Fluid Phase Equilibria 415 (2016) 88–100

Contents lists available at ScienceDirect

Fluid Phase Equilibria

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

On the evaluation of asphaltene precipitation titration data: Modeling and data assessment

Abdolhossein Hemmati-Sarapardeh [a], Forough Ameli [b, c], Bahram Dabir [a, b, **], Mohammad Ahmadi [a], Amir H. Mohammadi [d, e, f, *]

[a] Department of Petroleum Engineering, Amirkabir University of Technology, Tehran, Iran
[b] Department of Chemical Engineering, Amirkabir University of Technology, Tehran, Iran
[c] Islamic Azad University of Technology, North Tehran Branch, Tehran, Iran
[d] Thermodynamics Research Unit, School of Engineering, University of KwaZulu-Natal, Howard College Campus, King George V Avenue, Durban 4041, South Africa
[e] Institut de Recherche en Génie Chimique et Pétrolier (IRGCP), Paris Cedex, France
[f] Département de Génie des Mines, de la Métallurgie et des Matériaux, Faculté des Sciences et de Génie, Université Laval, Québec (QC), G1V 0A6, Canada

ARTICLE INFO

Article history:
Received 28 September 2015
Received in revised form
16 January 2016
Accepted 18 January 2016
Available online 21 January 2016

Keywords:
Asphaltene precipitation
Titration data
Least square support vector machine
Leverage approach
Outlier detection

ABSTRACT

Asphaltene precipitation causes several problems during different stages of oil production in the reservoirs. Experimental measurement of asphaltene precipitation is cumbersome, expensive and tedious. In this communication, the amount of asphaltene precipitation during titration experiments was modeled as a function of easily measureable parameters including temperature, type of solvent, and solvent to oil dilution ratio. A large data bank of asphaltene precipitation was collected from different sources, covering a wide range of thermodynamic conditions and different types of crude oils. Least square support vector machine (LSSVM) optimized with a stochastic algorithm named couples simulated annealing (CSA) was employed for the purpose of modeling. The data bank was divided into four sections based on the type of solvent and solvent to oil dilution ratio. Subsequently, for each section a model was proposed and the results showed that all of the proposed models can predict the amount of asphaltene precipitation with enough accuracy. In general, the proposed CSA-LSSVM models can predict asphaltene precipitation with an average absolute relative error of 9.46%. The proposed models were compared to pre-existing models and both graphical and statistical analyses indicated the superiority of the proposed CSA-LSSVM models over the pre-existing ones. Finally, a mathematical model was used which not only defines the applicability domain of the proposed models, but also evaluates the quality of experimental data and detects the probable outliers. The results demonstrated that all of the proposed models are statistically valid and only 3.3% of the data may be recognized as the probable outliers.

1. Introduction

One of the most important components of crude oil is asphaltene, which is defined as association of different structures including macromolecules and colloidal particles [1]. This structure is most likely to precipitate due to variations in temperature and pressure of the reservoir and crude oil compositions [2]. As it is stated in literature, asphaltene precipitation causes severe problems in petroleum reservoirs, production lines and facility equipment [1,3–8]. Many experimental and theoretical studies have been conducted in this regard. However, due to the complex nature of this structure, the findings may be limited. Very recently, Mohammadi et al. [9] classified the asphaltene precipitation models into five groups, including 'equation of state (EoS)' based models, 'association' models, 'activity coefficient' based models, 'scaling laws, corresponding state and correlations 'and 'colloidal/micellization' models.

In equation of state based models, asphaltene properties are applied for asphaltene precipitation studies. The validity of this

* Corresponding author. Institut de Recherche en Génie Chimique et Pétrolier (IRGCP), Paris Cedex, France.
** Corresponding author. Department of Petroleum Engineering, Amirkabir University of Technology, Tehran, Iran.
E-mail addresses: drbdabir@aut.ac.ir (B. Dabir), a.h.m@irgcp.fr, amir_h_mohammadi@yahoo.com (A.H. Mohammadi).

http://dx.doi.org/10.1016/j.fluid.2016.01.031
0378-3812/

approach depends on the reversibility experiments of the crude oil [10–12]. This model has been extensively used for modeling the deposition of heavy organic compounds, including Peng–Robinson (PR) [13], Soave–Redlich–Kwong (SRK) [13] Gupta [14], Nghiem et al. [15–17], Lindeloff et al. [18], Sabbagh et al. [19], and Soroush et al. [20]. The advanced EoS based models are based on the work of Wu et al. [21,22], Ting et al. [23], Buenrostro-Gonzalez et al. [24], Christensen et al. [25], Gonzalez et al. [26], and Tabatabaei-Nejad and Khodapanah [27]. PR and SRK EoSs were modified later by Vafaie-Sefti, Mousavi-Dehghani [28], Nikookar et al. [29]. Mohammadi and Richon [30] developed a more general Florry-Huggin equation and demonstrated that the existing Florry- Huggins model is a specific case of the current model. The results were validated by some experimental data. More recently, Mohammadi et al. [9] combined the chemical theory of associated solutions with Flory–Huggins polymer solution theory, and introduced a new thermodynamic model to predict the asphaltene deposition.

As stated, in activity coefficient and association models as well as EoS based models density, solubility parameter and the molecular weight of asphaltene are required. However, the latter is difficult to be measured due to the complex composition and chemical association behavior of asphaltene [5]. For the case of simulation, asphaltene structure is lumped into a pseudo-component. This leads to deviation of the properties and the need to use data fitting in order to accurately predict the amount of asphaltene precipitation [7]. Activity coefficient based models, are generally based on polymer solution theories, including Scatchard-Hildebrand, Flory–Huggins and Scott–Magat. Most of the Flory-Huggins based models do not consider the distribution of asphaltene and non-asphaltene compounds. In this modeling approach, the precipitation process is assumed reversible to use from molecular thermodynamics. There are two assumptions made for this theory. First, precipitated phase is only asphaltene and second, non-asphaltene compounds are also present in the precipitate phase without any asphaltene in the oil phase. Hirschberg model was developed based on the first assumption in which asphaltene volume fraction in precipitated phase is equal to 1. Cimino et al. [31] model was developed based on the second assumption. This model could only be used for determining the onset of asphaltene precipitation. On the other hand, by considering the presence of maltene in the precipitated phase and presence of asphaltene in oil phase, more reliable models were proposed in comparison to Hirschberg et al. [1] and Cimino et al. [31] models.

In colloidal approach, it is assumed that asphaltene is suspended in crude oil by resins and the precipitation process is irreversible. In addition to the stated procedures, Park and Mansoori [11] developed scaling laws approach for modeling the asphaltene precipitation. They stated that asphaltene precipitation is similar to aggregation phenomena and could be described by scaling theory. The advantages of this approach over the others include simple mathematical formulation and no requirement to asphaltene properties for the modeling [32]. Rassamdana et al. [32] proposed the first scaling equation which includes two exponents of Z and Z′ and was applied for the first time to predict the onset of the asphaltene precipitation and the amount of the precipitated asphaltene for an Iranian crude oil sample. The results stated that by fitting a limited set of experimental data, this approach was capable of predicting the asphaltene precipitation behavior at a fixed temperature. Despite the accuracy of this method, it suffers from the lack of involving temperature as a variable parameter. Later, Rassamdana and Sahimi [33] modified their scaling equation to include temperature effect. Also Hu et al. [34] studied this approach with data in the literature and examined the universality of Z and Z′ and obtained an optimum value for Z. Hu and Gua [35] applied this procedure for studying the effect of temperature and composition for prediction of the onset point and determined the amount of asphaltene precipitation. Results showed that the obtained equations were in good agreement with experimental data for different temperatures and compositions. Ashoori et al. [36] tested the above stated scaling equations for a core flood and obtained the amount of the precipitated asphaltene at different temperatures and alkane types. The results were compared with previous studies of Rassamdana et al. [32] and Hu and Guo [35] which were not promising with the previous scaling exponents; therefore, a new scaling equation was developed which needs further studies of asphaltenic crudes and subsequently field data. In fact, Ashoori et al. [36] developed two distinct models for solvent to oil ratios greater and lower than 7. Soulgani et al. [37] developed a new scaling equation by modifying the original equation of Rassamdana et al. [32] for asphaltene precipitation of a live oil sample while the pressure and temperature were changed. This model was developed by applying the bubble point and onset pressures, critical temperature and temperature of the live oil. The model was proposed with data of an Iranian oil reservoir and validated for other data from literature. Jafari-Behbahani et al. [38] developed a scaling equation for live oil to determine the amount of asphaltene precipitation as a function of PVT properties of bottom hole live oil including resin to asphaltene ratio, onset pressure, bubble point pressure, reservoir temperature, asphaltene content of bottom hole live oil and solution gas oil ratio. This model was verified using experimental data for asphaltene precipitation in bottom hole live oil, during pressure depletion with Iranian bottom hole live oil samples. This model correlated asphaltene deposition more accurately in comparison to PC-SAFT and Flory–Huggins equations. Manshad et al. [39] also developed a scaling equation for live oil as a function of pressure, temperature, molecular weight, dilution ratio (solvent). This equation was applied to determine the amount of asphaltene precipitation in presence of different solvents and the amount of solvent for the onset point. This model was more accurate in comparison to the other scaling equations. Parameters of the scaling equation were determined using genetic algorithm.

Intelligent models have been much attended in chemical and petroleum industries over the last few decades. Artificial neural networks (ANNs) have been used to model different properties in chemical and petroleum engineering. However, ANN methods require large number of data sets to give more reliable results. Moreover, this approach needs many adjustable parameters including weights and biases, which may lead to uncertainties while applied to different crude oil samples [40]. This methodology may also suffer from over fitting or under fitting problems. Recently, a new powerful intelligent model has been introduced for solving complex and nonlinear problems named least square support vector machine (LSSVM), which showed more accurate results compared to traditional ANNs and correlations. We have already used this modeling approach for predicting the amount of asphaltene precipitation during natural depletion of the reservoir in Iranian live crude oil samples [41]. Herein, we follow up our previously published work and develop an intelligent LSSVM model for prediction of asphaltene precipitation titration data of different dead oil samples [41]. For developing a reliable and consistent model, a large data bank covering a wide range of crude oil samples and thermodynamic conditions is required, which was gathered from literature sources. It is worthwhile to note that the previous scaling equations have been mostly developed by using one crude oil sample, while in this study several crude oil samples from different sources are used [42–44]. After selecting appropriate input parameters, the LSSVM model is developed and its parameters are optimized using a stochastic search method named