Chemical Engineering Science 78 (2012) 181–185

Contents lists available at SciVerse ScienceDirect

Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces

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A novel method for evaluation of asphaltene precipitation titration data

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ARTICLE INFO

Article history:
Received 16 February 2012
Received in revised form
23 April 2012
Accepted 7 May 2012
Available online 18 May 2012

Keywords:
Evaluation of data
Leverage approach
Asphaltene precipitation
Outlier diagnostics
Scaling equation
Titration data

ABSTRACT

In this work, we propose a mathematical method for detection of the probable doubtful asphaltene precipitation titration data. The algorithm is performed on the basis of the Leverage approach, in which the statistical Hat matrix, Williams Plot, and the residuals of the model results lead to identify the probable outliers. This method not only contributes to outliers diagnostics but also defines the range of applicability of the applied models and quality of the existing experimental data. Two available scaling equations from the literature are used to pursue the calculation steps. It is found from the obtained results that: I. The applied models to represent/predict the weight percent of asphaltene precipitation are statistically valid and correct. II. All the treated experimental titration data seem to be reliable except one. III. The whole data points present in the dataset are within the domain of applicability of the employed models.

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1. Introduction

Saturates, aromatics, resins, and asphaltenes (SARA) are generally assigned as the portions of crude oils (Leontaritis and Mansoori, 1988; Leontaritis et al., 1992; Mohammadi and Richon, 2007, 2008a,b; Thawer et al., 1990; Pan and Firoozabadi, 1996; Andersen and Speight, 2001; Mohammadi et al., 2012). The latter fractions (asphaltenes) are normally toluene/benzene soluble but *n*-heptane/*n*-pentane insoluble. It can be stated that asphaltenes are the most aromatic with highest molecular weight fraction of petroleum fluids that generally contain simple heteroatoms (C, H, N, O, and S) or even particular metal constituents like Fe, Ni, and V (Mohammadi et al., 2012). Asphaltenes have potential to be precipitated from the bulk of crude oils mainly due to changes in pressure, temperature, and fluid composition. For instance, there is a possibility of asphaltene precipitation as the oil pressure drops during production of some crude oils.

It is currently well accepted that asphaltene precipitations/depositions in petroleum reservoirs, production and/or processes facilities cause remarkable problems (Leontaritis and Mansoori, 1988; Leontaritis et al., 1992; Mohammadi and Richon, 2007; Thawer et al., 1990; Mohammadi and Richon, 2008a,b; Pan and Firoozabadi, 1996; Andersen and Speight, 2001; Mohammadi et al., 2012) Nevertheless, the real mechanism of asphaltene agglomeration, flocculation, and precipitation has been not completely understood so far mainly due to its complexity (Mohammadi and Richon, 2007; Mohammadi et al., 2012) There are still many debates on this subject (Mohammadi and Richon, 2007; Mohammadi et al., 2012).

To deal with clarification of this issue, many experimental techniques have been proposed in the literature. Perhaps, the most widely used ones are the titration tests. They are generally performed using core flood investigations accompanied by addition of different asphaltene precipitants such as n-alkanes (mainly *n*-C_5, *n*-C_6, and *n*-C_7). Different dilution ratios (the ratios of solvents/precipitants to the weight of the live/dead oil samples) are normally used to precipitate or dissolve asphaltene fraction in the bulk of crude at different temperatures (Andersen and Speight, 2001; Ashoori et al., 2003; Rassamdana et al., 1996; Rassamdana and Sahimi, 1996). The common experimental (filtration) procedure (which is generally performed on the basis of IP-143 procedure) is briefly as follows: (Rassamdana et al., 1999). The crude oil sample accompanied by the precipitants are mixed with each other (according to specified dilution ratios) in a suitable vessel using agitation system. Later, an asphaltene solvent (like toluene) is added to the system to dissolve the precipitated asphalts. The solvent would then evaporate and the remaining asphaltenes (precipitated asphaltenes) can be measured.

Although the available titration data seem to be adequate to investigate the amounts and onsets of asphaltene precipitations in various oil samples, no method has been proposed to check their reliability up to now. Furthermore, comparison between the various titration data as a method for checking the quality of the corresponding datasets may be conservative due to non-similar

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0009-2509/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.ces.2012.05.009

phase behaviors and/or structures of asphaltene fractions present in different oil samples.

Apart from that, the scaling equation developed by Rassamdana and co-workers (Rassamdana et al., 1996; Rassamdana and Sahimi, 1996) has generated number of attractions in the past decade to represent/predict the asphaltene precipitation titration data. Therefore, it is of much interest to propose a statistically-correct method for simultaneous detection of the doubtful titration data and their quality along with checking the validity and domain of applicability of the scaling equation. In this communication, our aim is to use the Leverage approach (Rousseeuw and Leroy, 1987; Goodall, 1993; Gramatica, 2007) for this purpose. To the best of our knowledge, this is the first time that this statistical method is used for evaluation of such data which are of interest in petroleum industry.

2. Theory

2.1. Leverage approach

Outlier diagnostics (or detection) are of much importance in developing the mathematical models. As a matter of fact, outlier detection is to identify individual datum (or groups of data) that may differ from the bulk of the data present in a dataset (Rousseeuw and Leroy, 1987). The corresponding methods generally consist of numerical and graphical algorithms (Rousseeuw and Leroy, 1987; Goodall, 1993; Gramatica, 2007; Gharagheizi et al., 2011). The Leverage approach (Rousseeuw and Leroy, 1987; Goodall, 1993; Gramatica, 2007) is considered to be a reliable algorithm for outlier detection that deals with the values of the residuals (i.e., the deviations of a model results from the experimental data) and a matrix known as Hat matrix composed of the experimental data and the represented/predicted values obtained from a model. The primary application criterion of this method is to use a model, which is capable of acceptable calculation/estimation of the data of interest.

The Leverage or Hat indices are calculated based on Hat matrix (H) with the following definition: (Rousseeuw and Leroy, 1987; Goodall, 1993; Gramatica, 2007; Gharagheizi et al., 2011)

$$H = X(X^t X)^{-1} X^t \tag{1}$$

where X is a ($n \times k$) matrix, in which n stands for the data (rows) and k denotes the parameters of the model (columns), and t stands for the transpose matrix. The Hat values of the data in the feasible region of the problem are, as a matter of fact, the diagonal elements of the H value.

Having evaluated the H values with Eq. (1), the Williams plot is sketched for graphical identification of the suspended data or outliers. This plot shows the correlation of Hat indices and standardized cross-validated residuals (R), which are defined as the difference between the represented/predicted values and the implemented data. A warning Leverage (H) is generally fixed at the value equal to $3n/p$, where n is number of training points and p is the number of model parameters plus one. The Leverage of three is normally considered as a "cut-off" value to accept the points within ± 3 range (two horizontal red lines) standard deviations from the mean (to cover 99% normally distributed data). Existence of the majority of data points in the ranges $0 \le H \le H^*$ and $-3 \le R \le 3$ reveals that both model development and its predictions are done in applicability domain, which result in a statistically valid model. "Good High Leverage" points are located in domain of $H^* \le H$ and $-3 \le R \le 3$. The Good High Leverage can be designated as the ones, which are outside of applicability domain of the applied model. In other words, the model is not able to represent/predict the following data at all. The points located in the range of $R < -3$ or $3 < R$ (whether they are larger or smaller than the H^* value) are designated as outliers of the model or "Bad High Leverage" points. These erroneous representations/predictions may be attributed to the doubtful data.

2.2. Scaling equation

In 1996, Rassamdana and co-workers (Rassamdana et al., 1996; Rassamdana and Sahimi, 1996) stated that the titration data of asphaltene precipitation including the dilution ratio, the molecular weight of solvent/precipitant, and the weight percent of precipitated asphaltene can be collapsed onto a single (and simple) equation (curve) (Rassamdana et al., 1996; Rassamdana and Sahimi, 1996). As a consequence, they proposed the following three-order polynomial for representation/prediction of the amounts/onsets of asphaltene precipitations against addition of n-alkanes: (Rassamdana et al., 1996).

$$Y = a + bX + cX^2 + dX^3 \tag{2}$$

where,

$$X = R_d / M^z \tag{3}$$

and

$$Y = W / R_d^{z'} \tag{4}$$

In the preceding equations, W is the weight percent of the precipitated asphaltene, R_d stands for the dilution ratio, and M denotes the molecular weight of the solvent/precipitant. They recommended the values of 1/4 and -2 for z and z' after adjusting these parameters against the obtained experimental titration data. Later, Rassamdana et al. (1999) and Ashoori et al. (2003) modified one of the parts of the original scaling equation to account for the effects of temperature on the amount of precipitations introducing a third parameter in Eq. (3) as follows:

$$X = R_d / T^n M^z \tag{5}$$

where T is the temperature. The value of 0.15 for the n parameter in Eq. (5) shows acceptable results for representation of the experimental titration values reported by Ashoori et al. (2003).

3. Experimental data

The experimental asphaltene precipitation titration data obtained and reported in the original publications of Rassamdana et al. (1996) and Ashoori et al. (2003) have been treated in this work.

4. Results and discussion

Tables 1 and 2 show the absolute relative deviations of the results using the original (Rassamdana et al., 1996) and the modified scaling equation. (Ashoori et al., 2003). As can be seen, the deviations of the models representations/predictions from the corresponding experimental data reported in the original articles (Ashoori et al., 2003; Rassamdana et al., 1996) are generally acceptable to be used for the Leverage statistical approach.

The evaluation steps have been followed on the basis of the aforementioned procedure (Section 2.1).

The H values have been calculated through Eq. (1). The Williams plots have been sketched in Figs. 1 and 2 for the results using the first model (Rassamdana et al., 1996) and corresponding experimental dataset (Rassamdana et al., 1996) and the second ones, (Ashoori et al., 2003), respectively. All the calculated H and R values are presented in Tables 1 and 2. Two warning Leverages

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