Evaluation of indices and of models applied to the prediction of the stability of crude oils

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ABSTRACT

In this work, indices developed for verification of the stability of oils or fractions were evaluated, as the Colloidal Instability Index (CII), Heithaus Parameter (P), and Toluene Equivalence (TE), and models of prediction of the compatibility of oils, as the BMCI–TE and the Oil Compatibility Model (Wiehe and Kennedy, 2000), were applied to the prediction of the stability. Possible relations between onset of precipitation (OP) and contents of saturates, aromatics, resins and asphaltenes (SARA) were also considered as indicative of the stability of oils. With the exception of the CII, these parameters have as a main limitation the necessity of calculations which depend on the experimental determination of the onset of precipitation of asphaltenes. In some of the oils studied it was not possible to determine the OP, then it was not viable to verify the efficacy of the models in the prediction of their stability. However, the CII, which does not present such restriction, showed to be the least efficacious. These indices, therefore, proved inefficacious in the evaluation of systems containing the Brazilian oils considered in this study, which proves the necessity of more research for its improvement or the development of new models and indices.

1. Introduction

Asphaltenes are heavy fractions of oils which show a tendency to aggregation (Spiecker et al., 2003; Espinat et al., 2004; Evdokimov et al., 2006). One of the main problems resulting from this characteristic is the deposition, which consists of a precipitation/flocculation followed by sedimentation (Kriz and Andersen, 2005; Ortega-Rodriguez et al., 2006), which can lead to the blockage of the equipment and pipe lines, besides modifying the original characteristics of the oil, compromising the attainment of some fractions and favoring the rise of the coke tax and residues to the end of the processing (Wiehe and Kennedy, 2000a; Byambajav and Ohtsuka, 2003).

There is not yet a complete understanding of the behavior of the asphaltenes in the oils, however, some studies admit that they represent a class of compounds soluble in the oil, which constitutes, in specific conditions of temperature, pressure and composition, a stable solution (Asomaning, 2003; Vicente et al., 2006). When variations in these conditions occur, the stability of the oils can be compromised and the precipitation of asphaltenes can happen.

In the conditions in which the oil does not present tendency to the asphaltenic precipitation, it is classified as stable (Holmes and Bullin, 1983); in case this precipitation is verified, the oil is considered unstable. Thus, the term *stability* can be understood as a measure of the tendency of the precipitation of asphaltenes in relation to the oil.

Some studies still point out the possibility of the asphaltenes being in the limit of the balance and, in this case, the stability of the oil would be considered inside a region of uncertainty (Asomaning, 2003).

As a matter of fact, it is verified that the identification of an oil as stable or unstable can be accomplished, for example, in the case of an unstable oil, by the presence of incrustations in equipment and/or blockage of the pipe lines involved in the diverse stages of the production and processing (Akbarzadeh et al., 2004). However, the tendency to the precipitation of the asphaltenes is of difficult quantification and researches have been carried out in this direction, considering the stability of asphaltenes as a function of diverse factors, such as, the balance between peptizing power of the medium and the peptizability of these fractions (Tojima et al., 1998; Schermer et al., 2004); balance among saturates, aromatics, resins and asphaltenes (Asomaning, 2003); or solubility parameters of the substances involved (Wiehe and Kennedy, 2000a; Wong and Yen, 2000).

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The stability of the oils is, consequently, function of the stability of the asphaltenes in the medium and it is related to the variation of diverse factors, which include composition, pressure, temperature (Hammami et al., 2000) and electrokinetics effects (Mansoori, 1997); it varies from oil to oil, but not all are susceptible to the deposition, and, apparently, the percentage of asphaltenes present in the medium does not represent, individually, a determinative factor to the precipitation (Asomaning, 2003), even though some studies indicate that the type and the amount of deposits formed in the oil vary in accordance with the relative amount of each fraction (SARA) (Mansoori, 1997; Wong and Yen, 2000).

Diverse indices and models have been developed and applied to the study of the stability of oils, such as the "Colloidal Instability Index" (CII), "Heithaus Parameter" (or Parameter *P*), "Toluene Equivalence" (TE) and "Bureau of Mines Correlation Index–Toluene Equivalence" (BMCI TE), which represent some of the parameters initially developed for the prediction of stability of asphalts, and also the "Oil Compatibility Model", developed for the prediction of the compatibility of mixtures of oils and also applicable to the evaluation of stability.

Some of these indices, however, involve the experimental determination of the asphaltenes' precipitation by the addition of a flocculant to the oils or solutions of oils in aromatic solvents. Other indices use composition data, as contents of saturates, aromatics, resins and asphaltenes (SARA). In both cases, the pieces of information are particular to each oil and depend on some factors, such as the methodology used, sensitivity of the equipment and ability of the analyst, consequently, the input data of these parameters may be insufficiently reliable, what can imply significant errors in the results of the prediction of the stability of oils.

Thus, in this article, a study was developed that provides the attainment of experimental data of the precipitation of asphaltenes in oils of different natures and the calculation of parameters related to the stability of asphaltenes, making possible a discerning evaluation of the indices and of the models applied to the description of the stability of oils.

1.1. Coloidal Instability Index (CII)

In the CII, Colloidal Instability Index, the oil is considered a colloidal system consisting of the pseudocomponents saturates, aromatics, resins and asphaltenes (SARA). That index expresses the stability of asphaltenes as a function of these fractions and it is defined as the mass ratio between the sum of asphaltenes and the unfavorable components to its stability in the oil, that is, its flocculants (saturates) and the sum of its peptizer agents (aromatics and resins), which constitute the components favorable to the stability of asphaltenes present in a specific oil (Asomaning, 2003), as shown in Eq. (1).

$$IIC = \frac{\% \text{ of Asphaltenes} + \% \text{ of Saturates}}{\% \text{ of Resins} + \% \text{ of Aromatics}} \tag{1}$$

The lesser the value of this index, the greater is the stability of asphaltenes in the medium, therefore, the stability determined by this way is relative and allows us to evaluate if an oil is more, or less, stable in relation to another one.

Asomaning (2003) evaluated oils whose SARA contents were determined by liquid chromatography (ASTM D2007-03, 2008) and by the standard method IP 143/84 (1989), and experimental evidence showed that when IIC ≥ 0.9, the asphaltenes are unstable in the medium; when 0.7 ≤ IIC < 0.9, there is uncertainty about the stability; and if IIC < 0.7, the asphaltenes are stable in the oil.

Considering that the percentages of saturates, aromatics, resins, and asphaltenes depend on the determination procedure, the limits of stability of this index are also susceptible to many variations.

1.2. Heithaus Parameter (Parameter P)

This parameter was developed by Heithaus (1962) for the prediction of the stability of heavy oils and asphalts, through the determination of the index *P* (Tojima et al., 1998; Schermer et al., 2004). Thus, a solution of the oil, or fraction, in an aromatic solvent, as toluene or α-methyl-naphthalene, is titrated with a paraffin, as n-heptane or iso-octane or n-hexadecane, until the precipitation occurs (Heithaus, 1962; Gawel et al., 2005). At this point, the volumetric fraction of the aromatic solvent in relation to the total volume of solvent (V_S) + titrant (V_T) is called flocculation rate (*FR*) and is calculated by Eq. (2):

$$FR = \frac{V_S}{V_S + V_T} \tag{2}$$

Similarly, the concentration of the oil (*C*) is given by the fraction (in weight) of the oil in relation to the total volume of solvent + titrant in this exact point (Eq. (3)).

$$C = \frac{W_A}{V_S + V_T} \tag{3}$$

where V_S is the volume of the solvent, V_T is the volume of the titrant and W_A is the mass of oil, or fraction, in the sample (Tojima et al., 1998; Redelius, 2000; Schabron et al., 2001).

The titration must be repeated for, at least, four different concentrations of oil (Redelius, 2000). The values of *FR* and *C* obtained by this way are used in the construction of a graph, whose linear regression supplies the intersection with the ordinate axis, called FR_{max}, and with the abscissa axis, C_{min}. The FR_{max} factor represents the solvent and titrant ratio in which the oil is soluble in all the concentrations, while the C_{min} factor is the minimum amount of oil that must be present in a specific titrant concentration to keep its complete solubility (Heithaus, 1962; Redelius, 2000; Schabron et al., 2001). In reality, the C_{min} factor can be interpreted as another form to represent the onset of precipitation (OP), which represents the minimum amount of necessary n-heptane so that the precipitation of the asphaltenes in the absence of toluene occurs (Escobedo and Mansoori, 1995; Mousavi-Dehghani et al., 2004), normally expressed in volume of n-heptane per mass of oil (mL g^{-1}). In the OP, V_S is equal to zero and the sample contains only the oil and the titrant.

From these measures, three characteristic parameters of the oils are determined: P_a, P_o and *P* (Heithaus, 1962; Tojima et al., 1998; Redelius, 2000; Schabron et al., 2001). The first one, P_a, represents the peptizability of the asphaltenes and it is calculated through Eq. (4). High values of P_a indicate that the asphaltenes are more easily peptized in this medium.

$$P_a = 1 - FR_{max} \tag{4}$$

The second parameter, P_o, obtained in accordance with Eq. (5), represents the peptizer power of the maltenes (other fractions of the oil, without the asphaltenes) and the higher its value, the higher is the solubility power of the medium.

$$P_o = FR_{max}[(1 / C_{min}) + 1] \tag{5}$$

Finally, the parameter *P*, or Heithaus Parameter, indicates the global state of peptization of the system and represents its stability. The relation among the three parameters is normally expressed by Eq. (6) (Heithaus, 1962; Tojima et al., 1998; Redelius, 2000).

$$P = P_o / (1 - P_a) \tag{6}$$

When *P* < 1, the oil is defined as unstable, or of low colloidal stability, and there is a great possibility of the formation of precipitate (Tojima et al., 1998); on the other hand, the higher the peptization