Experimental evaluation of asphaltene inhibitors selection for standard and reservoir conditions

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ABSTRACT

Asphaltene precipitation is a serious technical problem in petroleum industry. Several procedures are used to remove or prevent asphaltene precipitation, but the uses of asphaltene inhibitors provide the most practical and economical solution for deposits treatment. In this study, several effective impacts of inhibitors (salicylic acid, phthalic acid, nonylphenol, phenanthrene, benzoic acid and IR95) on asphaltenes were investigated including decrease in the amount of asphaltene precipitation at standard and reservoir condition, onset shifting, and asphaltene deposition at reservoir condition. During static and onset shifting tests, the hydroxyl group in inhibitors creates a compact planar phenol structure which seems to make a stable π–π interaction with the asphaltenes. In this case, salicylic acid creates an effective π–π interaction with the asphaltenes in a way that the carboxyl functional group and the extra hydroxyl group (–OH) on benzoic ring can strengthen the attachment with the asphaltenes because of the polarity. Results of dynamic test reveals that the adsorption of anionic chemicals in carbonate reservoirs is expected to be high because of the expected positive surface charge of carbonate minerals. The amount of adsorption of anionic chemicals on minerals is expected to depend on the surface charge of the mineral. Salicylic acid has an extra hydroxyl group on benzoic ring and with 34% asphaltene precipitation reduction has the best efficiency among non-commercial inhibitors. On the other hand, high capability of IR95 to be adsorbed on the porous media restarts the ability of asphaltene particles for precipitation on the pore surface.

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1. Introduction

Several authors defined asphaltene over the years, from 1924 by Nellensteyn (1924) up to 2006 by Wang et al. (2006). They described asphaltene as the portion of oil that is soluble in aromatics like benzene and toluene and insoluble in straight chain n-alkenes such as n-pentane or n-heptanes.

The phenomenon of asphaltene deposition has become a severe problem to almost all petroleum production, processing and transportation facilities. The precipitation of heavy organic solids especially asphaltenes in reservoirs, wells, and facilities has a detrimental effect on the economics of oil production because of reduction in well productivity and clogging up of the production facilities.

Asphaltenes remain in solution under reservoir temperature and pressure conditions and begin precipitating when the production temperature or pressure drops below onset conditions. 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 (Kokal and Sayegh, 1995).

The Colloidal Instability Index (CII) is one accurate test for measurement of stability of asphaltenes in crude oils. It considers the crude oil a colloidal solution made up of the pseudo components: saturate, aromatic, resin and asphaltene 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 oils.

$$CII = \frac{Asphaltene + Saturate}{Aromatic + Resins}$$

Empirical evidence has shown that values of 0.9 and more indicate 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 (Gaestel et al., 1971).

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Measures for solving and stabilizing asphaltene precipitation and deposition problems are typically three fold: (a) the development of theoretical models (Vasquez and Mansoori, 2000; Pacheco-Sanchez and Mansoori, 1998; Victorov and Firoozabadi, 1996; Islam, 1994); (b) the study of asphaltene interfacial and colloidal behavior in crude oils and model systems (Ramos, 2001; Ramos et al., 2001; Mohamed et al., 1999a; Carbognani, 2001) and; (c) the estimation of chemical additives for the inhibition of asphaltene precipitation (Chang and Fogler, 1994a, 1994b; Mohamed et al., 1999b; Gonza´lez and Middea, 1991; Rogel and Leo´n, 2001).

Minssieux (1997) studied the flow properties of asphaltenic crudes and carried out core floods experiments with an oil asphaltene content in the range of 0.1–6% weight in various rock materials. It was concluded that the gradual surface deposition is the damage mechanism in pore space.

Different chemistries for asphaltene inhibition have been developed and evaluated at recent years (Squicciarini and Yen, 2007). Asphaltene inhibitors act in a way similar to resins, peptizing the asphaltenes and keeping them in solution. The effectiveness of inhibitors is controlled primarily by their chemical and structural characteristics. However, the inhibitor ability to stabilize asphaltenes depends also on the solvent or dispersion medium (Chang and Fogler, 1993).

A few studies have presented alternatives to identify and develop more effective substances. Nevertheless, due to the complex nature of the crude oils it is necessary to estimate these substances with as many types of crude oils as possible in order to obtain more sustainable results. Usually, the studies have addressed the use of nonionic amphiphiles, such as the ethoxilated nonylphenol for asphaltene stabilization process (Gonza´lez and Middea, 1991; Loh et al., 1999; Mohamed et al., 1999b; Ramos et al., 2001; Ibrahim and Idem, 2004a), and the importance of acid–base interactions for asphaltene dissolution process in aliphatic solvents (Chang and Fogler, 1993, 1994a, 1994b; Ramos et al., 2001).

Conceptually, there are at least two mechanisms by which a chemical inhibitor could prevent asphaltene deposition in the reservoir and down-hole facilities:

In the first case, the inhibitor may be effective in the bulk of the crude oil so that when it is dissolved above a given concentration, it keeps asphaltenes either in solution or as a stable dispersion. This is the way in which inhibitors are generally supposed to be effective and is the case for which quantitative conclusions have been drawn in this work by the static and onset shifting tests.

Alternatively, the asphaltene inhibitor may act on the surfaces of rock by limiting the rate of deposition/adhesion of asphaltene particles. IR95 as a commercial asphaltene inhibitor is presently known to act in this way in Iran, and the analysis performed also allows some qualitative conclusions to be drawn for this second mechanism by dynamic tests.

In the technical literature, a few case histories of squeeze treatments for asphaltene inhibition are reported (Bouts et al., 1995; Allenson and Walsh, 1997). Also in the present work; an attempt has been made to experimentally evaluate the efficiency of such treatments and briefly compare the economics of the solvent-washes with the squeeze treatments.

In this study, several effective impacts of inhibitors on asphaltenes were investigated including decrease in the amount of asphaltene precipitation at standard and reservoir condition, onset shifting, and asphaltene deposition at reservoir condition. Examined inhibitors consist of five non-commercial inhibitors namely benzoic acid, nonylphenol, phenanthrene, phthalic acid and salicylic acid and one commercial inhibitor namely IR95 with patent number 70680 in Iran. The non-commercial inhibitors are selected based on their functional groups to investigate the effect of hydroxyl and carboxyl functional groups on asphaltene stabilization (Karambeigi et al., 2015). As we all know, benzoic acid has one carboxyl functional group, nonylphenol has one hydroxyl functional group, salicylic acid has one hydroxyl functional group and one carboxyl functional group, phthalic acid has two carboxyl functional groups and phenanthrene does not have any functional groups. Among various commercial inhibitors, IR95 showed good effects on asphaltene precipitation reduction during a three-stage inhibitor injection.

However, it can be verified that the conditions along the processing and production of crude oils are different from those found in the laboratory.

2. Material and experimental procedure

2.1. Crude oil, core and inhibitors properties

Oil sample used in this work belongs to an Iranian oil field. The properties of reservoir and crude oil are given in Tables 1 and 2.

A carbonate core sample was used in the experiments. Petrophysical properties of the core samples used are given in Table 3. Porosity and permeability are measured by VINCI TECHNOLOGIES setup.

To make synthetic live oil in laboratory, the oil recombination was performed by charging a specified amount of dead oil into a recombination cell. The corresponding gasses were then injected into the recombine cell. Recombine cell was pressurized to 5000 psia and was shaken continuously for 14 days by an electric motor (100 rpm) to ensure complete mixing of oil and gas into single phase liquid.

D2007 (SARA test) is a method to separate crude oil into four fractions based on their solubility properties. These four fractions are saturates, aromatic, resin and asphaltene. In this method, the maltenes (the oil without asphaltene obtained from IP/143 test) were separated into saturates, aromatics, and resins using a chromatographic column packed with aluminum oxide. These fractions were sequentially eluted and collected using different solvents: saturates and aromatics were eluted using toluene-*n*-heptane mixtures, while resins were obtained using a mixture of methanol, acetone, and chloroform. Asphaltenes were obtained using IP/143 method.

Table 4 display the results of D2007 test.

Results of D2007 test show that CII = 1.61. It reveals that the examined oil is very unstable (Gaestel et al., 1971; Asomaning et al., 2000; Asomaning., 2003).

Examined inhibitors consist of five non-commercial inhibitors namely benzoic acid, nonylphenol, phenanthrene, phthalic acid and salicylic acid and one commercial inhibitor namely IR95. Physical properties of non-commercial inhibitors are given in Table 5.

All above inhibitors were purchased from Merck (Merck Company), with purity higher than 99%. The commercial inhibitor is IR95.

2.2. Experimental procedure

2.2.1. Standard condition tests

At first, the standard test was conducted at standard condition

Table 1
Properties of reservoir.

Specification	Result
Initial Pressure (Pisa)	5750
Saturation Pressure (Pisa)	3904
Temperature (°F)	241.7