Iraqi Journal of Oil & Gas Research, Vol. 1, No. 1 (2021)

Iraqi Journal of Oil & Gas Research

Journal homepage: https://ijogr.uotechnology.edu.iq/

Prediction of Asphaltene Precipitation Behaviour of Khasib Formation / Halfaya Oil Field

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Article information

Article history:
Received: July, 19, 2021
Accepted: October, 5, 2021
Available online: October, 8, 2021

Keywords:
Asphaltene Precipitation,
Asphaltene Deposition,
Asphaltene Precipitation Modeling

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Abstract

Asphaltene precipitation from reservoir fluids during oil production is a serious problem because it can result in plugging of the formation, wellbores and production facilities. An efficient modelling technique based on the representation of the precipitated asphaltene from live oil of Khasib Formation / Halfaya Oil Field as a pure dense phase is presented. The success of the approach is based on the division of the heaviest component in the oil into a nonprecipitating and a precipitating component. This case study described the procedure for modeling the precipitation of asphaltene from a live reservoir oil due to pressure depletion. The thermodynamic model used to describe the precipitation of asphaltene. The precipitation of asphaltene is modelled using a multiphase flash calculation in which the fluid phases are described with an equation of state (Peng-Robinson equation of state) and the fugacities of components in the solid phase are predicted using the solid model. The used model showed that there was asphaltene precipitation problem of the selected fluid at specified conditions and approaching these conditions should be avoided during production to provide treatment costs.

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1. Introduction

The capability of a petroleum production system to carry fluid from porous media via pipelines and surface facilities and finally to the point of sales during the project life refers to flow assurance. This capability will degrade by pores plugging or formation damage due to asphaltenes deposition. Other hindrance factors such as slugging, deposition of wax, scale, formation of hydrate and corrosion are also considered as flow assurance. Among these main flow assurance issues, asphaltenes problems are the least understood [1].

Asphaltenes are the solubility fraction of oil, which are insoluble in alkane such as n-heptane and soluble in aromatic solvents, such as toluene [2-4]. There are different reasons of precipitation of asphaltenes such as changes in pressure, temperature or crude oils chemical composition and also operations like acidizing or EOR process such as dilution of oil with diluents and CO2 [5].

Asphaltene precipitation have been predicted by many approaches. The most hard-working approaches consider asphaltenes exist as macromolecules with the other constituents of crude oil in a non-ideal solution [3]. Asphaltene precipitation modeling and prediction are depended on one of the two theories either solubility or

colloidal. The approach of solubility supposes that the asphaltenes are solvated in crude oil and when the solubility falls below a certain level of threshold, the precipitation will occur [6]. The two theories of regular solution and equation of state (EOS) are main approaches of solubility theory. The theory of colloidal considers that the asphaltenes presence as colloidal particles settled by resins adsorbed onto surfaces of asphaltene [7]. The solubility of asphaltene depends on resins distributing between the medium of the surrounding and the colloidal surface. The destabilization and precipitation of asphaltene occur when resins desorb with a sufficient amount [8].

In this study, the thermodynamic model was used to describe the precipitation of asphaltene. The modelling of asphaltene precipitation is made by using calculation of a multiphase flash. In this model, the fluid phases are characterized by using an equation of state (Peng-Robinson equation of state) and the fugacities of components in the solid phase are predicted by using the solid model.

2. Thermodynamic Model

Nghiem et al. supposed that the precipitated asphaltenes exist as a dense and pure phase in the crude oil. They divided the crude oil heaviest component (C_{31+}) into non-precipitating (C_{31A+}) and precipitating components (C_{31B+}). The precipitating components contain dissociated asphaltene and precipitated asphaltene-resin micelle while the nonprecipitating component contain heavy paraffins and non-precipitated or undissociated asphaltene-resin micelle. There are identical critical properties (critical pressure and critical temperature) and acentric factors (an indicator of the molecules non-sphericity) of precipitating and non-precipitating components, but the interaction coefficients between these components and light components were different [9]. The solid, liquid and vapor phases are represented by this models as follows:

Solid phase: The precipitated asphaltene is described as a pure solid and the solid phase fugacity is found by:

$$\boldsymbol{ln\, f_s = ln\, f_s^* + \frac{V_s(p-p^*)}{RT}} \qquad (1)$$

Liquid and vapor phases: The liquid and vapor phases are modeled by an EOS with volume shift parameters. The component i fugacity in phase j (j = oil, gas) is given by:

$$\boldsymbol{ln\, f_{ij} = ln\, f_{ij}^{eos} + \frac{s_i b_i p}{RT}} \qquad i=1,\ldots n_c;\ j=v,1 \qquad (2)$$

The phase j molar volume with volume shift is given by:

$$\boldsymbol{V_j = V_j^{eos} + \sum_{i=1}^{n_c} y_{ij} s_i b_i} \qquad (3)$$

Peneloux et al. was first introduced the volume shift parameter to improve the predictions of liquid density. The volume shift parameter was not supposed by Nghiem et al. in their modeling technique. It is shown that this parameter is essential in asphaltene precipitation modeling due to pressure change. It also recompenses for the error in the solid volume V_s[10].

When the solid, liquid and vapor phases coexist, the following equation of thermodynamic equilibrium are fulfilled:

$$\boldsymbol{ln\, f_{iv} = ln\, f_{il}} \qquad (4)$$

$$\boldsymbol{ln f_{n_n v} = ln\, f_{n_c l} = ln\, f_s} \qquad i=1,\ldots n_c \qquad (5)$$

3. Peng-Robinson equation of state

Peng and Robinson proposed the following equation of state (PR EOS), as a basis for creating his perfected model [11]:

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)+b(v-b)} \quad (6)$$

where:

$$a(T) = a_c \alpha(T) \quad (7)$$

$$a_c = 0.42747 \frac{R^2 {T_c}^2}{P_c} \quad (8)$$

$$b = 0.07780 \frac{RT_c}{P_c} \quad (9)$$

$$\alpha(T) = \left(1 + m\left(1 - \sqrt{\frac{T}{T_c}}\right)\right)^2 \quad (10)$$

$$m = 0.3796 + 1.54226\omega - 0.2699\,\omega^2 \quad (11)$$

4. Precipitation Calculation

Flash calculations are performed in a stage-wise manner as shown in figure 1. More details can be found in Nghiem et al. [9].

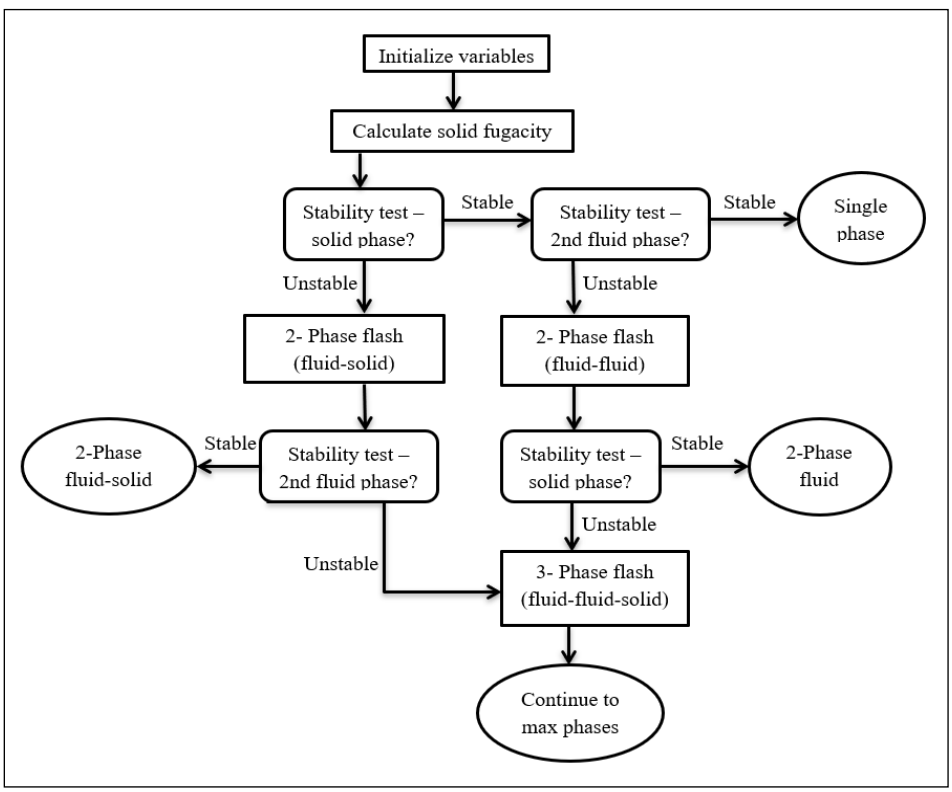

Figure 1: Three-phase vapor/liquid/solid flash calculation flow charts [9].

The existence of a solid phase satisfies the following criteria:

The solid phase exists if:

$$\ln f_{n_c l} \geqslant \ln f_s$$

$$\ln f_{n_c j}^{eos} + \frac{s_{n_c} b_{n_c} p}{RT} \geqslant \ln f_s^* + \frac{V_s(p-p^*)}{RT} \qquad (12a)$$

The solid phase does not exist if:

$$\ln f_{n_c l} < \ln f_s$$

$$\ln f_{n_c j}^{eos} + \frac{s_{n_c} b_{n_c} p}{RT} < \ln f_s^* + \frac{V_s(p-p^*)}{RT} \qquad (12b)$$

5. Application of Thermodynamic Model

The thermodynamic model was used in this study as follows:

Outline:

The modeling of the phase behaviour of asphaltene precipitation during primary depletion is illustrated using the experimental data live oil of Khasib Formation / Halfaya Oil Field. An interpretation of the mechanistic aspect of the model is given.

Experimental data:

The experimental PVT and precipitation data for the sample of oil from Khasib Formation / Halfaya Oil Field was taken from fluid analysis studies report on bottom hole samples of the selected well [12]. The sample information is presented in table 1.

Table 1: Sample identification and sampling Details.

Sample identification	Sampling details
Type of sample	BHS
Sampling depth	2500
Formation	Khasib
Reservoir conditions (Psia / ˚C)	4849.1/90.4
Water content	<1
Nature of Sample	Black Oil
Bubble point pressure (psia)	4000
GOR (scf/stb)	940
Density (g/cc)	0.912
API	23.5
Compressibility at Reservoir Pressure ($psia^{-1}$)	11.00×10^{-6}

The measured oil composition which was obtained from the report is shown below in table 2.

Table 2. Sample composition.

Compound	Mole%
Nitrogen	0.51
Carbon dioxide	0.93
Hydrogen sulphide	0.00
Methane	42.12
Ethane	9.34
Propane	5.79
Iso-Butane	1
Normal-Butane	3.17
Iso-Pentane	1.45
Normal-Pentane	1.83
Hexane	2.98

Plus heptane	30.89

The specific gravity and molecular weight of plus heptane fraction are 0.924 and 267.39 respectively.

The detailed asphaltene flow assurance study was conducted on a sub-sample from monophasic bottom hole sample by using fixed Wavelength near infrared red (NIR) light transmittance technique to measure the Asphaltene Onset Pressure (AOP) at reservoir temperature of 90.4°C. The result of this technique via using Solid Detection System (SDS) cell is shown in figure 2. Based on the NIR light transmittance through the sample in the SDS, the AOP is observed at around 4154 psia.

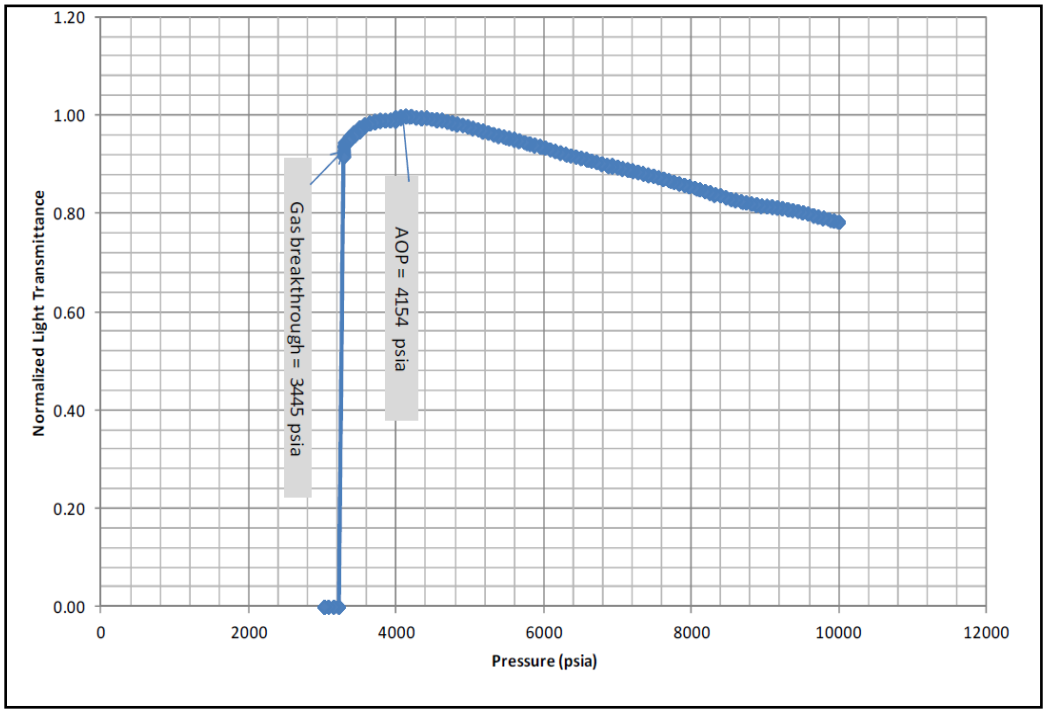

Figure 2: NIR Scan for Asphaltene Onset Pressure.

Also asphaltene content of stock-tank oil samples is conducted using the IP-143 (French Institute of Petroleum) procedure and the weight percent of asphaltene content was 4.8%. Other PVT tests such as constant composition expansion (CCE), differential liberation at reservoir temperature (DL), separator and viscosity of live fluid at reservoir temperature were also take from fluid analysis studies report on bottom hole samples of the selected well to use these data in building PVT model by using PR EOS equation for tuning the simulated data.

Methodology:

The following steps are required to create an asphaltene precipitation model:

1. Characterization of the fluid.

2. Regression on experimental fluid PVT properties.

3. Solid model parameters specification.

4. Asphaltene precipitation behavior prediction.

1. Characterization of the fluid: This case study is started by preparing a data set in order to make a characterization of the fluid by describing the compositions of components until hexane and pseudo-components defining the plus heptane fraction as shown in table 2. The data of composition of components extending to hexane has been used, and a calculation of plus fraction splitting has been specified with the molecular weight

and specific gravity of plus heptane. The plus fraction has been lumped into four pseudo components, and the correlations of Lee-Kesler critical property has been used and finally the specification of system component was updated.

2. Regression on experimental fluid PVT properties: After splitting and lumping, the model of the equation of state has been tuned to all available PVT data with regression by preparing the regression data set of PVT tests from fluid analysis studies report on bottom hole samples of the selected well.
3. Solid model parameters specification: The asphaltene component was identified by dividing the oil heaviest component into precipitating and non-precipitating components (the heaviest component in the oil (e.g. C_{31+}) is split into a precipitating component (C_{3IB+}) and a non-precipitating component (C_{3IA+})). The critical properties and acentric factors for these two components are the same, however the light components up to about pentane have higher binary interaction coefficients with the precipitating component. The same binaries for carbon dioxide and nitrogen were entered of C_{31B+} and C_{31A+}, then the values of 0.2 for the interactions with methane through normal-pentane were used. All other values of C_{31B+} put as zero.
The asphaltene component mole fraction can be calculated from the following relation:

$$x_{Asph}\, MW_{Asph} = w_{Asph}\, MW_{Oil} \qquad (13)$$

The oil molecular weight (MW_{oil}) was determined from the result of the regression run as 102.62. From fluid analysis studies report on bottom hole samples of the selected well, the asphaltene content (W_{Asph}) of the stock tank oil is specified as 4.8 wt% and this ratio has been used for the live oil because of small weight percent of gas in the live oil. From the table of components after regression run, the precipitating component (C_{31B+}) molecular weight (MW_{Asph}) was 604.014. By substituting pervious information of oil and asphaltene molecular weights and mole fraction of asphaltene in equation (13), this resulted in a mole fraction of 8.155×10^{-3} for the precipitating component (X_{Asph}). The composition was modified by entering the mole fractions of 8.155×10^{-3} for the precipitating component (C_{3IB+}) and 0.0383147 for the non-precipitating component (C_{3IA+}).
Because the predictions of the fluid phase behaviour will be affected by splitting the heaviest component into precipitating and nonprecipitating components and adjusting the asphaltene component binaries, the regression process also must be executed once more to ensure that the used model will detect the correct behaviour of fluid and solid phase. In this case study data set, the stock tank oil API of 23.5 and the saturation pressure of 4000 psia were added in the regression process to match between simulated and experimental values of these properties and the parameters of the volume shift of the heavy fraction pseudo components were modified.
The solid component fugacity in the solid phase can be determined by equation (1). For the asphaltene model, the reference fugacity specification was computed by making the reference fugacity the same as the precipitating component which determined at an experimental onset pressure of asphaltene precipitation by the equation of state for a given temperature. This confirms that the model will detect or determine the onset pressure correctly. For other pressure conditions, the comparison well make between the solid component fugacity in the solid phase and the solid component fugacity in the liquid phase as detected by the equations of state. If the solid component fugacity in the liquid phase is greater than the solid component fugacity in the solid, asphaltene will precipitate. From the modern detection system of solid precipitation as shown in fluid analysis studies report on bottom hole samples of the selected well, onset pressure can be determined very accurately and it was shown at around 4154 psia and this value has been entered to the asphaltene precipitation model. The reference fugacity after that has been set equals to the precipitating component fugacity in the liquid phase which calculated by the equation of state.
The molar volume of the solid in equation (1) has been set to a value somewhat higher than the precipitating component molar volume calculated via the equation of state. For checking the regression on the PVT data of the fluid and for viewing the molar volume of the solid component detected by the equation of state, the data set has been run at this point. The summary table of the regression showed that there was an exact match of stock tank API and the saturation pressure. The different solid model parameters are given in a list at the end of the regression output file. The molar volume of the solid was given as 0.59242 L/mol. An initial value of 0.67 L/mol was selected as a good value to enter for the molar volume of the solid.
4- Asphaltene precipitation behavior prediction: To make asphaltene precipitation prediction, the composition of the whole live fluid, not the composition modified for the calculation of reference fugacity has been used as follows:

A reservoir temperature of 194.72 °F, a minimum pressure of 14.7 psia, a maximum pressure of 6014.7 psia, a step of pressure of 200 psia and a pressure steps number of 31 have been entered. The flash calculation was performed at every 200 psia from 14.7 to 6014.7 psia by this specification. At this point, the reference fugacity for the asphaltene precipitation model was put as the same value determined in the previous flash calculation of asphaltene and also other properties like molar volume, reference temperature and reference pressure used previously were set at this step. As shown earlier, executing the regression within the data set of asphaltene precipitation modeling causes the model to detect the correct behavior of fluid PVT if the asphaltene component interaction parameters are altered. The molar volume of the solid component was changed to reach the desired maximum precipitation amount. A value of 0.69 L/mol was used to give acceptable results in this case.

6. Results and Discussion

Regression on Fluid PVT Results: By using Peng-Robinson equation of state (PR-EOS), the simulated data were tuned to experimental data of PVT tests (constant composition expansion (CCE), differential liberation at reservoir temperature (DL), separator and viscosity of live fluid at reservoir temperature) through regression process.

1- The results of tuning (regression) of CCE test data are shown below:

The relative volume verses pressure relationship of the fluid was showed a good agreement between the simulated data by PR-EOS and experimental data as shown in figure 3. The relative volume is the ratio of fluid volume at each pressure to fluid volume at saturation pressure. From figure 3 it is illustrated that there was a alteration from the system of the single phase to the system of the two phase. It must be indicated that the slope change is associated and attributed to the compressibility of the fluid due to the single phase transition to the two phase state. The saturation pressure is the point at which the transformation from the single phase to the two phase state takes place and for this fluid was equal to 4000 psia. There was no difference between the simulated and experimental values of bubble point pressure of the fluid.

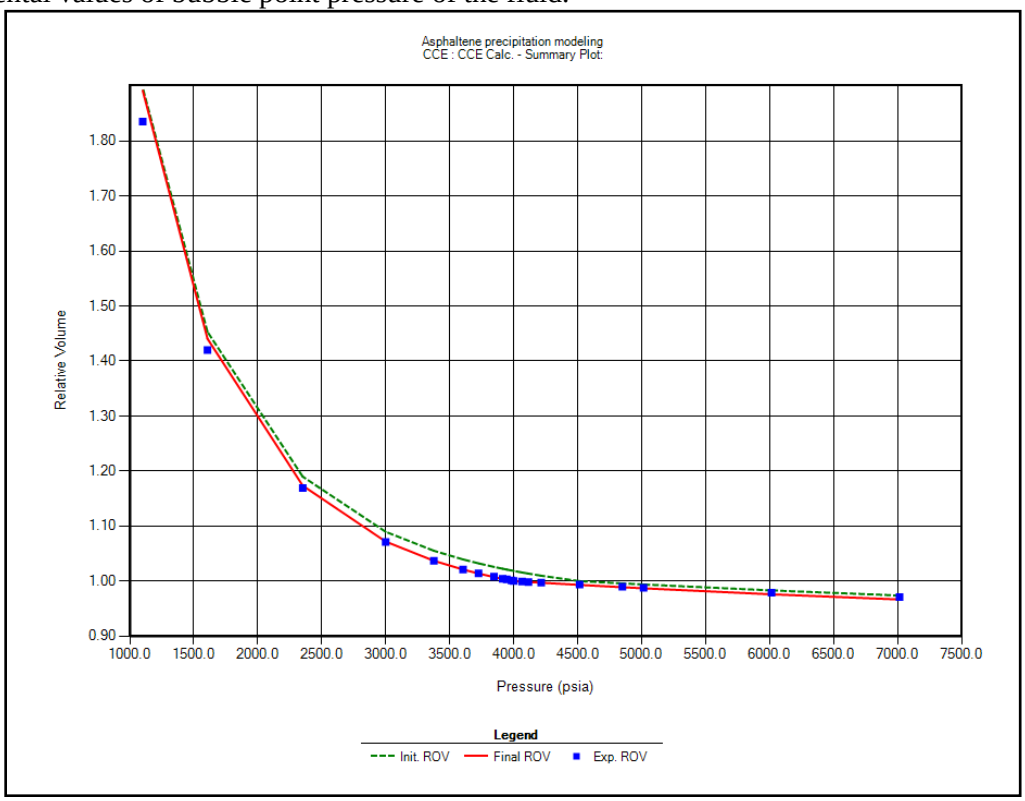

Figure 3: Relative volume tuning.

The relationship of oil density verses pressure of the reservoir fluid above saturation pressure (bubble point pressure) is plotted in figure 4. In this figure, the oil density form PVT report of the fluid (Experimental measurement) and from PR-EOS (calculated one) with pressure declining are shown.

There was a deviation in simulated data from real data (experimental data) and approximately equals 1% and this represented the best tuning after many trial and error attempts. By tuning the simulated data to experimental data

of oil density, the difference between these two data was decreased (Final oil density approached the experimental values) and bubble point presser reached the real value of 4000 psia. There was a deflection point at pressure equals 4000 psia which represents the transformation from the test of constant composition expansion (CCE) or flash liberation of the single phase to differential liberation (DL) test of the two phase and above bubble point pressure oil density increases with pressure increasing because of the increasing in the volume of oil above the pressure of bubble point due to gas expanding with pressure decreasing. A sharp increase or erratic values of density around the pressure of bubble point might indicate problems of flow assurance (asphaltene precipitation problem) depending on the method introduced by Ahmed, 2007 [13].

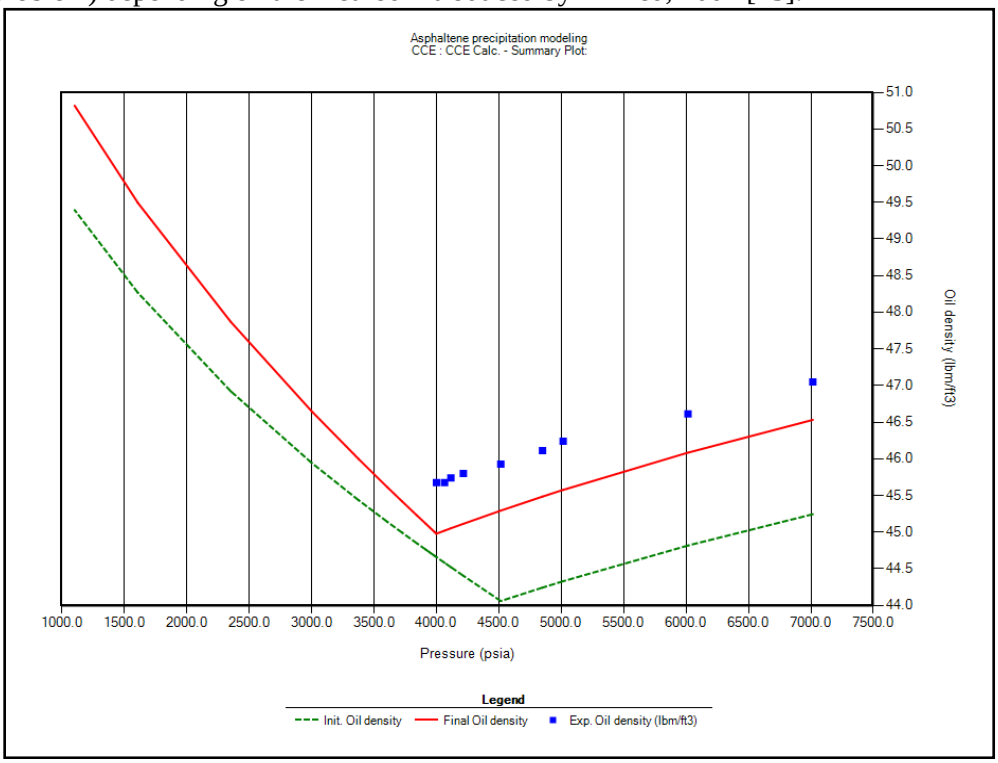

Figure 4: Oil density tuning.

The oil compressibility measured by the CCE test and calculated by PR-EOS and the difference between them is observed in figure 5 below. The minimum deviation was at bubble point pressure which equals approximately 8% and the deviation increased as the pressure moved away from the pressure of bubble point and reached the maximum value at pressure 7015psia.

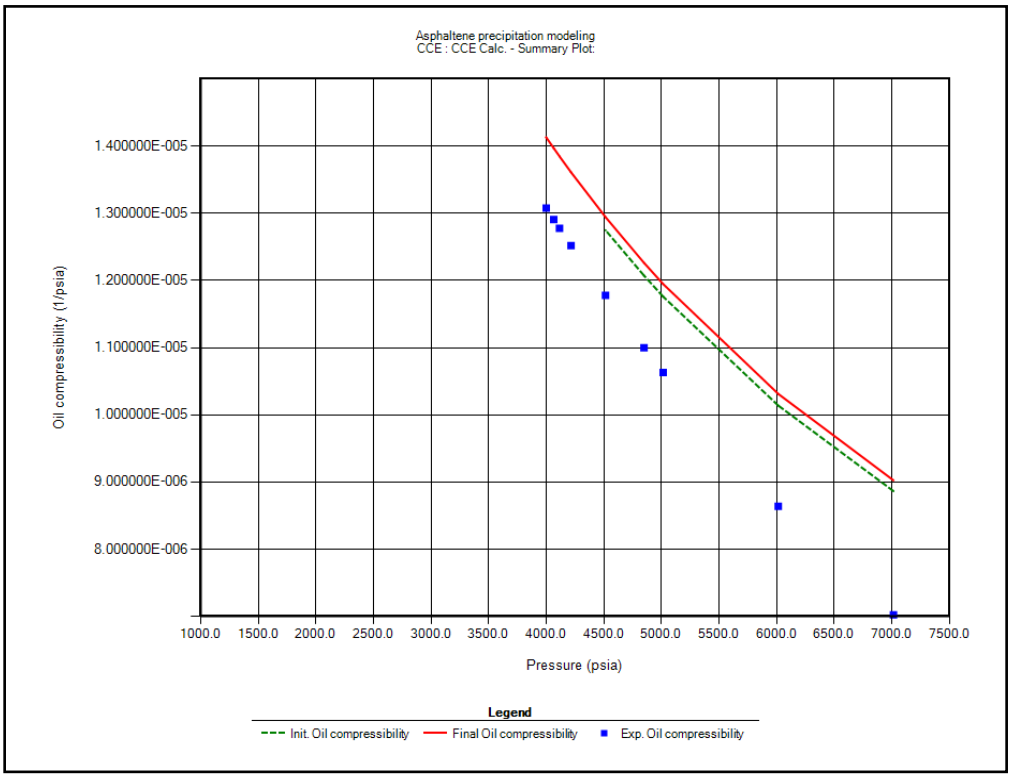

Figure 5: Oil compressibility tuning.

2- The results of tuning process of Dl test data are shown below:

Solution gas-oil-ratios (GOR) and relative oil volume (Bo) verses pressure relationships are shown in figure 6. For Solution gas-oil-ratios (GOR), there was a good matching between simulated and experimental values of GOR at all pressure steps except bubble point pressure (4000 psia) at which the deviation was 3.5%. Above bubble point pressure, solution gas-oil-ratios (GOR) remains constant because there is no gas liberating and at this point, the maximum value of solution gas-oil-ratios is observed because of high volume of gas. Below bubble point pressure, solution gas-oil-ratios decreases with pressure decreasing because of gas liberating and leaving the oil. For relative oil volume (Bo), also there was a good matching between simulated and experimental values of GOR at all pressure steps except at lower pressure (less than 915 psia) there was small difference between simulated and measured data of Bo. As the pressure decreases through differential liberation test, the oil formation volume factor increases up to reaching the pressure of bubble point due to gas expanding that increases the volume of oil at reservoir condition relative to the volume at surface condition. When the pressure reaches bubble point, maximum value of Bo is observed after this point Bo is decreased because of gas liberating.

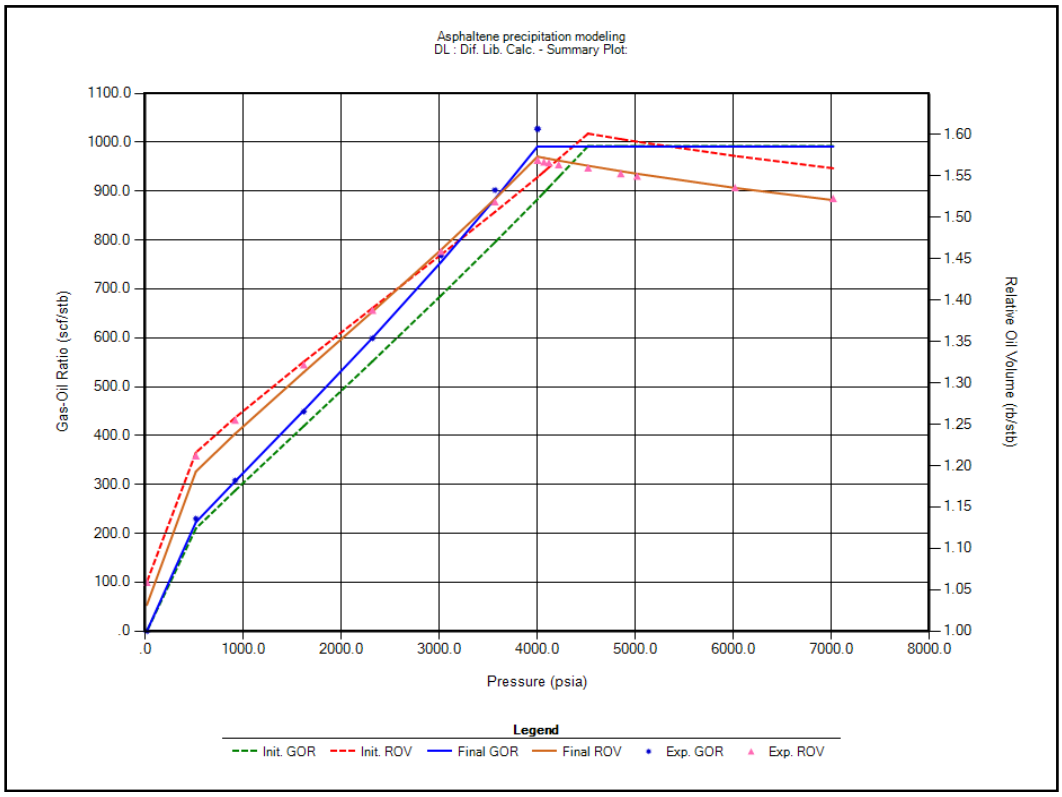

Figure 6: GOR and Bo tuning.

Gas compressibility factor (Z factor) and gas formation volume factor (Bg) verses pressure relationships are shown in figure 7. The simulated and measured values of Z factor with respect to pressure values are acceptably matched. The maximum deviation was at 3015 psia and equaled 2%. It was illustrated that at extremely low pressure, the ideal gas behavior conditions are more possible to be found (z-factor equals 1.0) because the molecules are adequately far away from each other. At moderate pressure, the molecules are sufficiently close to each other to applying some attractions between these molecules. This attraction causes the actual volume to be somewhat less than the volume predicted by ideal gas equation, that is, the z-factor will be less than 1.0. Gas formation volume factor (Bg) verses pressure relationship was obtained with a good agreement between simulated and experimental data of this property as shown in Fig. 5. Bg increased as pressure decreased below bubble point pressure and there was a sharp increase in Bg at low pressure below 515 psia because gas deviation factor (Z) increased sharp from approximately 0.926 to 1 which causes gas volume factor (Bg) at high value. While above 515 psia, the difference between two pressures gave low difference in gas deviation factor (Z) that causes steady increase as the pressure decreased because gas volume factor (Bg) is directly proportional to gas deviation factor (Z).

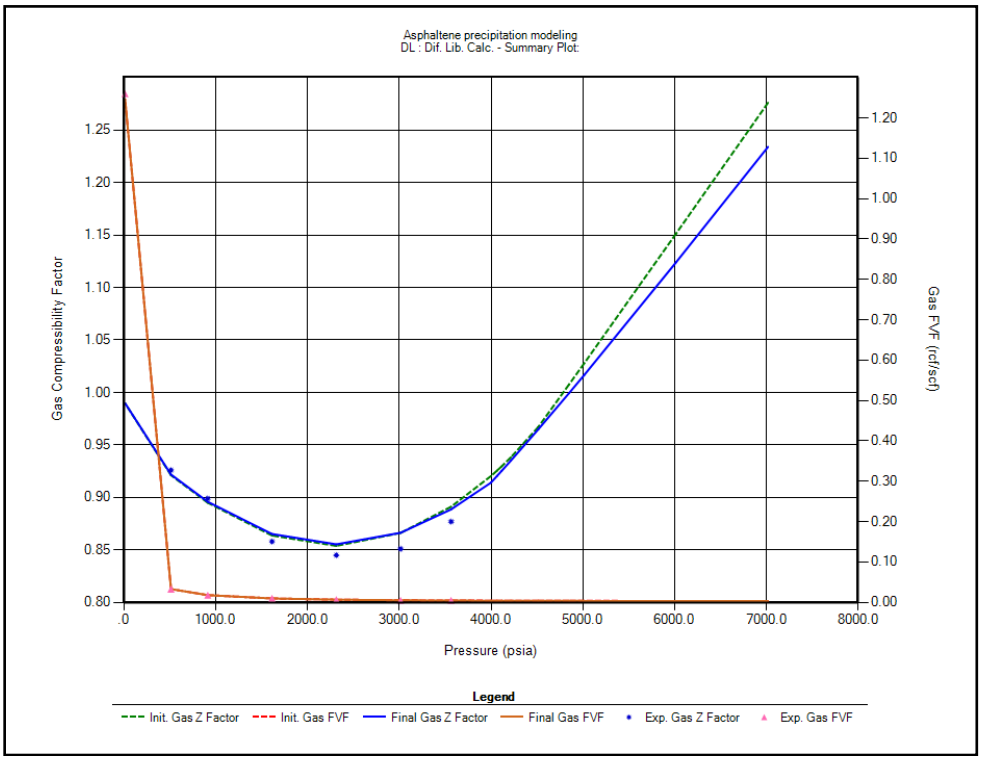

Figure 7: Z factor and Bg tuning.

The measured and calculated values of specific gravity of oil and gas depending on pressure declining are shown in figure 8. For oil specific gravity, below bubble point pressure there was good match between simulated and measured value while above bubble point pressure there was a deviation of 2%. For gas specific gravity, the maximum deviation of simulated value from experimental value was at 915 psia and was equaled 8%.

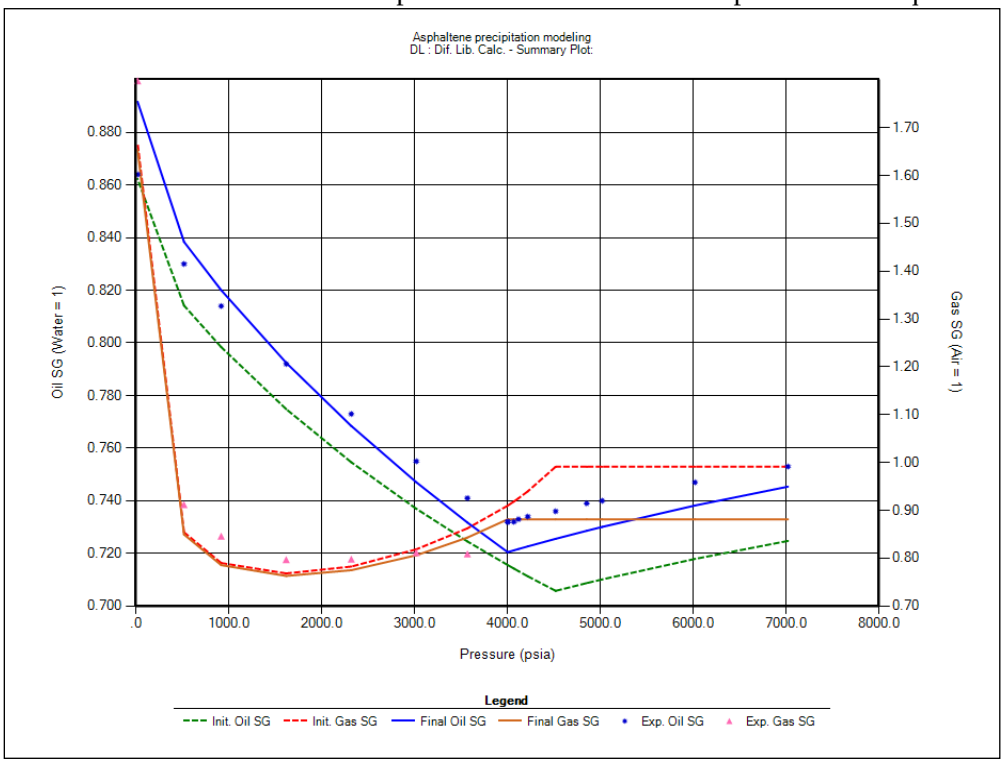

Figure 8: Oil and gas specific gravity tuning.

3- Prediction of Precipitation Behavior Result:

Finally, the asphaltene precipitation for the study zone was predicted as shown in figure 9. The result of this study accepted with the results of study of Tavakoldavani and Ashoori, 2017 [14]. As the model of solid

precipitation (asphaltene precipitation) used in this research was thermodynamic model, as against kinetic, precipitation reversibility is possible (the liquid phase can redissolve precipitated solids).

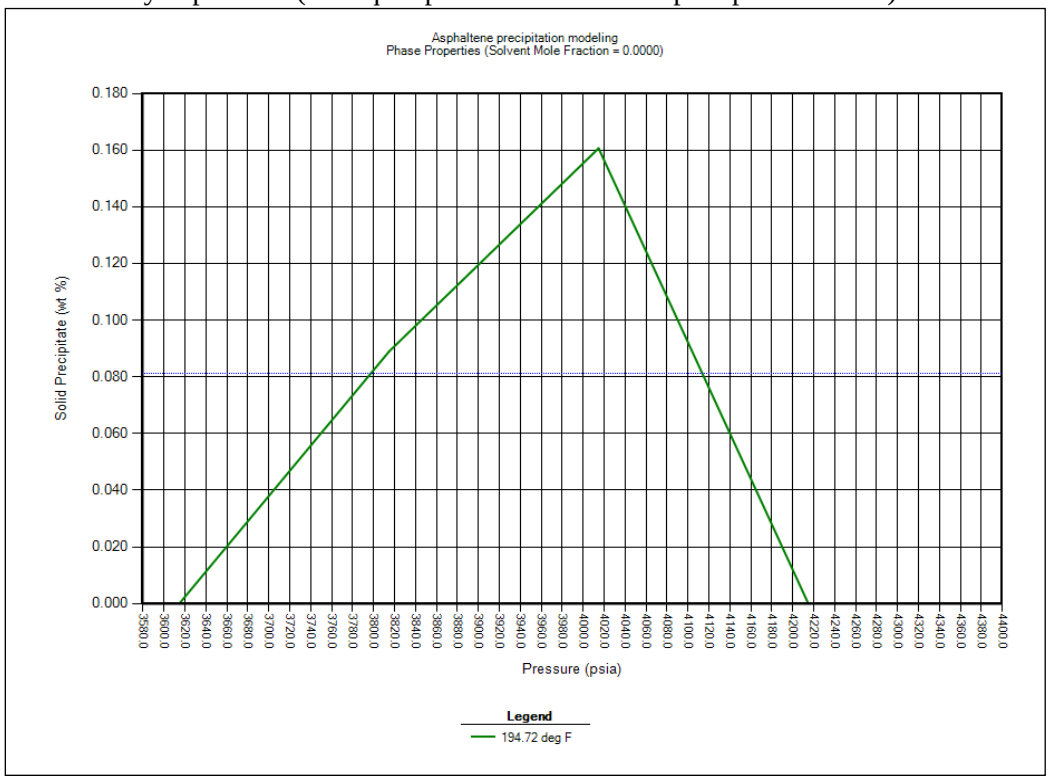

Figure 9: Asphaltene precipitation prediction.

Usually, the maximum asphaltene precipitation amount occurs close to the fluid saturation pressure. Under this pressure, the gas liberation from the oil alters the parameter of solubility of the liquid phase and permits redissolving of the asphaltene that precipitated. It is feasible to find at enough low pressures, the entire precipitated asphaltenes will return to dissolve in the solution. The maximum precipitation of asphaltene was at bubble point pressure and was equaled 16% while at asphaltene onset pressure was 4.8%. The asphaltene precipitation problem of this reservoir fluid was because of high ratio of methane (CH_4) in this fluid which equaled 42% of the total weight of the reservoir fluid (Monophasic fluid) as in table 2. Methane causes the asphaltene precipitation problem because it desorbs the resin around the asphaltene molecules and allow them to collect causing the precipitation problem of asphaltene according to the study of Siyamak et al., 2012 [15]. Although this fluid precipitated asphaltene experimentally and by EOS modeling, the reservoir will produce oil without precipitating asphaltene because its pressure is above asphaltene onset pressure (AOP). With time and oil production, the reservoir pressure will decrease and the fluid will enter the asphaltene precipitation zone causing deposition problems and treatment costs will increase, therefore it must monitor well and reservoir pressure continuously to avoid reaching this problem.

Conclusions

The thermodynamic model was used in this study to describe the precipitation of asphaltene of a live oil of Khasib Formation / Halfaya Oil Field in Iraq. The following conclusions are obtained

1- For fluid characterization and regression on fluid PVT by PR-EOS model, the saturation pressure (bubble point pressure) and other fluid properties gave an acceptable match with experimental data of these properties.

2- For prediction of asphaltene precipitation, the thermodynamic model showed good match of asphaltene onset pressure at reservoir temperature.

3- Although this fluid precipitated asphaltene experimentally and by thermodynamic modeling, the reservoir will produce oil without precipitating asphaltene because its pressure is above asphaltene onset pressure (AOP). With time and oil production, the reservoir pressure will decrease and the fluid will enter the asphaltene precipitation zone causing deposition problems and treatment costs will increase, therefore it must monitor well and reservoir pressure continuously to avoid reaching this problem.

Acknowledgment
The author wish to thank the Petroleum Technology Department at the University of Technology - Iraq for facilitating this work.

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Nomenclature

b	The EOS parameter
b_i	The EOS "b" parameter for Component i
b_{n_c}	The EOS "b" parameter for Component n_c
f_s	The fugacity of pure solid asphaltene at pressure of p
f_s^*	The fugacity of pure solid asphaltene at pressure of p*

f_{ij}	The component i fugacity in Phase j with translation
f_{ij}^{eos}	The component i fugacity in Phase j without translation
f_{iv}	The component i fugacity in vapor
f_{il}	The component i fugacity in liquid
$f_{n_n v}$	The component n_c fugacity in vapor
$f_{n_c l}$	The component n_c fugacity in liquid
$f_{n_c j}^{eos}$	The component n_c fugacity in Phase j without translation
P	Pressure
P_c	Critical pressure
R	The universal constant of a gas
s_i	The dimensionless parameter of volume shift of Component i
s_{n_c}	The dimensionless parameter of volume shift of Component n_c
T	Temperature
T_c	Critical temperature
V	Molar volume
V_j	The molar volume of phase j with volume shift
V_j^{eos}	The molar volume of phase j without translation
V_s	The molar volume of solid asphaltene
y_{ij}	Component i mole fraction of in Phase j
ω	Acentric factor