Review article

Methods for determining asphaltene stability in crude oils

Roque Guzmán [a,b], Jorge Ancheyta [a,*], Fernando Trejo [b], Silvano Rodríguez [a,b]

[a] Instituto Mexicano del Petróleo, Eje Central Lázaro Cárdenas Norte 152, Col. San Bartolo Atepehuacan, Mexico City 07730, Mexico
[b] Instituto Politécnico Nacional, CICATA-Legaria, Legaria 694, Col. Irrigación, Mexico City 11500, Mexico

A B S T R A C T

Different tests used to predict asphaltene stability in crude oils, such as colloidal instability index, colloidal stability index, Stankiewicz plot, qualitative-quantitative analysis, stability cross plot, Heithaus parameter, toluene equivalence, Bureau of Mines correlation index – toluene equivalence, and oil compatibility model are reported in this work. In addition, SARA fractionation, asphaltene flocculation point, P-value, S-value, separability number, stationary column stability test, compatibility test, and spot test are disclosed. Using experimental data reported in literature, each test is carried out in order to evaluate its accuracy finding that some tests predict the asphaltene stability better than other ones. It was found that qualitative-quantitative analysis and stability cross plot behaved better than colloidal instability index and Stankiewicz plot.

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* Corresponding author.
  E-mail address: jancheyt@imp.mx (J. Ancheyta).

1. Introduction

Incompatibility and instability are responsible of asphaltene precipitation in crude oils and their blends. Asphaltene precipitation commonly causes plugging of pipelines and process equipment such as pumps, heat exchangers, or separator tanks. Various studies have been reported in order to understand asphaltene precipitation [1,2] and predictive models have been proposed taking into account the changes in crude oil composition [3–7]. Most of models are focused on predicting asphaltene precipitation from pure crude oils diluted with solvents [8]. By carrying out flocculation tests in parent crude oils, stability of blended crude oils is commonly reported [9,10].

Other tests have been proposed in order to study the stability of crude oils, i.e., colloidal instability index (*CII*), colloidal stability index (*CSI*), Stankiewicz plot (*SP*), qualitative-quantitative analysis (*QQS*), stability cross plot (*SCP*), Heithaus parameter (or parameter P), toluene equivalence (*TE*), Bureau of Mines correlation index – toluene equivalence (*BMCI-TE*), and oil compatibility model (*OCM*). The latter is currently used to predict the compatibility of blended crude oils and their stability. In some cases, asphaltene precipitation is required by adding solvent to pure or blended crude oils. On the other hand, saturates, aromatics, resins, and asphaltenes (SARA) fractions are needed.

In this work, SARA fractions and onset of asphaltene precipitation in different crude oils are taken from the literature and the aforementioned tests are applied to predict the stability of the crude oils. A comparison among the different methods is carried out.

2. Asphaltene properties

Asphaltenes are macromolecules containing aromatic and naphthenic cores, aliphatic chains, and heteroatoms such as oxygen, nitrogen, or sulfur [11]. Asphaltene is typically defined as the insoluble fraction in paraffinic hydrocarbons, i.e., *n*-heptane, but soluble in aromatics such as toluene. Even in low concentrations, asphaltene molecule is prone to aggregate and precipitate, thus causing major damage in the different stages of the petroleum processing. The polarity of asphaltene molecule is caused at local level by electrons in atoms such as sulfur, oxygen, and nitrogen. Electrons are able to bonding when metals are present in catalyst, i.e., Ni, Co, Mo, etc. In this case, a bond is formed and poisoning of catalysts occur. In addition, asphaltenes have amphiphilic or natural surfactant characteristics, which significantly influences on their self-association (micelles) both in solvents and in crude oil.

Sediments are closely related to sludge in crude oils. There is also thought but not always true that sediment is a deposit formed from inorganic constituents of crude oil, i.e., metalloporphyrin or from adsorption of contaminants during upstream/downstream processes. Salt, sand, rust, etc. can be considered as sediments. However, sediments can be also formed from organic material in petroleum in different process. Commonly sediments are formed when hydrocracking reactions take place at high temperature [12].

Coke is a carbonaceous black deposit insoluble in solvents commonly deposited on catalysts because of phase separation in crude oil. Its formation is caused by thermal or even catalytic reactions involving free radicals that lead to condensation reactions and dehydrogenation promoted at high temperatures. Coke deposition on catalyst surface reduces the catalytic activity by pore plugging. In order to recover the catalytic activity, regeneration of catalyst is needed [13,14]. A review involving conversion of crude oils in conventional refining processes focused on the production of high quality fuels, as well as deactivation processes by coke and poisoning is reported elsewhere [15].

Different separation methods are employed to separate or identify asphaltenes, sediments, or coke. These methods are based mainly on solubility in solvents. In the case of asphaltenes, they are isolated by following standardized methods such as ASTM D4124 [16], in which four fractions are obtained. Crude oil is mixed with *n*-heptane and two fractions are obtained: (1) Insoluble, that correspond to asphaltenes, and (2) Deasphalted oil, which can be further separated into saturates, aromatics, and resins. Sediments are obtained by extraction from crude oils or fuels using toluene as solvent. Commonly, the sediment concentration ranges from 0.01 to 0.40 wt%; however, higher values are also reported [17].

Coke is deposited on catalyst surface after catalytic reactions. In a laboratory test, pellets of spent catalyst are washed under reflux with toluene to remove hydrocarbons. Insoluble and darkness deposits on catalyst correspond to coke. However, in coke from thermal process is also formed in the inner walls of equipment because of bond breaking and polymerization reactions through free radicals. It is important to mention that asphaltenes are soluble in toluene whereas coke is insoluble. Trejo et al. [18] studied the tendency to coke formation of different petroleum fractions and determined that under thermogravimetric analysis, asphaltenes yielded 47 wt% of coke in nitrogen atmosphere whereas resins only produced 9 wt%. It is drawn that asphaltenes are coke precursors according to these results.

3. Stability of crude oils

An important issue in petroleum industry is the understanding of the compatibility and fouling behavior of crude oils. Correlations have been developed to characterize the crude oils and translate typical assay parameters into fouling and compatibility tendencies [19]. The destabilization of asphaltenes in crude oils can cause stable oil-water emulsion problems, heat exchanger fouling and coke deposits in furnace tubes. Furthermore, incompatible crude oil blends can result in the flocculation and deposition of asphaltenes. The determination of insolubility number and solubility blending number are important parameters in predicting flocculation when dealing with incompatible crude oil blends [20]. A review of asphaltene solubility and fluid compatibility has been reported where the oil compatibility model is disclosed [21]. Saleh et al. [22] determined the compatibility parameters of oils based on flocculation titrations and SARA analysis. Fouling rates for individual crude oils diminished with decreasing asphaltene content and increasing the solubility blending number. The importance of particulate fouling was proven by decreasing the amount of suspended solids. The fouling rate was linearly related to the magnitude of this decrease.

Alvarez et al. [23] used ellipsometry to evaluate the compatibility of crude oil blends. The procedure implies the evaluation of the real part of the refractive index of the crude oils and their mixtures, which can be linked to the density of the mixture. The ellipsometric measurements fit well to theoretical predictions obtained using a Cauchy dielectric function for the pure crude oils and the Maxwell-Garnett effective medium model for the mixtures. Östlund et al. [24] used a method based on transmittance of light in order to evaluate the crude oil stability when adding *n*-heptane.

Sollaimany and Bayandori [25] studied the influence of different factors on the asphaltene stability such as compositional and structural characterization of resins and asphaltenes to study a possible relationship between these properties and asphaltene deposition behavior. According to their results, the stability behavior of asphaltenes was influenced strongly by their structural characteristics. Colloidal stability indices such as the $(Ar + R)/(As + S)$ ratio and $(Ar + R)/As$ ratio do not play a key role in the asphaltene stability for the studied crude oils by which the compositional ratios are