



### Effects of Increment or Decrement Operational Factors on Asphaltene Deposition in Shahid Mansoori Oilfield of Iran

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### Abstract

Keywords:	In this article asphaltene precipitation models are described and in a case study the precipitated asphaltene is represented by an improved solid model. The main purpose of this study is to
Asphaltene, Precipitation, APP diagrams, Reservoir.	model and anticipate the effects of major parameters on formation of asphaltene precipitation and deposition at reservoir conditions, in order to provide a better understanding of the factors that may enhance asphaltene precipitation or deposition. The oil and gas phases are modeled with Peng-Robinson equation of state. The effect of several factors such as solid molar volume and injected solvent gas composition as well as thermodynamic condition variations (such as pressure and temperature) on the predictions made by this model will be investigated too. Eventually, with regard to the experimental data that has been obtained from one of the oil wells located at the South Oil Zones of Iran's oilfields, the accuracy of modeling and anticipating of asphaltene precipitation will be checked. All of the related calculations have been done by Winprop software from CMG package.

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### 1. Introduction

Nowadays the asphaltene deposition's problems in oil industries are growing much higher compare to the past time. These depositions can be seen especially during the solvent gas injection for enchanted oil recovery and also after a certain part of well's life has been passed (at the same time that pressure drop in the well starts). Obviously for fully understanding the asphaltene deposition problems and performing effective preventive procedures for confronting with this phenomenon; there should be a comprehensive study about the effective parameters and related factors that have the most influence on this topic. The main goal of this article is considering and analyzing such reviews. We also should mention that there are some differences between the Deposition and Precipitation, deposition is occurring when asphaltene is separated from crude oil and forming a single solid

phase whereas Precipitation occurs when asphaltene sticks to a solid surface like pipes or oil stone surfaces. Therefore the problems which are made by asphaltene precipitation can be removed by proper anticipation and exact controlling of asphaltene deposition. On other words, asphaltene precipitation can be formed only when asphaltene deposition occurs. Since that recognizing asphaltenes behavior, need complete and comprehensive information about crude oil compositions, first of all we will pay attention to expression generalities about crude oil compositions properties.

### 2. Reviewing the Thermodynamics Models for Asphaltene Precipitation

The most important models that have been presented and developed so far are these models:

#### A. Dissolving Model (1984)

With regards to the common definitions for asphaltene (like its solubility in aromatics) a thermodynamic model can be developed for asphaltene deposition. Hirschberg et al. [1] presented a model by using these definitions and assumptions. In this model, the related calculations to liquid and gas phases equilibrium and flash calculation has been done by SRK equation of state [2]. In this model it is assumed that asphaltene deposition (if formation be done) has no effect on gas liquid equilibrium. By defining the maximum volume of solved asphaltene in the oil in form of  $(\phi_a)_{max}$ ; this model can be presented as equation 1:

$$\ln\left(\phi_{a}\right)_{\max} = \frac{v_{a}}{v_{1}} \left[1 - \frac{v_{1}}{v_{a}} - \frac{v_{1}}{RT} \left(\overline{\delta}_{a} - \overline{\delta}_{1}\right)^{2}\right]$$
(1)

In this equation, the molar volume of asphaltene is a function of its molar weight and specific weight. As regards to this fact that almost all of the developed methods for determination of molecular weight are relating to molecular collision effects in solution, the exact value of  $(\phi_a)_{max}$  is not measurable at equation 1 and this is the biggest weak point of this equation. Solubility parameter,  $\overline{\delta}$  in this equation can be estimated by determination of solubility amount of asphaltene in different solvents and specifying the way that asphaltene react with these solvents per increasing asphaltene solubility. Therefore, asphaltene solubility parameter is reported as the asphaltene dissolution on the best solvent. This parameter also can be defined as a linear function of temperature as equation 2:

$$\overline{\delta} = a + bT \tag{2}$$

Where 'a' and 'b' are constants [3].

### **B.** Thermodynamic Model of Collision (1987)

With assuming asphaltene as a suspended solid particle within crude oil which is surrounded by resins; Mansoori presented a thermodynamic model. In this model, according to experimental data about initial point of asphaltene forming, a critical chemical potential is estimated for resins and then this critical chemical potential can be used for anticipation of the initial deposition point in other conditions [4].

# C. Thermodynamic Model of Micellars Formation (1987)

According to formation method of asphaltene sediment cells which known as micellars and minimizing Gibbs energy, Firozabadi&Pen presented thermodynamic model for asphaltene deposition. This model is highly accurate and can confirm the experimental data with high precision. Nevertheless some efforts for improving this model are in progress that has had no success so far [4].

### D. Solid Model (1988)

This model is one of the simplest models for anticipating asphaltene deposition which asphaltene assume as a pure solid and single phase within oil and its gaseous solution. In this model oil and gas phase behavior is simulating by cubical equation of state. Pure solid fugacity (asphaltene) can be determined from equation 3 as below:

$$\ln f_{s} = \ln f_{s}^{*} + \frac{v_{s} (P - P^{*})}{RT}$$
(3)

It is worth mentioning that some of the experimental data which gained by scientists was used for testing above equation and the result was not very satisfactory for a part of these data [5]. The other presented models for asphaltene deposition are generally complex and have too many configurable parameters that lead to a more complicated model. An overall comparison between the presented models will be discussed in next section of this article.

### 3. Comparison of Models

Model 4 (solid model) was based on calculation of fugacities while models 1-3 were formed according to activity factors. Solid model is using the same components that were used in equations of state for modeling of gas and oil phase, while in two previous models, first gas-oil two phase flash calculations have been done for dividing oily mixture into oil and gas phase and then oil phase is divided into different components for modeling of asphaltene deposition. So that in model 1 the oil phase is divided into two components which asphaltenes contain one of these components and the other component includes nonasphaltenes. In models 2 and 3 an extra component for including the micellars and along resins effect on simulating has been applied.

Although that deposition rate clearly has influence on oil and gas phase equilibrium, the first three models neglects this effect, which this ignoring may lead to occurring some errors in oil-gas phase calculations (note that heavy components like asphaltene have major effects on equilibrium conditions of saturated vapor solution).

Briefly, if the purpose of simulation is applying thermodynamic model with a multi-components modeling, using model 4 is recommended. This exclusive property makes model 4 (solid model) one of the best possible choice for usage in related simulating programs like Winprop.

#### 4. CASE STUDY

In this section according to experimental data that is gained from one of the oil reservoirs in south of Iran, suggested thermodynamic models in Winprop

Table 1: Reservoir oil properties.

	Value	Unit
Reservoir temperature	378.7	K
Saturated pressure	9515	Kpa
Asphaltene volume percentage	7.71	%Wt
Reservoir oil molecular weight	166	
GOR	278.35	SCF/STB

Table 2: Heavy components properties.

	Value
Molecular weight of heavy components C <sub>12</sub> +	330
Molecular weight of C <sub>12</sub> +	0.9636

software (from CMG software package) will be investigated and the results will be compared with experimental data. Eventually to anticipate the amount of thermodynamic equilibrium conditions (such as temperature, pressure, oil molar fraction and ...) effects on increasing or decreasing of asphaltene deposition, these results will be used too.

Tables 1, 2 and 3 are showing overall properties of crude oil and thermodynamic conditions of reservoir during oil extraction.

Table 3: Crude oil composition in one of the southernIranian oilfield.

Components	Oil Reservoir (%mol)
C1	19
$C_2$	7.1
C <sub>3</sub>	5.21
iC4	1.11
nC <sub>4</sub>	2.9
iC5	1.1
nC <sub>5</sub>	1.1
C <sub>6</sub>	5.4
<b>C</b> <sub>7</sub>	4.1
C <sub>8</sub>	3.4
<b>C</b> 9	3.07
C <sub>10</sub>	2.95
C <sub>11</sub>	2.59
$C_{12}^{+}$	39.62
$N_2$	0.3
CO <sub>2</sub>	0.9

### A. Specifying Asphaltene Component

The very first step in simulation is specifying the related asphaltene components. Using separation or accumulation abilities in Winprop software can help us to reach this goal. C12+ components can be broken

up to C21+ or C31+, in both case those components will mark as Ultra heavy or asphaltene part of oil.

Therefore, if we want to divide the components up to C21+ by using the approved methods, it is necessary to have an estimate about critical and physical conditions of divided hydrocarbon groups such as IC<sub>4</sub>-

NC<sub>4</sub>  $(IC_5-C_6, C_7-C_{15}, C_{16}-C_{20})$  and  $C_{21}+$ . The critical conditions estimate for heavy components with having some data about special mass and molecular weights of  $C_{21}+$  component, is calculating by Lee-Kesler equations [6], [7]. Physical conditions of mixture are estimated by Teo equations. Applying regression analysis on hydrocarbon heavy group's data for achieving more accurate and valid results seems essential of course. This analysis applies by Winprop software itself. It should be mentioned that the oil and gas phase have been modeled by Peng-Robinson

equation of state [8]. Table 4 shows the crude oil sample data after regression and dividing the heavy component up to  $C_{21}$ +. Similarly these divisions are applicable up to  $C_{31}$ + group. Table 5 shows these results after regression analysis. To determine which components of asphaltene will sediment for certain, we need to divide heavy component (such as  $C_{21}$ + or  $C_{31}$ +) into two different parts, one part that is able to sediment.

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	P <sub>c</sub> (atm)	T <sub>c</sub> (K)	ω	Mw	Z	Vc(l/mol)	SG	Mol%
CO2	72.8	304.2	0.225	44.01	0.2736	0.094	0.818	0.93
N2	33.5	126.2	0.04	28.013	0.2905	0.0895	0.809	0.3
C1	45.4	190.6	0.008	16.043	0.2876	0.099	0.3	18.91
C2	48.2	305.4	0.098	30.07	0.2789	0.148	0.356	7.2
C3	41.9	369.8	0.152	44.097	0.2763	0.203	0.507	5.21
IC4-NC4	36.679	422.805	0.208199	58.124	0.27182	0.2582	0.57827	4.04
IC5-C6	31.792	499.214	0.260697	81.1134	0.26541	0.3446	0.66932	7.66
C7-C15	28.26942	614.7636	0.466133	117.8796	0.25672	0.5485	0.80087	29.16
C16-C20	19.48304	735.1288	0.731515	198.5777	0.24694	0.8634	0.8743	15
C21+	12.14509	875.1478	1.106591	347.3872	0.22982	1.4187	0.94981	11.59

Table 4: Crude oil component's properties (after lumping to C21+).

Table 5: Crude oil component's properties (after lumping to C31+).

	P <sub>c</sub> (atm)	T <sub>c</sub> (k)	ω	Mw	Z	V <sub>c</sub> (l/mol)	SG	Mol%
CO2	72.8	304.2	0.225	44.01	0.2736	0.094	0.818	0.93
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C3	41.9	369.8	0.152	44.097	0.2763	0.203	0.507	5.21
IC4	36	408.1	0.176	58.124	0.275	0.263	0.563	1.11
NC4	37.5	425.2	0.193	58.124	0.2728	0.255	0.584	2.93
IC5	33.4	460.4	0.227	72.151	0.2716	0.306	0.625	1.05
NC5	33.3	469.6	0.251	72.151	0.2685	0.304	0.631	1.14
FC6	32.46	507.5	0.27504	86	0.271261	0.344	0.69	5.44
C07-C15	25.90178	652.5765	0.451664	147.2724	0.265039	0.521218	0.827641	16.15
C16-C25	16.00509	809.8804	0.789045	279.2312	0.250012	0.927762	0.91395	2.572
C26-C30	12.07802	899.7084	1.014742	389.5274	0.239198	1.248509	0.959793	10.3
C31+	6.808553	1075.737	1.423258	665.624	0.207435	2.197911	1.044126	6.758

The part that is able to sediment marks with B and the other part marks with A. equation 4 can calculate asphaltene molar fraction which sediment in oil [9].

$$x_{asph-B}Mw_{asph} = w_{asph}Mw_{oil} \tag{4}$$

In continue APP diagrams (Asphaltene deposition Per Pressure) and the effect of changes in different thermodynamic conditions on those diagrams will be discussed.

### B. Deposition diagram

By dividing crude oil hydrocarbon's group up to  $C_{21}$ + and applying the listed methods, the rate of asphaltene

deposition per pressure diagram can be drawn. This diagram is comparable with experimental data which is listed on table 6. Figure 1 shows this diagram versus table 6. Is it clear that there is an acceptable agreement between APP diagram and experimental data before the bubble pressure of oil, while this agreement goes away after the bubble pressure. Figure 2 shows App diagram for broken components of oil up to  $C_{31}$ +. After comparing the diagram with experimental data, we realize that unlike the previous figure, in this case, there is a good agreement between APP diagram and experimental data after the bubble pressure while this agreement is almost vanished for lower pressure than bubble pressure.

Table 6: Experimental data for asphaltene deposition.

Asphaltene Deposition (Wt%)	Pressure (Kpa)
2.71	6895
3.21	8963
2.86	13789
1.96	20684



Fig. 1: APP diagram after lumping to C21+.



Fig. 2: APP diagram after lumping to C31+.

### C. Anticipation of molar volume of sediment component effect on solid precipitate

As it can be seen, a decrease in molar volume will lead to a contraction in APP diagram and thus reduction in deposition.

Figure 3 shows the APP diagram for different molar volume of  $C_{31}B$ + component in asphaltene deposition.



Fig. 3: Effect of sediment component's molar volume increment on APP diagram.

### D. Anticipation of temperature effect on solid precipitate

Temperature increment in temperatures below the bubble point (in here between 278 to 311 K) will

cause relative reduction in asphaltene deposition (figure 4). While in temperatures above the bubble point (between 380 to 434 K) temperature increment has an inverse role and will lead to a growth in deposition (figure 5).



Fig. 4: Temperature increment (278-311 K) effect on APP diagram.



Fig. 5: Temperature increment (380-434 K) effect on APP diagram.

### E. Anticipation of solvent gas injection effect on solid precipitate

In this section, injection effect of different and common gaseous solvents (that usually are being used for enhanced oil recovery from reservoirs) on amount of asphaltene deposition changes in APP diagrams will be investigated. The major pure gases that their effects (in various volumes) on amount of deposition will be studied, are CO<sub>2</sub> and N<sub>2</sub>. First with regards to injected gas data, changes mode of asphaltene deposition per different injected molar parts toward

extracted crude oil will be investigated. These data are listed in table 7. It must be pointed out that majority part of returned gas to the oil mixture are contain of light hydrocarbon components such as  $C_1$ ,  $C_2$ , and  $C_3$ than components like N<sub>2</sub> and CO<sub>2</sub>. Figure 6 shows the related APP diagram which according to that, per pressures below bubble point, amount of increment in deposition, during increase of molar volume of injected gas are much lower than pressures above bubble point. Moreover, higher molar fraction of injected gas will lead to a sharp increase in asphaltene deposition.

Component	Injected gas (%mol)
$N_2$	0.79
CO <sub>2</sub>	2.49
C1	50.6
$C_2$	18.45
C3	12.72
iC4	2.17
nC4	6.26
iC <sub>5</sub>	1.9
nC <sub>5</sub>	2.14
C <sub>6</sub>	1.77
<b>C</b> <sub>7</sub>	0.64
C <sub>8</sub>	0.07

Table 7: Sample injected gas compositions.



Fig. 6: Effect of injected gas (in table 7) on APP diagram.

#### E.1. CO<sub>2</sub> injection

Effect of  $CO_2$  injection on APP diagram is indicated on figure 7. A very small increase in deposition increment before the bubble pressure is detectable while on pressures above the bubble point increase in deposition during injection even in low amounts of  $CO_2$  is relatively high.



Fig. 7: Effect of various amounts of CO2 injection on APP diagram.

#### E.2. N<sub>2</sub> injection

The effect of injecting this gas is almost reverse as  $CO_2$  injection effect. As it can be seen on figure 8, per each increment on amount of injected  $N_2$  up to a specific pressure, a noticeable decrease in asphaltene

deposition will take place and then it will increase slightly per smaller mol fractions. While injection of  $N_2$  gas on higher amount is happening, Asphaltene maximum amount reduction will take place and it begin to stretch to right side of the diagram (higher pressures) on figure 8.



Fig. 8: Effect of various amounts of N2 injection on APP diagram.

#### 5. CONCLUSION

When pressure is above the bubble point pressure and below the formation point of asphaltene, reduction of pressure leads to an increment in solid deposition and vice versa when pressure is lower than reservoir bubble pressure, reduction of reservoir pressure leads to a reduction in solid asphaltene amount. The forecast APP graphs shape will change by using different molar ranges. Temperature increase may lead to an increment in asphaltene deposition problems or decrease this deposition amount. Gas injection significantly will increase asphaltene maximum deposition amount, also initial deposition point will take place on higher pressure (much faster).

Increment in injection of some gases like  $CO_2$  on reservoir cause an expanding on APP diagrams and consequently will increase the deposition for pressures higher than bubble point, while injection of  $N_2$  gas leads to shrinkage on APP diagram at pressures below the bubble point and will bring deposition reduction in these areas. APP diagrams can be used for estimation of asphaltene deposition details like when, how much and where (such as inside of reservoir or around of reservoir edges and...) it will happen inside oil wells.

To obtain high accuracy APP diagrams, at least three points of APP graph should be studied and compared by experimental data. These data are asphaltene initial pressure point, weight percentage and a pressure between initial point and bubble point and eventually a weight percentage of the component that will deposit and a pressure below bubble point.

#### NOMENCLATURE

R =Gas global constant (8.314 kPa.m<sup>3</sup> /kmol.K) T = Temperature (K)

 $v_a$  = Molar volume of asphaltene (m<sup>3</sup>/kmol)

 $v_l$  = Non oil asphaltene–solvent mixture molar volume (m<sup>3</sup>/kmol)

 $\overline{\delta}_{a}$  = Asphaltene dissolution parameter (kPa<sup>0.5</sup>)

 $\overline{\delta}_1$  = Oil-solvent mixture dissolution parameter (kPa<sup>0.5</sup>)

 $f_s$  = Asphaltene solid phase fugacity (kPa)

 $f_s^*$  = Reference fugacity for solid phase (kPa)

P = Pressure (kPa)

 $P^*$  = Reference pressure (kPa)

 $v_s$  = Solid asphaltene deposition molar volume

(m<sup>3</sup>/kmol)

 $x_{asph-B}$  = Molar fraction of asphaltene in crude oil mixture which will sediment

 $M_{W_{asph}}$  = Asphaltene molecular weight

 $W_{asph}$  = Weight fraction of asphaltene in crude oil mixture

 $M_{W_{oil}}$  = Crude oil molecular weight

*GOR* = Gas/oil ratio (SCF/STB)

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