in deposition, however, could be of effective contribution in deposition process [19,20].

Asphaltene precipitation is a function of pressure, temperature and crude oil composition [21]. In contrast, deposition depends on amount of adsorbed clusters adhered on the solid surface [22]. After deposition, flocs could be totally or partially dissociated into smaller aggregates which are called *Flocs Dissociation*. During deposition process, flocs could clog holes of porous media or break into smaller particles due to shear forces [23,24]. Fig. 1 illustrates sequential mechanisms of asphaltene precipitation and deposition phenomena.

As a matter of fact, there are three distinct transition phases during asphaltene separation from bulk of oil phase, in sum:

1) Asphaltene Precipitation Onset (APO)
2) Asphaltene + Resin-Flocculation Onset (ARFO)
3) Asphaltene + Resin-Deposition Onset (ARDO)

APO, ARFO and ARDO are defined as the points at which asphaltene start to precipitate, flocculate and deposit, respectively, once adding paraffinic hydrocarbons into oil [25,26]. Accurate estimation of APO, ARFO and ARDO is of practical importance for design of oil-related processes and operations [25,27].

To date, various methods have been proposed to characterize asphaltene formation phenomena, including: visual microscopic measurement, particle size distribution, fluorescence spectroscopy, density measurement, acoustic methods, and so forth [28–30]. In this regard, some questions have intrigued researchers. Firstly, which onset is determined by these methods, precipitation or flocculation? What is the range of applicability of each method? And, most importantly, are these methods applicable for live oil?

In spite of sparse investigations reported in asphaltene literature, it is worth examining different onset determination techniques to approach preceding questions. To this end, present work gives a critical review to evaluate aforementioned techniques based on their advantages and drawbacks. Also, we attempt to answer accurately and scientifically the foregoing questions.

2. Methods for determining onset of asphaltene precipitation

There are different approaches used to record onset of asphaltene precipitation in crude oil, such as: viscosity measurement [31], filtration techniques [3,32,33], heat transfer-based approaches [34], electrical conduction [35] and density-based techniques [36]. It should be noted again that precipitation means forming a solid-like phase, and so all the preceding methods investigate appearance of this phase. Contrary to common belief, flocculating is aggregation state where asphaltene is still in solution phase [37]. Detailed discussion of preceding methods are presented in following sections.

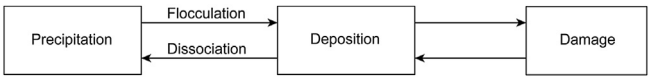

Fig. 1. Mechanism of asphaltene precipitation phenomenon [58].

2.1. Viscosity measurement

Mansoori and Escobedo investigated crude oil viscosity alteration by adding precipitant solvent [31,38]. They observed a point where viscosity is markedly increased, which is considered as the onset of precipitation, as shown in Fig. 2. Such increase in viscosity was attributed to incipient of precipitation process and entanglement of asphaltene molecules.

2.2. Filtration technique

In this method, contents of a PVT cell are mixed together using a magnetic mixer during the whole period of depressurizing process, and then a small amount (about 10 ml) of mixed fluid is passed through a 0.45 micrometer hydrophobic filter at high pressure and temperature [3,32,33]. Filtration is done at ambient condition. The back of filter is pressurized using stable hydrocarbon gas at lab pressure. Remaining material on the filter is analyzed based on SARA separation [33].

2.3. Heat transfer-based approach

Pruden and Clarke obtained onset of asphaltene precipitation by measuring heat transfer in a layer of deposition at the bottom of solution formed by mixing a precipitant solvent with crude oil. This method is applicable for high pressure and temperature systems [34].

2.4. Electrical conductivity

Measuring crude oil electrical conductivity during adding precipitant solvent could be an identification method for onset of asphaltene precipitation [39]. By gradually increasing the

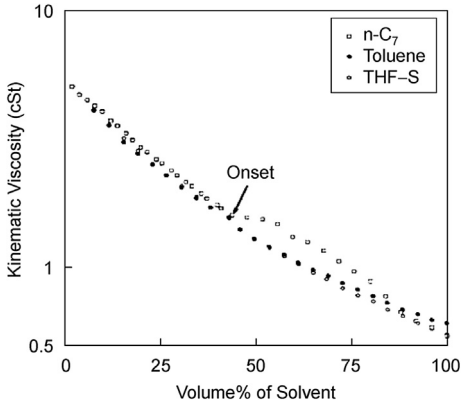

Fig. 2. Kinematic viscosity versus volume % of added n-heptane to oil sample [31,59].