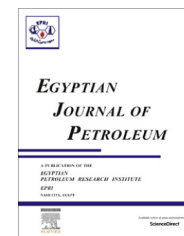




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FULL LENGTH ARTICLE

The relationship between SARA fractions and crude oil stability

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KEYWORDS

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 CII;
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Abstract Asphaltene precipitation and deposition are drastic issues in the petroleum industry. Monitoring the asphaltene stability in crude oil is still a serious problem and has been subject of many studies. To investigate crude oil stability by saturate, aromatic, resin and asphaltene (SARA) analysis seven types of crudes with different components were used. The applied methods for SARA quantification are IP-143 and ASTM D893-69 and the colloidal instability index (CII) is computed from the SARA values as well. In comparison between CII results, the values of oil compositions demonstrated that the stability of asphaltenes in crude oils is a phenomenon that is related to all these components and it cannot be associated only with one of them, individually.

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1. Introduction

Crude oil can be fractionated into four components (SARA). A reliable compositional characterization of crude oil fractions is very important for optimization of, products performance evaluation, refining processes, structure property, oil source correlations, and environmental issues [1].

Chromatographic techniques have been extensively used for hydrocarbons group type determination, such as SARA fractionation. Studies of this area were first done by Jewlle et al. [2]. In these four fractions, asphaltenes have an important role in organic deposition during petroleum production and processing [1].

Deposition of asphaltenes is a well-known problem that generates an enormous cost increase in the petroleum industry. This phenomenon seriously affects petroleum production and refining operations as well. A small change in petroleum components causes asphaltene dropouts [3].

According to the Classical colloidal model, solid particles exist with a core formed by stacks of asphaltenes surrounded by resins and aromatic molecules [4]. The idea is to identify the ratio of asphaltene sources that may cause asphaltene deposition [5]. Also, reservoirs with deposited asphaltene might not

Abbreviations: As, asphaltene; Re, resin; Sa, saturated; Ar, aromatic.
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be those with large amounts of asphaltene in the oil; on the contrary they might be those with high saturate fractions [2].

The colloidal instability index (CII) is one approach to determine the instability of heavy oil which is based on the chemical composition of crude oil [6]. The colloidal instability index (CII), suggested by Yen et al. is also applied as a widely-used monitoring criterion to recognize the asphaltene deposition potential of petroleum systems [7]. In this article, a study was developed that provides experimental data of the petroleum (SARA) fractions in different crude oils and the role of these fractions on the stability of asphaltenes.

2. Materials and methods

2.1. Residua

The samples studied in this work were obtained from South Azadegan field of Iran related to Oil and Gas Arvandan Company.

2.2. Asphaltene fraction measurement

Asphaltene fraction is one of the fractions in a categorization of crude oil samples in saturate, aromatic, resin and asphaltene (SARA) forms. Having the highest molecular weight with most enigmatic compounds of crude oils, asphaltene fractions toluene/benzene are soluble but n-heptane and n-pentane are insoluble. Asphaltene fractions are obtained from seven dead crude oils by the standard method (IP 143) [8,9]. The results obtained are given in Table 1.

2.3. Resin, saturate and aromatic fractions measurement

The analyses of saturates, aromatics and resins of crude oils are obtained from ASTM D893-69. All weight percentages related to petroleum fractions have been demonstrated in Table 1.

From Table 1, it can be seen that the resin and asphaltene fractions are smaller than saturate and aromatic fractions.

3. Theory

3.1. Colloidal instability index (CII)

Yen et al. applied a monitoring scale to identify the asphaltene deposition potential of petroleum systems. The CII is expressed as the sum of asphaltenes and saturates per the sum of aromatics and resins [10,11]:

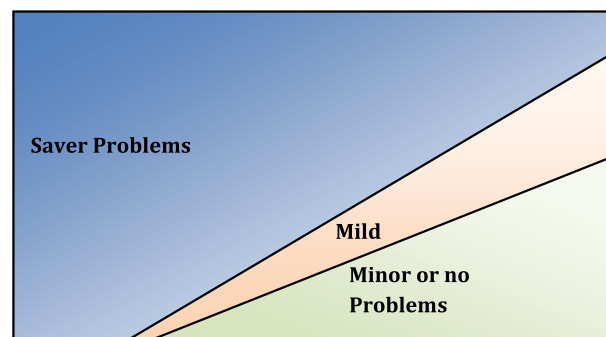


Figure 1 Colloidal instability index could be used to determine area where asphaltene deposits problems occur.

$$CII = \frac{\text{Saturates} + \text{Asphaltenes}}{\text{Aromatics} + \text{Resins}} \quad (1)$$

If oil has a CII value below 0.7, it is defined as stable and if the CII is higher than 0.9 is considered as unstable. For better illustration, Fig. 1 shows in which part the oil is stable, mild or unstable with asphaltene deposit problems in terms of CII value. For determination of this parameter we need to carry out hydrocarbon group type analysis [5,6].

Those practical methods are considered as a preliminary screening analysis for asphaltene deposit problems. It is strongly recommended to have more studies on laboratory experiments to solve the potential problems [5]. From Table 2, it can be seen that the ratio of asphaltenes to resins (As./Re.) and saturates to aromatics (Sa./Ar.), as well as the results of CII are tabulated for the seven crude oils.

Based on the results from Table 2 for the seven crudes analyzed, the CII value from sample No. 2, is between 0.7 and 0.9. Also, this value in sample No. 6 is less than 0.7 but in another cases these values are higher than 0.9.

3.2. Correlation between asphaltene and CII

Asphaltene is the heaviest and most polar crude oil fraction that is soluble in toluene and insoluble in n-heptane (Standard method D2007-80). [4,5]. Asphaltene is also the heaviest and most polar molecule in crude oil [12]. According to the approach of Pan–Firoozabadi and Victorov–Firoozabadi on the reversible micellization [13], the assumption that molecules of asphaltene are insoluble solid particles is relaxed [14]. Even though sweet crude oil contains low asphaltene, this does not mean that it has a lower tendency to precipitate than crude oil that has high asphaltene content [15]. Various researches have shown that crude oil with lower asphaltene content can

Table 1 The weight percentages of maltenes fractions.

Sample No.	Saturates (%)	Asphaltenes (%)	Resines (%)	Aromatics (%)
1	56.3288	3.2987	12.11	28.2325
2	40.5662	5.4408	14.6309	39.3621
3	72.65	1.7269	9.24	16.3831
4	54.2236	3.9691	11.2407	30.5665
5	53.1343	9.4302	14.07	23.3655
6	36.435	2.1034	6.56	54.9016
7	63.056	6.7903	12.7053	17.4484

Table 2 Hydrocarbon groups ratios and CII results.

Sample No.	As./Res.	Sat./Arm	CII
1	0.27239427	17.07606027	1.4769336
2	0.37187049	7.455925599	0.8520919
3	0.18689394	42.06960449	2.9027284
4	0.35310079	13.66143458	1.3919301
5	0.67023454	5.634482832	1.6712612
6	0.32064024	17.32195493	0.6270322
7	0.53444625	9.28618765	2.3163426

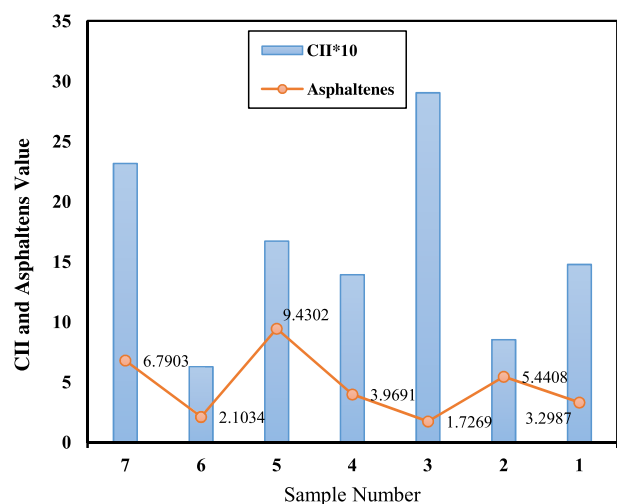


Figure 2 Comparison between CII variations with change in asphaltene value.

also have a higher tendency to precipitate comparing with those possessing high asphaltene content [16–18].

From Fig. 2 it can be seen that in some cases with high asphaltene component the CII values decrease and on the other hand, low asphaltene cases have an increment in CII values.

3.3. Correlation between resins and CII

The resin component and the CII were studied together to understand resin behavior and find a correlation between them. Resin has polar constituents [19]. With the colloidal viewpoint, the associated asphaltene molecules are considered to form a stack, which is surrounded and dispersed in the oil by the resin component [20].

Asphaltene molecules in petroleum are stabilized by resin molecules, preventing any major aggregation of the asphaltene [12]. From Fig. 3 an increment of resin value can be seen only in some cases leading to a decrease in CII.

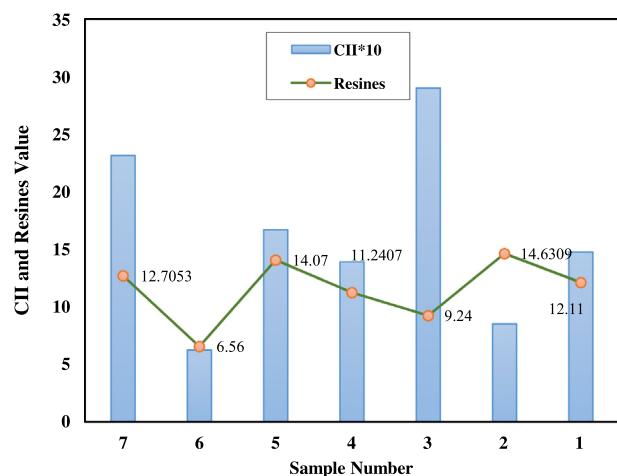


Figure 3 Comparison between CII variations with change in resin value.

3.4. Correlation between saturate and CII

The saturate components are not polar materials in crude oil [5]. The oils which have a high content of saturate fraction have low content of aromatic and resin fractions, therefore these crude oils could be highly unstable [21]. Carbognani and Espidel reported that reservoirs with deposited asphaltene problems might not be those with large amounts of asphaltene components in crude oil; on the contrary might be those with high saturate fractions [22]. Fig. 4 depicts the relationship between saturate and CII values from seven types of crude oil.

According to the Fig. 4, it can be seen that generally in cases with lower saturate values the colloidal instability index is higher. Fan et al. illustrate that the saturate, makes a negative contribution to colloidal stability in crude oil [23,24].

3.5. Correlation between aromatics and CII

The aromatic components are more polarizable than other fractions of crude oil. On the other hand, asphaltene as a polar part of petroleum in the form of a complex molecular structure

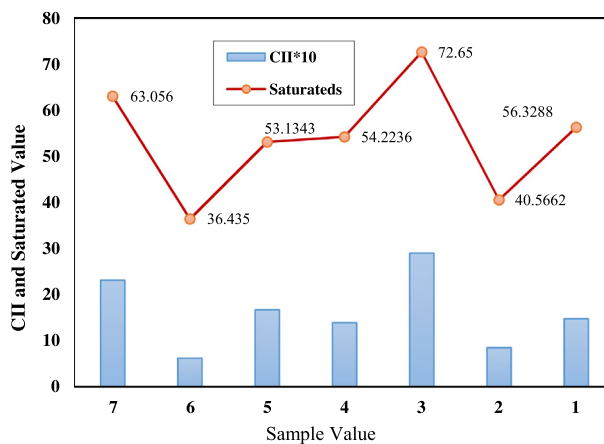


Figure 4 Comparison between CII variations with change in saturate value.

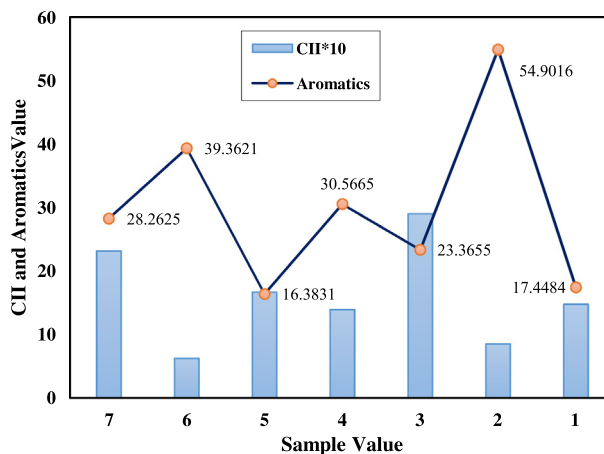


Figure 5 Comparison between CII variations with change in aromatic value.

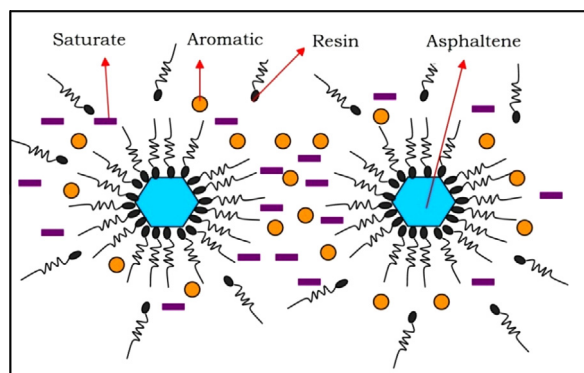


Figure 6 An illustration of force balance on asphaltenes.

has aromatic chains [5,19]. Asphaltene is the heavy fraction of the oil, which is insoluble in paraffin but soluble in aromatics. In 1940 Pfeiffer and Saal showed that asphaltenes consist of high molecular hydrocarbons of a predominantly aromatic character. Fig. 5 shows the relationship between aromatic and CII values. From this figure it can be seen that oils which have higher aromatics are more stable.

Aromatics are a good solvent for asphaltene molecules [19]. Aromatics, acting as a bridge between the mixed micelle and saturates, make the mixed micelles effectively dispersed in saturates [23].

Furthermore, it can be seen that CII has an agreement trend to the saturate-aromatics ratio. The lower values of CII indicate higher asphaltene stability due to the dispersant effect of aromatics and saturates [5].

4. Result

According to the above figures it is generally accepted that each of fractions influence the stability of crude oil. Stable oil has higher polar fraction values i.e. for asphaltene, resin and aromatic. Nonpolar fraction causes saturation of crude oil which has an important role in stability as well and in petroleum that has a higher value of saturate the probability of a decrease in stability becomes apparent.

5. Discussion

By spot colloidal model provisions and achieved results it may be concluded that precipitation is believed to occur when the resins are stripped from the colloid allowing aggregation and phase separation to occur [20]. Resins have a strong tendency to associate with asphaltenes due to their opposite charge and are absorbed by asphaltenes to become a protective shield for asphaltene [3]. When this protective shield of resins is removed, it might lead to the precipitation of asphaltenes [25]. Alkafeef et al. pointed out that the destabilization (i.e. flocculation) of colloidal asphaltenes in oil production systems depends principally on breaking up the balance of attraction forces between the adsorbed resin molecules and asphaltene particles. The resins are considered to be the crucial component in holding the asphaltene micelles in suspension [23]. An illustration of the resin can be described in Fig. 6 showing a force balance

between the adsorbed resin molecules and asphaltene particles where the polar heads of the resins are covering asphaltenes. Both resin and asphaltene have polar constituents but the difference between them depends on miscibility with n-pentane or n-heptane, asphaltene is insoluble, while resin is miscible [5,19]. Resins have a strong tendency to associate with asphaltenes. A larger precipitation of asphaltene results in a decrease in resin content [11,20].

Resins adsorb onto the asphaltene aggregates and keep them dispersed in the crude oil medium [26]. Pfeiffer and Saal suggested asphaltenes are the centers of micelles formed by adsorption or even by absorption of resins onto the surfaces or into the interiors of asphaltene particles as well. Hence for asphaltenes to stay in solution, resins must be present. The core of the micelle is occupied by one or several asphaltene “molecules” and is surrounded by interacting resins. Resins are surrounded by aromatics which ensure a progressive transition to the bulk of petroleum where saturated hydrocarbons are usually predominant [27]. Asphaltenes and resins are hetero compounds and form the most polar fraction of crude oil. Dilution of the resins below a certain threshold will cause asphaltenes to precipitate. Deplete the resins and the aromatics that kept the asphaltenes dispersed in solution [28].

It is generally accepted that the asphaltene molecules are dispersed in the oil by the polar molecules, aromatics, and resins, thus stating that the asphaltenes are colloidal dispersed in crude oil [29]. Considering crude oil as a colloidal system, and asphaltenes and resins comprise the dispersed phase while saturates and aromatics form the continuous phase. The overall structure would be of a micellar type: the cores of the nature of asphaltenes together with the nature of the dispersion medium are also important factors that determine the relative stability of crude oils and related materials [2]. The interaction among both phases and their influence on the stability of the system is related to the peptizing power of the resins, the solvent effect of the aromatics, the precipitant properties of saturates and the flocculation tendency of asphaltenes. As mentioned before resins are the most polar fraction, and aromatic species are present in deasphalted oil and, it has been suggested, contribute to the enhanced solubility of asphaltenes in crude oil by solvating the polar and aromatic portions of the asphaltenic molecules and aggregates. In opposition to the contents of saturates, a higher percentage of aromatics and resins could confer to the oils a higher capacity to keep asphaltenes in solution. The attractive interactions experienced by colloidal-sized asphaltene aggregates near the onset of precipitation are probably dominated by nonpolar Van Der Waals forces. It is generally accepted that the asphaltene molecules are dispersed in the oil by the polar molecules, aromatics, and resins, thus stating that asphaltenes are colloidal dispersed in crude oil [6,26].

6. Conclusion

The study of the crude oil composition (saturates, aromatics, resins and asphaltenes) demonstrates that the stability of asphaltenes in crude oils is a phenomenon that is related to all these components behavior, the percentage of each component is shown in Tables 1 and 2 and the influence of each fraction on another fractions according to their polarity as well, but it cannot be associated only with one of them, individually.

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