



Original Article

## A new thermodynamic model for the prediction of asphaltene precipitation in crude oil

Alireza Fazlali<sup>1,\*</sup>, Sayedmohsen Hosseini<sup>1</sup>, Gholamreza Pazuki<sup>2</sup> and Esmaeel Khosrobeigi<sup>1</sup>

<sup>1</sup> Department of Chemical Engineering, Faculty of Engineering,  
Arak University, Arak, Iran

<sup>2</sup> Department of Chemical Engineering,  
Malek ashtar University of Technology, Tehran, Iran

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### Abstract

It has been proved that asphaltene precipitation is a difficult problem to define and study. Precipitation of these complex and heavy organic compounds can cause serious problems in crude oil production and transportation, residual oil processing and heavy oil combustion. Several theories have been proposed to explain the mechanism of asphaltenes precipitation. The Flory-Huggins (F-H) is one of the famous models, which are used to describe the asphaltene precipitation mechanisms in the same ways as polymeric solutions. In this research, the F-H model has been modified to predict the phase behavior of asphaltene precipitation process during adding non-polar (normal alkane) solvents. The adjustable parameters of this model are computed by using a least-square approach between the modeling results and experimental data. Then, the results of these models are compared with the obtained results of the original F-H and the experimental data at different conditions. According to the interaction parameter as an adjustable parameter, four new functionalities have been used for this target. According to the obtained results, the modified model with a second order equation can predict the amount of asphaltene precipitation better than the others with a minimum error. The calculation shows good agreement between the experimental data and the results of the modified model.

**Keywords:** asphaltene, precipitation, solvent, modeling, crude oil

### 1. Introduction

Crude oil is a complex mixture of hydrocarbons, and can be divided into several fractions of materials, such as saturates, aromatics, resins, and asphaltene compounds. Asphaltenes comprise the most polar fraction of oil, which is insoluble in normal alkanes. Deposition of these complex mixtures as solids causes many problems in crude oil production, transportation, and processing. In fact, asphaltene tends to precipitate under various conditions and can be stabi-

lized as a water-in-oil emulsion (Fazlali, 1999). Asphaltene precipitation around the wellbore, well tubing, flow lines, separators, pumps, and tanks are some examples that can threaten the economical oil recovery or can considerably increase the production costs. Recently, some phenomena such as pH variations, mixing of crude oil streams, incompatible organic chemicals, stimulation, pressure depletion, or streaming potential charged bare metal surface have been reported as different causes of asphaltene deposition (Fazlali, 1999). Asphaltene precipitation has been proved to be a difficult problem to define and study. In such a case, models are needed based on theoretical considerations and experimental results, which can help in the prediction of asphaltene precipitation. Several theories have been proposed to explain

\*Corresponding author.

Email address: A-Fazlali@Araku.ac.ir

the mechanism of asphaltene precipitation. The first important approach in modeling asphaltene precipitation in petroleum engineering was given by Hirschberg *et al.* (1984). A rather simple model for the asphaltene precipitation is the single-component solid model, which was tested by Gupta (1986) and Thomas *et al.* (1992). The previous approaches are based on molecular thermodynamics and are suitable for modeling the situations where the asphaltene/resin micelles precipitate as the essential and unalterable elements (Fazlali, 1999). Leontaritis *et al.* (1987) proposed a different approach for asphaltene flocculation based on a thermodynamic-colloidal model (Fazlali, 1999). A model has also been used to describe the asphaltene precipitation mechanism by a polymeric solution theory. In this case, large asphaltene molecules are supposed to be similar in their structures and behaviors to polymer molecules and the deasphalted oil acts as a solvent (Burke *et al.*, 1990; Fazlali, 1999; Pazuki *et al.*, 2006). In this research, the Flory-Huggins, or F-H model has been modified to predict the phase behavior of the asphaltene precipitation process by adding non-polar (normal alkane) solvents. The adjustable parameters of this model, which are new functionalities for the solubility parameter of the F-H model, are computed by using the Least-Square approach between the selective functions and experimental data of asphaltene precipitation. Then, the results of these models are compared with the original F-H and experimental data at different conditions.

## 2. The Modeling of Asphaltene Precipitation

In this research a vapor-liquid-liquid equilibria model has been used. Separately, vapor-liquid equilibria and liquid-liquid equilibria calculations have been used to predict the phases, which can split (vapor, asphaltene, crude oil), and the SRK equation of state (EOS) has been used for the estimation of the component properties for the lighter fraction and equilibrium calculation. The properties of the heavy fractions in the crude oil system are determined by using empirical correlations (Riazi *et al.*, 1996; Pazuki *et al.*, 2006). As the asphaltene is supposed to be a polymeric like substance dissolved in crude oil, the polymeric solution theory was used for the prediction of asphaltene precipitation in crude oil. The F-H model is a simple model, which has been suggested for the study of the polymeric solution behavior (Fazlali, 1999). According to the F-H theory, the chemical potential of the polymeric compound is calculated as follow:

$$\frac{\mu_p - \mu_p^0}{RT} = \ln \varphi_p + (1 + \frac{V_p}{V_s}) \varphi_s + \frac{V_p}{RT} (\delta_p - \delta_s)^2 \varphi_s^2 \quad (1)$$

where  $\mu$ ,  $\phi$  and  $V$ ,  $\delta$  are chemical potential, volume fraction, molar volume, and solubility parameter, respectively, and the subscripts  $P$  and  $S$  are related to polymer and solvent phases. The solubility parameter is written as below:

$$\delta_i = \left( \frac{\Delta U}{V} \right)_i^{0.5} \quad (2)$$

where,  $\Delta U$  is the vaporization internal energy at constant temperature. The values of  $\Delta U$  and  $V$  are calculated by the SRK equation of state. Therefore  $\Delta U$  is calculated as follows:

$$\Delta U = \int_v^\infty [P - T(\frac{\partial P}{\partial T})_{V, n_T}] dV \quad (3)$$

Then, by using the SRK equation of state and substituting it in the above equation:

$$\Delta U = \int_v^\infty \left[ \frac{RT}{V-b} - \frac{a}{V^2+bV} - \frac{RT}{V-b} \right] dV = - \int_v^\infty \left[ \frac{a}{V^2+bV} \right] dV \quad (4)$$

$$\Delta U = \frac{a}{b} \ln \frac{V+b}{bV} \quad (5)$$

Finally, by the combination of Equation 2 and 5:

$$\delta_i = \left( \frac{a}{bV} \ln \frac{V+b}{bV} \right)^{0.5} \quad (6)$$

The thermodynamic model of F-H does not give a proven reason for not having an adjustable parameter. In this study, the F-H model is modified as follow:

$$\frac{\mu_p - \mu_p^0}{RT} = \ln \varphi_p + (1 - \frac{V_p}{V_s}) \varphi_s + \frac{V_p}{RT} ((\delta_p - \delta_s)^2) \varphi_s^2 + \lambda_{ps} \delta_p \delta_s \quad (7)$$

where  $\lambda_{ps}$  is the interaction parameter between polymer and solvent. The modified F-H model (Equation 7) with different possible functions is used for the estimation of the asphaltene precipitation in crude oil. In this study, it is assumed that the asphaltene phase is a pure liquid pseudo-component where the asphaltene precipitation has no effect on the liquid-vapor equilibrium. Also, crude oil is considered as a binary homogeneous mixture of asphaltene and solvent (Fazlali, 1999; Pazuki *et al.*, 2006). Based on the above assumptions and by considering  $P$  and  $S$  indices for asphaltene and solvent, Equation 7 will be simplified as below:

$$\frac{\mu_p^L - \mu_p^0}{RT} = \ln \varphi_p + (1 - \frac{V_p^L}{V^L}) + \frac{V_p}{RT} ((\delta_p - \delta^L)^2) + \lambda_{ps} \delta_p \delta_s \quad (8)$$

When the differential chemical potentials of asphaltene component are equalized in the two phases of asphaltene and liquid, then we have:

$$\varphi_p^L = \exp \left[ \left( \frac{V_p^L}{V^L} - 1 \right) - \frac{V_p^L}{RT} ((\delta_p - \delta^L)^2) + \lambda_{ps} \delta_p \delta_s \right] \quad (9)$$

where the superscription L is for liquid phase. In respect to the above equation the weight fraction of asphaltene precipitation is calculated as below:

$$\omega_p = \frac{(1 - \varphi_p^L)(Mw^L/V^L)}{(1 - \varphi_p^L)(Mw^L/V^L) + \varphi_p^L(Mw_p/V_p)} \quad (10)$$

Also the  $\lambda_{ps}$  is a function of asphaltene and solvent properties (e.g. molecular weight), and solvent ratio (volume ratio of n-alkane solvent to crude oil). Several functions have been examined for this including:

$$\lambda_{PS,1} = \alpha_1 X + \beta_1 \quad (11)$$

$$\lambda_{PS,2} = \alpha_2 X^2 + \beta_2 X + \gamma_2 \quad (12)$$

$$\lambda_{PS,3} = \alpha_3 X^3 + \beta_3 X^2 + \gamma_3 X + \xi_3 \quad (13)$$

$$\lambda_{PS,ln} = \alpha_4 \ln X + \beta_4 \quad (14)$$

where X is described as following equation:

$$X = \frac{(1+SR)Mw_p}{Mw_{oil} + SR * Mw_s} \quad (15)$$

and SR is the volume ratio of added solvent and crude oil.

The coefficients of the equations are obtained by using a least-square approach between the experimental data of asphaltene precipitation and calculated values from the model. In general, the F-H model has been modified by an interaction parameter, which is based on the molecular weight of asphaltene, crude oil, and solvent, and the volume ratio of the added solvent. Then the amount of asphaltene precipitation was determined by using the SRK EOS and the modified F-H model.

### 3. Results and Discussion

In this study, the amount of asphaltene precipitation in an oil sample from south west Iran has been calculated at different proportions of n-Heptane, n-Hexane, and n-Pentane precipitants based on the F-H model and the modified F-H model. The specifications of oil sample are shown in Table 1 (Rassmdana *et al.*, 1996). The SRK EOS and the sample mixing roles have been used for calculation of the solubility parameter and the molar volume. Based on the studies, the amount of asphaltene precipitation is very sensitive to the differential solubility of asphaltene and solvent parameters (Fazlali 1999; Pazuki *et al.*, 2006). These variations of solubility parameters is due to the change in the nature of liquid phase, their interaction, variation of molecular weight and the amount of polar compound in the liquid phase (Fazlali 1999; Pazuki *et al.*, 2006). The values of  $\alpha_i$ ,  $\beta_i$ ,  $\gamma_i$ ,  $\xi_i$  for each of the organic solvents of n-C<sub>5</sub>, n-C<sub>6</sub> and n-C<sub>7</sub> are indicated in Table 2.

Table 1. The mole fraction of crude oil components (Rassmdana *et al.*, 1996).

| Component                      | Mole % |
|--------------------------------|--------|
| C <sub>1</sub> -C <sub>3</sub> | 0      |
| i-C <sub>4</sub>               | 0.05   |
| n-C <sub>4</sub>               | 0.64   |
| i-C <sub>5</sub>               | 1.69   |
| n-C <sub>5</sub>               | 2.21   |
| n-C <sub>6</sub>               | 4.23   |
| C <sub>7</sub> <sup>+</sup>    | 91.18  |

Asphaltene Content 11%, Molecular Weight of Oil, 200; Specific Gravity, 0.8778.

The comparison between asphaltene precipitation based on the modified F-H models, F-H, experimental data (Rassmdana *et al.*, 1996) and different solubility ratios are indicated in Figure 1 to 3.

### 4. Conclusions

According to Table 3, it can be seen a good agreement between predictions and experimental data, thus the modified model's credibility becomes distinct. According to the results, the SRK EOS and the modified F-H model along with the second degree polynomial for interaction parameter

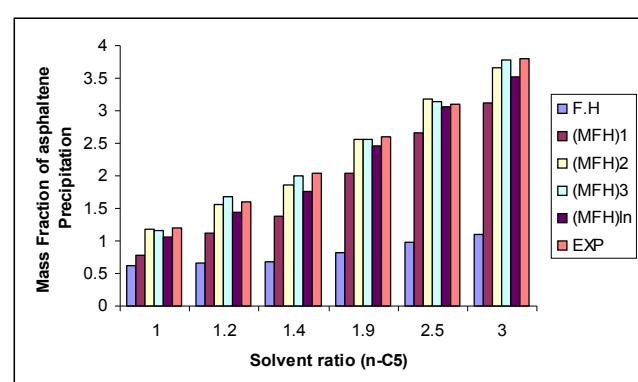


Figure 1. Comparison between the values of asphaltene precipitation obtained from modified Flory-Huggins models and Flory-Huggins models and the experimental data in different ratios of n-C<sub>5</sub>.

Table 2. Adjustable parameters for modified model.

| Solvent          | $\alpha_1$ | $\beta_1$ | $\alpha_2$ | $\beta_2$ | $\gamma_2$ | $\alpha_3$ | $\beta_3$ | $\gamma_3$ | $\xi_3$ | $\alpha_4$ | $\beta_4$ |
|------------------|------------|-----------|------------|-----------|------------|------------|-----------|------------|---------|------------|-----------|
| n-C <sub>5</sub> | 0.0003     | -0.0022   | -1E-5      | 0.0005    | -0.003     | 8E-5       | -0.0022   | 0.0194     | -0.0571 | 0.0028     | -0.0055   |
| n-C <sub>6</sub> | 1.8881     | -13.558   | 0.7389     | -9.2299   | 28.213     | 4.6331     | -103.94   | 778.6      | -1946.9 | 14.179     | -27.957   |
| n-C <sub>7</sub> | 0.662      | -4.4736   | -0.165     | 3.07      | -13.252    | 6.112      | -133.98   | 979.29     | -2386.4 | 4.8294     | -9.2394   |

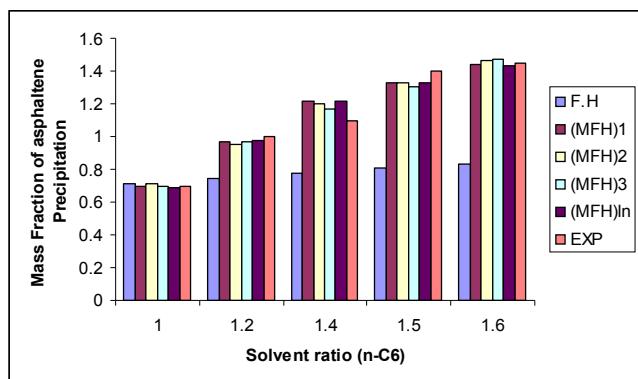


Figure 2. Comparison between the values of asphaltene precipitation obtained from modified Flory-Huggins models and Flory-Huggins models and the experimental data in different ratios of *n*-C<sub>6</sub>.

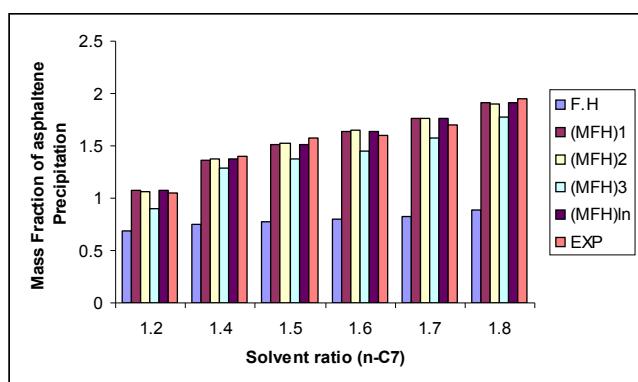


Figure 3. Comparison between the values of asphaltene precipitation obtained from modified Flory-Huggins models and Flory-Huggins models and the experimental data in different ratios of *n*-C<sub>7</sub>.

Table 3. Average relative error for each  $\lambda_{ps}$  and F-H model.

| Solvent          | (E) <sub>1</sub> | (E) <sub>2</sub> | (E) <sub>3</sub> | (E) <sub>ln</sub> | (E) <sub>F-H</sub> |
|------------------|------------------|------------------|------------------|-------------------|--------------------|
| n-C <sub>5</sub> | 0.2512           | 0.0353           | 0.0236           | 0.0829            | 0.6365             |
| n-C <sub>6</sub> | 0.0402           | 0.0437           | 0.0361           | 0.0414            | 0.2822             |
| n-C <sub>7</sub> | 0.0276           | 0.0255           | 0.1014           | 0.0269            | 0.4793             |

predict well the asphaltene precipitation values with different solubility values, which have a suitable coordination with experimental data. Based on the results, it is concluded that, as the ratio of solvent to oil (SR) increases the weight fraction of asphaltene precipitation increases and accelerates with the increase of solvent molecular weight. It can be further concluded that the differential solubility parameter acts as a driving force in the formation of asphaltene precipitation. By considering the limited amount of asphaltene after some time, the further addition of precipitant will lead to a constant value in asphaltene precipitation (Fazlali 1999; Pazuki *et al.*, 2006).

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