

ASPHALTENE MODELING BY SARA TEST RESULTS, AN INTRODUCTION OF SIMPLE AND ACCURATE EMPIRICAL MODEL

Mahdi Hasanvand¹, Mohammad Shadadeh¹, Mohammad Ali Ahmadi²

¹ Research Institute of Petroleum Industry, Tehran, Iran

² Petroleum University of Technology, Ahwaz, Iran

Received April 11, 2018; Accepted June 27, 2018

Abstract

Asphaltene precipitation problems cause millions \$ of cost annually. Reservoir skin effect, Well inflow capacity decreasing, Oil flow decreasing, and well column blockage and production facilities break-out are examples of asphaltene related problems. The basic step to control and solve these problems is accurate prediction of asphaltene molecule precipitation. Asphaltene content oil is experience different thermodynamic conditions in the flow path from underground original reservoir zone to oil and gas separation facilities. It is obvious that thermodynamic instability of asphaltene is related to oil composition and its fraction entities. Although the direct effect of different fraction of crude oil (Saturate, Aromatics, Resins and Asphaltene (SARA)) may be unclear but by increasing the experimental data of precipitation an empirical model can be developed. The developed empirical model is the first model to predict the weight percent of asphaltene in a wide range of temperature and pressure (130-250 °F and 600-8600 Psi). The correlation is proposed based on 84 precipitation data point of 10 different crude oils. The least square of errors (R^2) of correlation is more than 93% which is so accurate rather than common thermodynamic models of asphaltene precipitation.

Keywords: .

1. Introduction

Asphaltene related problems are going to increase every day, as the oil fields production life becomes more, and reservoirs become more depleted. The cost of wellbore tubing washing, oil production delay and environment damages are dramatic tragedies associated with asphaltene precipitations. So the best solution here is to avoid asphaltene precipitation and deposition rather than thinking of removal methods.

There are different ways to avoid asphaltene precipitation such as inhibitor and solvent injection, thermal ways like heating and ultrasonic methods and finally making conditions out of Asphaltene Deposition Envelope (ADE). In all of this ways, the knowledge of asphaltene thermodynamic behavior is essential. To optimize these processes, it is necessary to have accurate predictions of the amount of asphaltene precipitation as a function of the amount of solvent, temperature, and pressure [1].

The thermodynamic behavior of asphaltene molecule is unique and vague from an oil field to another. The common trend is precipitating in a pressure above bubble point as onset pressure, increasing asphaltene precipitation to bubble point and decreasing after that. The temperature trend is vague and it is believed that in heavy crude oils by increasing the temperature the asphaltene precipitation increased and in light crude oils the trend is contradict. Some different cases are reported in literature [2-3].

To modeling and simulating asphaltene behavior some experiments are defined. Onset pressure of this molecule is detected by Near Infra-Red ray in solid detective suspended equipment [4]. Additionally, asphaltene weight precipitation change by pressure is detected by High Pressure High Temperature (HPHT) Filtration device and associated IP143 tests [5] or by Visual

HPHT microscope [6]. All of these experiments are special, time consuming and done in high pressure and temperature conditions. The results of these Laboratory studies are used to modeling of molecule behavior. But the common models have failed to produce a consensus about the physical state of asphaltenes in crude oil. Most of these models need special properties such as molecular weight, enthalpy of fusion, volume shift and so on of asphaltene molecule which is not identical during precipitation, so it makes procedure more problematic [7-9]. The number of variables is another problem of common models of asphaltene behavior [10]. A list of common models of asphaltene behavior is taken in table 1. All together it can be said that estimates of models to asphaltene properties are more speculative than conclusive [9,11]. This is mainly due to the extreme chemical complexity of both the asphaltenes and crude oil [12-13].

So there are two problem in asphaltene modeling, the hardship of laboratory experiment and the ease of procedure and precise of thermodynamic model.

Table 1. Asphaltene Mmain models, type, properties, advantages and disadvantages

Model name	Proposer	Type	Summary
Hirschberg model	[14]	Based on Flory (1953) lattice theory.	The parameters are mole fraction, molar volume, and solubility parameter for each individual component. The entropy of mixing of mono-disperse polymer-like molecules can be accounted by using Flory (1953) lattice theory. He investigated the effect of temperature and pressure on the asphaltene color and precipitation.
Micellization Models	[10]	Based on minimum Gibbs Energy theory.	The liquid phase Consists of a mixture of monomer asphaltenes, monomer resins, asphalteneresin micelles, and Other oil species. Total Gibbs Energy of system is calculated by fugacity calculation. a large number of parameters such as interaction parameters, the size of the micellar core, the average characteristic length of molecules, the interfacial tension, the thickness of micelle, and the adsorption energy, are needed in the model
Statistical Thermodynamic model	[36]	Based on Statistical Associating Fluid Theory (SAFT)	Asphaltenes are assumed to be large spherical molecules with multiple association sites that can bind to other asphaltenes and resins. An advantage of the SAFT approach is that the complexity of the problem can be significantly reduced by formulating molecular theory. Furthermore, the model can account for the effects of resins addition and asphaltene solvent addition on the solubility of asphaltenes.
Oligimerization Model	[37]	Based on Colloidal theory.	Asphaltene association was modeled analogous to linear polymerization. This model is very complex and need lots of parameters for modeling. It can fit the molar mass data and solubility so.
Developed Oligimerization Model	[1]	Based on Colloidal theory.	This model requires two fit parameters (the association constant and molar ratio of terminator to propagator) and two estimated parameters (the monomer molar masses of terminators and propagators). The model can predict the effect of carbon number precipitant, temperature, solvent and resin concentrations.
Micellar Models	[38]	Based on surfactant behavior.	Asphaltene is a very large structure that made of several monomers it can act as a surfactant, this model explain micellar structure for asphaltene. Akbaezadeh 2005 showed neither molar mass nor IFT variation show the existence of CMC. Therefore, asphaltene cannot have the micellar structure.
Regular Solution Model	[8]	Based on vapor-liquid-liquid equilibrium.	The model uses the concept of material balance by coupling with thermodynamic model. The separate VLE and LLE can be used to find the composition of different fractions (vapor, asphaltene, crude oil). By some assumption the predict precipitation of asphaltene in different pressure and temperature.

Our alternative way is modeling of asphaltene behavior by the results of concentration of Saturates, Aromatics, Resins and Asphaltene fraction of crude oil (SARA Test). This test is an easy handling experiment and is a standard of heaviness of crude oil. This experiment includes titration or addition of solvents and is a basic experiment that most of models about asphaltene precipitation are using. These tests are mostly conducted in atmospheric pressure or low pressures.

In this work we present a correlation model based on results of SARA test of more than 10 different crude oils. This model is a predictive empirical correlation on asphaltene precipitation behavior due to reduction or increase of pressure. The model has appropriate results for reservoir natural depletion cases or in reverse during secondary recovery when trying to increase reservoir pressure for improves recovery without considerable change in temperature.

Unfortunately in this study we could not do any predictions about onset of asphaltene precipitation due to lack of experimental data, however we believe that we can have a rough estimate which is not too bad to have an estimate of onset pressure.

2. Thermodynamic modeling of asphaltene precipitation

Today still there is not a unique predictive model that could describe asphaltene behavior at different conditions for different oil samples. This is due to complexity and nature of asphaltene and crude oils [12]. Different thermodynamic models have been proposed to predict asphaltene phase behavior. Precipitation is the formation of an asphaltene solid phase (or possibly dense liquid) due to change in the thermodynamic equilibrium between the oil components. Three general categories of thermodynamic models are 1-EOS approach, 2-Polymer solution models and 3-Colloidal models. As models become more complicated sometimes accuracy improves, but generally new parameters introduced are not available in the literature and should be determined experimentally for each sample, and this will limit their application.

An earlier model [14], which has been used for predicting asphaltene solution data by several investigators [15] employs the Flory - Huggins model of polymer solubility [16]:

$$\ln \phi_{a,max} = (V_a / V_l - 1) + (\phi_a - \chi \phi_l^2) \dots \quad (1)$$

where $\phi_{a,max}$ the maximum volume fraction of asphaltene solute; V_a and V_l are the molar volume of asphaltene and liquid solvent, respectively; χ is the Flory interaction parameter and ϕ_l is the solvent volume fraction. The Flory interaction parameter, χ , can also be estimated from:

$$\chi = V_a / RT (\delta_a - \delta_l)^2 \dots \dots \quad (2)$$

The two parameters which are essential in the performance of this model are the molar volume and solubility parameter of the asphaltene components. The molar volume is dependent on the molecular weight and the density. Density is a measurable parameter whereas the molecular weight is much more difficult to measure with any degree of accuracy. Most methods for the determination of molecular weight produce data that show a dependence on the ability of the asphaltenes to aggregate [17]. The solubility parameter is depended to aggregation and this dependency makes the results of modeling inexact.

The simplest model for precipitated asphaltene is the single-component solid model that was tried by [18] and [19]. The precipitated asphaltene is represented as a pure solid while the oil and gas phases are modeled with a cubic EOS [20]. The fugacity of the pure solid is given by:

$$\ln f_s = \ln f_s^o + \frac{v_s (P - P^o)}{RT} \dots \dots \dots \quad (3)$$

where f_s^o is reference solid fugacity and v_s is solid molar volume.

The model basically uses the same calculation as vapor liquid equilibrium calculation, but here it uses another flash calculation between solid and liquid. It could be assumed that solid liquid has an effect on liquid vapor equilibrium or not. The method uses EOS parameters of heavy or plus fraction as tuning parameters to predict the experimental data. Large number

of tuning parameters limits the ability of the model to predict different condition. This model is not able to predict the effect of temperature on asphaltene precipitation.

Colloidal model for prediction of asphaltene precipitation has been used as a model which has a focus on effect of resin on asphaltene precipitation and deposition. This model is presented by [21]. The model is based on the assumption that asphaltenes exist in the oil as solid particles in colloidal suspension, stabilized by resins adsorbed on their surface. It is also assumed that the short range intermolecular repulsive forces between resin molecules adsorbed on different asphaltene particles keep them from flocculating. This repulsive force can be overcome or neutralized by mechanical (large pressure drop, agitation) or electrical (opposing streaming potential) means.

The modeling of precipitation needs to calculate the concentration of the resins in the liquid phase. In the absence of the equilibrium constant data for resin adsorption on the surface of asphaltene particles for calculating the critical chemical potential of the oil mixture, implementation of the proposed model will require some experimental data of the onset of asphaltene deposition for fitting purposes. The model can then be used to predict the onset at different liquid compositions, provided that the resin and asphaltene fractions remain as they were when the fitting point was determined.

All above models are consuming time, have try and error steps, needs expensive and time consuming experiments background and have many variables.

3. Data gathering

The SARA separation was originally designed for characterization of residuals [22]. The heavy end of a crude oil can be separated into four distinct fractions namely saturates, aromatics, resins, and asphaltenes using the experimental SARA procedure. SARA analysis separates the sample in saturated, aromatics, resins, and asphaltenes compounds through the action of n-alkane solvents, toluene and dichloromethane, and the interaction between the oil with a stationary phase. The SARA analysis starts with the precipitation of asphaltenes in n-alkane solvents such as pentane or heptane. Subsequently, the de-asphalted oil is separated by chromatography methods with the help of different stationary phases and solvents of varied polarity [23-25].

A crude oil usually contains a considerable amount of volatile material that must be removed prior to performing SARA separation of the crude oil. Although there are different and accurate method to investigate the SARA weight fractions of crude oil [26-27], Vazquez and Mansoori [28], proposed a simple, inexpensive, forward standard method to separate SARA fractions based on liquid absorber chromatography. This is accomplished by performing a vacuum batch distillation at 10 mm Hg and room temperature until the weight of the residue reaches a constant value.

The first fraction to be separated from the vacuum residue is the nC₅-asphaltenes. The 0.2 micro meter filtrate collected from the separation of the nC₅ asphaltenes is commonly known as maltenes. It contains the remaining three fractions, saturates, aromatics and resins. These three fractions are separated using open-column liquid chromatography.

Saturate hydrocarbons in present of n-pentane as solvent phase, are not absorbed on activated silica under the conditions specified. The saturate fraction of the oil is eluted from the column with 1/L of n-pentane volume at 5 mL/min. The solvent is removed using a rotary vacuum evaporator to recover saturates fraction.

Aromatic hydrocarbons are adsorbed on activated silica in the presence of n-pentane, and desorbed by toluene after removal of the Saturates under the conditions specified. The aromatic fraction of the oil is eluted from the chromatographic column using toluene at 5 mL/min. The resin fraction of the oil is eluted from the chromatographic column using a 90/10 toluene/MeOH solution at 5 mL/min. This fraction is reported as wt. %. prepared Silica gel column and separation of maltene fractions during SARA test.

This procedure is done for 10 crude oil sample before HPHT filtration to develop Asphaltene Deposition Envelope (ADE). The results of SARA test and specific properties of crude oils are presented in Table 2.

Table 1. SARA test results of 10 crude sample and their specifications such as GOR, Ps and density

Crude No	Saturated wt. %	Aromatic wt. %	Resin wt. %	Asphaltene wt. %	GOR Scf/Stb	Saturation pressure, psia	Density, g/cc
1	63.79	31.67	2.61	0.89	1300	4260	0.829
2	60.49	33.84	3.23	2.11	1100	3290	0.865
3	55.14	30.73	10.88	3.25	1120	2980	0.861
4	54.67	28.89	12.66	3.8	1080	2513	0.857
5	52.49	41.04	5.48	0.99	1037	6267	0.898
6	52.07	35.87	8.93	3.17	900	3045	0.865
7	50	25	21	3.9	654	1963	0.873
8	44.84	34.83	12.21	8.10	240.43	1067	0.987
9	30.1	42.1	13.36	13.75	450	1722	1.076
10	26.82	67.69	4.47	0.66	540	1524	1.103

After SARA test, the high pressure high temperature set up was prepared for measuring Asphaltene Precipitation in different thermodynamic conditions. The Whatman paper filter of 0.2 micrometer diameter was pert by helium gas between two thick steal cylinders. After crude oil stabilization in specific thermodynamic condition, the crude oil is transported through paper filter and the asphaltene content of filtrated oil is measured by IP143 procedure. The difference of asphaltene contents before and after filtration is equal to asphaltene precipitation in specific temperature and pressure. This test is done and repeat for each crude oil in reservoir temperature and 8 different pressures. At the final, 84 data point is resulted and reported in 8 series: temperature, pressure, saturates, aromatic, resins, asphaltenes content, and asphaltene precipitation wt% .

4. Methodology

Genetic programming (GP) [29] is an exciting method to model various petroleum engineering issues. The major benefit of the GP-based models against other intelligent based solutions like as artificial neural network, fuzzy logic and least square support vector machine (SVM) is their capability to create estimation correlations without presuming first form of the existing correlation like as previous work of the authors [30-31]. Gene expression programming (GEP) is a new division or branch of Genetic Programming which evolved by Ferreira [32]. This approach has capability to generate computer programs with various sizes and shapes while conventional Genetic Programming and other intelligent tools like as fuzzy logic are restricted to fewer engineering areas [30-31].

Genetic Programming is a branch of genetic algorithms (GAs) which is a modern regression approach with a giant capability to automatically develop computer programs. It worth mentioning that, the evolutionary algorithm followed by the GP procedure is inspired from the Darwinian theory of natural collection [30].

Based on symbolic regression experiments by Koza in 1992, Genetic Programming (GP) was introduced and developed [29]. The major difference between the original Genetic Algorithm (GA) and Genetic Programming (GP) methods is that the developing programs in Genetic Programming (GP) are parse trees rather than fixed-length binary strings in conventional Genetic Algorithm (GA) [30]. A typical pc programme based on the Genetic Programming (GP) formula is demonstrated in Figure 1, [29,31].

Gene expression programming (GEP) is a new subarea of Genetic Programming (GP) was firstly introduced and evolved by Ferreira, [30,32]. Gene expression programming (GEP) consist Function set, terminal set, fitness function, control parameters, and termination condition which are the main parameters of the addressed method. The generated outcomes of Genetic Programming (GP) are depicted as tree topologies and presented in a functional programming language [29-30]. It should be noted that the genetic operators perform on the chromosome level in GEP approach which leads to an extreme simplification in the generation of genetic diversity [30]. As known Gene Expression Programming (GEP) has a multi-genic nature. There-

fore; more complicated models with various sub-models can be created through the evolutionary process. A gene in Gene Expression Programming (GEP) is comprised a list of symbols while the addressed symbols are parameters of function or terminal sets. A typical GEP gene is illustrated as following as [30]:

$$+./.\times.\sqrt{.}.^{.}5.X.Y \dots\dots\dots (4)$$

where X, Y and 5 are elements of the function set; +, /, $\sqrt{}$, \times and \wedge are the terminal nodes, and "." is the element separator for user friendly reading [30]. The above addressed expression is called Karva notation or K-expression [32]. A K-expression can be demonstrated by a diagram as an Expression Tree (ET) while the first position in the K-expression stands for the root of the addressed Expression Tree (ET) [30]. i.e. example, the pure mathematical equation

$\sqrt{\frac{(X \times Y)}{(X^Y)}}$ can be easily demonstrated as an expression tree (ET) which depicted in Figure 2, with the Karva language illustration of */Q ^ X Y (Q represents the square root function).

It worth mentioning that, the size of the relevant Expression Trees changes through the GEP evolutionary process while the valid length of each expression is same to or less than the length of the gene [30].

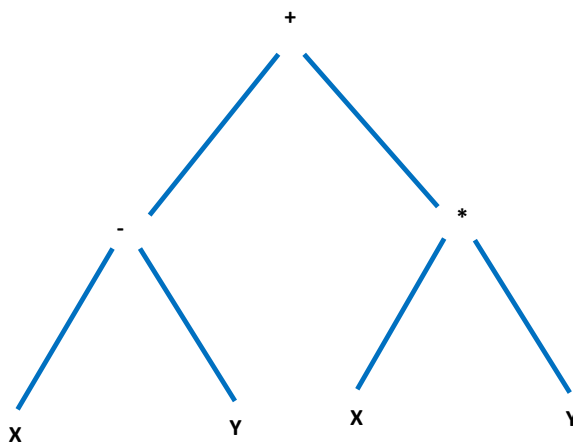


Figure 1. A typical computer LISP program in the GP algorithm represented as a parse tree (expression tree), which stands for the algebraic expression [(X-Y)+(X*Y)] by a two-gene chromosome

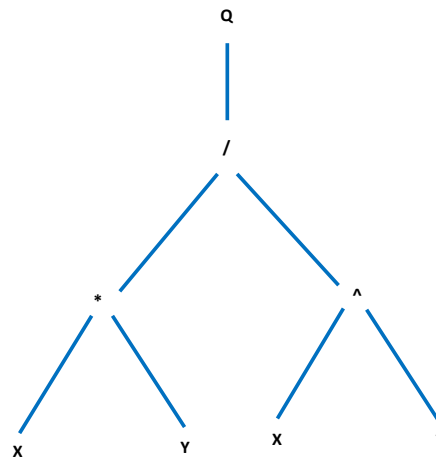


Figure 2. A typical Karva Language program in the GEP strategy, which represents the algebraic expression $[\sqrt{\frac{(X \times Y)}{(X^Y)}}]$ by a two-gene chromosome

5. Results and discussion

One of the exciting advantages of the GEP method [33] is that there is no need to take on special functional topologies to gain the best prediction/estimation of the real measured data. As a result, the most integrate and robust and effective correlation topologies consisting of the most efficient independent parameters are figured out through the evolutionary algorithm itself [34]. As illustrated earlier in this text, no accurate and integrate model or correlation exist for prediction of amount of asphaltene precipitation of crude oil samples. The majority of the amount of asphaltene precipitation of the crude oils can be correlated by the GEP principle parameters such as saturates, aromatics and resins. In this paper, it is firstly assumed that the RI can be formulated as the functions of the addressed parameters as follows:

$$\text{Amount of asphaltene precipitation} = f(\text{saturates, aromatics, resins, } \dots) \quad (5)$$

Based on the above assumption and GEP procedure which demonstrated in Figure 3, the required correlation was developed. Results of the evolved correlation discussed in detail in next section.

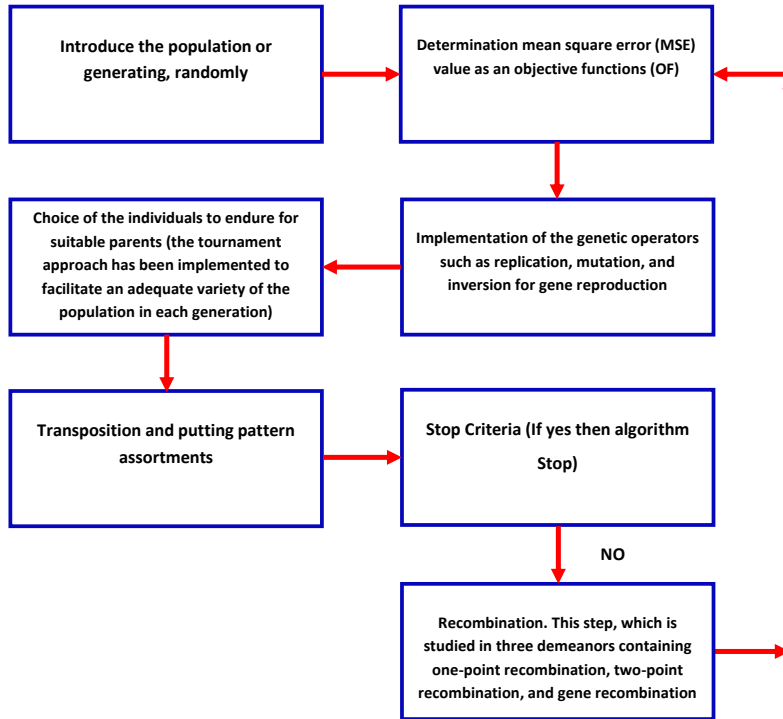


Figure 3. Chart box of the gene expression programming (GEP)

The asphaltene weight percent for 9 crude oils in reservoir temperature and different pressures have been resulted by HPHT filtration experiment. For crude oil number 10 the lower and upper onset pressures for 4 different temperatures have been got, and finally 84 different data point is developed for all 10 crudes. Each data point has 7 data includes Saturates wt%, Aromatic wt%, Resin wt%, Asphaltene wt%, Pressure, Temperature and finally precipitated Asphaltene wt%. The results of crudes oil are quantitatively follows known trend of pressure effect in literatures [35]. In high pressures by decreasing the pressure the asphaltene precipitation increased to reach a summit on bubble point. After that the amount of precipitated asphaltene decreased to reach the lower onset pressure. As it is shown in figure 6 all crude oils except crude number 8 follow this trend so this exception may be because of laboratory errors and we can ignore this test.

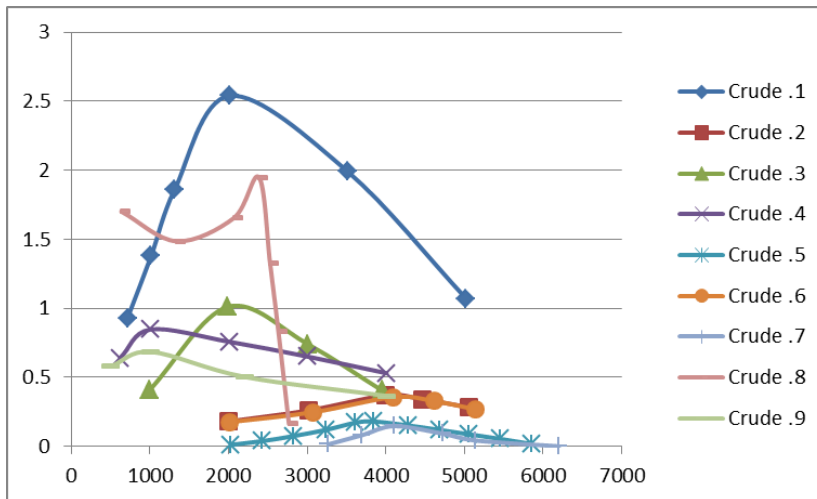


Figure 4. Asphaltene precipitation weight percent vs. pressure for different crude oils

The results of filtration and SARA tests are used for developing an algorithm to predict the asphaltene precipitation. The following correlation is the best match for the data points. In this correlation the input data are SARA fractions, temperature and pressure and in other hand Asphaltene weight precipitation is the output.

$$\begin{aligned} \text{AspPrecipitation wt\%} &= 0.048694 - 3.61035 \times B \times A + 0.923329 \times A^2 + 19.3559 \times B \times C \\ &- 7.96925 \times C^2 + 0.590678 \times B - 8.37478 \times B^2 \\ A &= 0.164042 - 0.0160959 \times R \times As - 6.62471 \times 10^{-6} \times R \times P + 0.00555145 \times R^2 + 0.0193652 \times As^2 \\ B &= -0.0242789 + 5.29966 \times D^2 + 0.574105 \times E - 5.34385 \times E^2 + 0.530724 \times F \\ C &= -0.257337 + 0.13385 \times R + 0.0149444 \times R \times D + 0.182241 \times R \times G - 0.0107369 \times R^2 \\ &+ 1.22226 \times D \times G - 0.558429 \times G - 1.77068 \times G^2 \\ D &= -38.621 + 1.16607 \times S + 0.00405818 \times A \times S - 0.156774 \times S \times As - 0.00814875 \times S^2 - 0.699435 \times A \\ &- 0.0578714 \times A \times As + 0.0110473 \times A^2 + 12.342 \times As - 0.285922 \times As^2 \\ E &= -4.33206 + 0.134702 \times S - 0.00867193 \times S \times R - 0.0266438 \times S \times As - 0.000960369 \times S^2 \\ &+ 0.404947 \times R + 0.00290696 \times R^2 + 1.78279 \times As - 0.0695639 \times As^2 \\ F &= -3.1253 + 0.134334 \times S - 0.00629117 \times S \times R - 0.001273119 \times S^2 + 0.268575 \times R \\ &- 1.69761 \times 10^{-6} \times R \times P + 0.00465625 \times R^2 + 2.1573 \times 10^{-5} \times P \\ G &= -0.913686 + 0.119983 \times S - 0.000701052 \times S \times T + 2.26418 \times 10^{-6} \times T \times P + 6.6136 \times 10^{-5} \times T^2 \\ &- 0.000644618 \times P + 1.58863 \times 10^{-8} \times P^2 \end{aligned}$$

which A, B, C, D, E, F and G are variable coefficients of S, Ar, R, As, P and T. S, Ar, R, As, P and T are Saturates, Aromatic, Resins, Asphaltenes, Pressure and Temperature respectively.

The results of comparison between estimated and actual data are depicted in figure 5. The least square average of correlation is $R^2=0.9384$.

The deviation of correlation data and actual data is presented in figure 6. The figure shows there is an accurate prediction in correlation results.

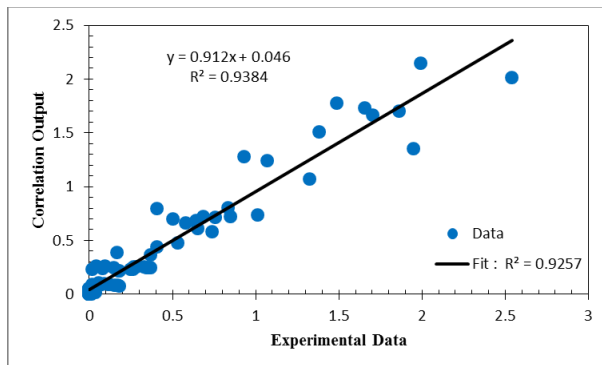


Figure 5. Comparison of correlation output vs. experimental data

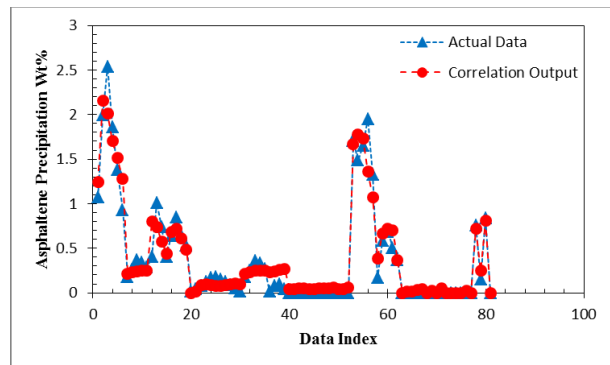


Figure 6. Predicted data and actual data of asphaltene precipitation

Before this study the SARA fraction is routinely used for qualitative analysis of stability of asphaltene in crude oils at reservoir conditions. De-Boer, proposed 4 plots based on SARA results to predict stability of asphaltene molecules [36]. But in this study it is proved that SARA results could predict asphaltene precipitation quantity rather than qualitatively analysis.

6. Conclusion

In this study a novel empirical correlation to model asphaltene precipitation based on SARA fraction test is developed. The developed empirical model is the first model to predict the weight percent of asphaltene in a wide range of temperature and pressure (130-250°F

and 600-8600 Psi). The correlation is proposed based on 84 precipitation data point of 10 different crude oils. The least square of errors (R^2) of correlation is more than 93% which is so accurate rather than common thermodynamic models of asphaltene precipitation.

References

- [1] Agrawala M, Yarranton HW. An Asphaltene Association Model Analogous to Linear Polymerization. *Ind. Eng. Chem. Res.*, 2001; 40: 4664-4672.
- [2] Nakhli H, Alizadeh A, Moqadam SM, Afshari S, Kharrat R, Ghazanfari MH. Monitoring of asphaltene precipitation: Experimental and modeling study. *Journal of Petroleum Science and Engineering*, 2011; 78(2): 384-395. .
- [3] Hasanvand M, Shahsavani B, Anooste A. Study of temperature effect on asphaltene precipitation by visual and quantitative methods. *Journal of Petroleum Technology and Alternative Fuels*, 2012; 3(2): 8-18.
- [4] Hasanvand MZ, Kharrat R, Behbahani SS. Thermodynamic Modeling of Asphaltene Precipitation, the Role of Pressure and Temperature. 2012: LAP LAMBERT Academic Publishing, ISBN-10: 384849244X.
- [5] ASTM, Standard Test Method for Determination of Asphaltene (Heptane Insolubles) in Crude Petroleum and Petroleum Products. 2000.
- [6] Zanganeh P, Ayatollahi S, Alamdari A, Zolghadr A, Dashti H, and Kord S. Asphaltene Deposition during CO₂ Injection and Pressure Depletion: A Visual Study. *Energy & Fuels*, 2012; 26(2): 1412-1419.
- [7] Shirani B, Nikazar M, Naseri N, Ali, Mousavi-Dehghani SA. Modeling of asphaltene precipitation utilizing Association Equation of State. *Fuel*, 2012; 93: 59-66.
- [8] Pazuki GR, Nikookar M. A modified Flory-Huggins model for prediction of asphaltene precipitation in crude oil. *Fuel*, 2006; 85(7-8): 1083-1086.
- [9] Speight JG, and Plancher H. Molecular Models for Petroleum Asphaltenes and Implications for Asphalt Science and Technology. in *Proc., Internat. Symp. on the Chemistry of Bitumens*. 1991.
- [10] Pan H, Firoozabadi A. Thermodynamic Micellization Model for Asphaltene Aggregation and Precipitation in Petroleum Fluids. *SPE Prod. & Fac*, 1998: 118.
- [11] Cimino R, Corraera S, Del Bianco A, and Lockhart TP. Solubility and Phase Behavior of Asphaltenes in Hydrocarbon Media. in *Asphaltenes: Fundamentals and Applications*, E.Y.S.a.O.C. Mullins, Editor. 1995, Plenum Press: NY: 97-130.
- [12] Mullins OC, Seifert DJ, Zuo JY, and Zeybek M. Clusters of Asphaltene Nanoaggregates Observed in Oilfield Reservoirs. *Energy Fuels*, 2013; 27(4): 1752-1761.
- [13] Groenzin H, and Mullins OC. Asphaltene Molecular Size and Structure. *J. Phys. Chem. A*, 1999; 130(50): 11237-11245.
- [14] Hirschberg A, de Jong LN, Schipper BA, Meijer JG. Influence of Temperature and Pressure on Asphaltene Flocculation. 1984, KoninWijke/Shell E&P Laboratorium.
- [15] Burke NE, Hobbs RE, and Kashou SF. Measurement and modeling of asphaltene precipitation. *Journal of Petroleum Technology*, 1990; 42(11): 1440-1446.
- [16] Prausnitz JM, Lichtenthaler RN, and Azevedo EGD. *Molecular Thermodynamics of Fluid Phase Equilibria*. 3rd ed. 1999, Upper Saddle River, NJ: Prentice Hall PTR.
- [17] Speight JG, Long RG, and Trawbridge TD. Factor Influencing the Separation of Asphaltenes from Heavy Petroleum Feed stocks. *Fuel*, 1984; 5: 616.
- [18] Gupta AK. A model for Asphaltene Flocculation Using an Equation of State. in *Department of Chemical and Petroleum Engineering*. 1986, University of Calgary: Calgary, Alberta.
- [19] Thomas FB, Bennion DW, and Hunter BE. Experimental and Theoretical Studies of Solids Precipitation from Reservoir Fluid. *Journal of Canadian Petroleum Technology*, 1992; 31: 22-31.
- [20] Nghiem L. Phase Behavior Modeling and Compositional Simulation of Asphaltene Deposition in Reservoirs. 1999, University Of Alberta: Edmonton, Alberta.
- [21] Leontaritis KJ, and Mansoor, GA. Asphaltene Flocculation during Oil Recovery and Processing: A Thermodynamic-Colloidal Model. in *SPE International Symposium on Oil Field Chemistry*. 1987, SPE: San Antonio, TX,.
- [22] Jewell DM, Albaugh EW, Davis BE, Ruberto RG. Integration of chromatographic and spectroscopic techniques for the characterization of residual oils. *Ind. Eng. Chem. Fundam*, 1974; 13(3): 278-282.
- [23] ASTM, Standard Test Method for Separation of Representative Aromatics and Non-aromatics Fractions of High-Boiling Oils by Elution Chromatography. 1995.

- [24] ASTM, Standard Test Methods for Separation of Asphalt into Four Fractions. 1997.
- [25] ASTM, Standard Test Method for Characteristic Groups in Rubber Extender and Processing Oils and Other Petroleum Derived Oils by the Clay-Gel Absorption Chromatographic Method. 2008.
- [26] Meléndez LV, Lache A, Orrego-Ruiz JA, Pachon Z, Mejia-Ospino E. Prediction of the SARA analysis of Colombian crude oils using ATR-FTIR spectroscopy and chemometric methods. *Journal of Petroleum Science and Engineering*, 2012; 90-91: 56-60.
- [27] Sanchez-Minero F, Anachyeta J, Silva-Oliver G, Flores-Valle S. Predicting SARA composition of crude oil by means of NMR. *Fuel*, 2013; 110: 318-321.
- [28] Vazquez D, Mansoori GA. Identification and measurement of petroleum precipitates. *Journal of Petroleum Science and Engineering*, 2000; 26(1-4), 49-55.
- [29] Koza JR. Genetic programming, on the programming of computers by means of natural selection. Cambridge (MA. 1992, MIT Press.
- [30] Mollahasani A, Alavi AH, Gandomi AH. Empirical modeling of plate load test moduli of soil via gene expression programming. *Computers and Geotechnics*, 2011; 38(281-286).
- [31] Ahmadi, M. A., Zendehboudi, S., Bahadori, A., James, L., Lohi, A., Elkamel, A., & Chatzis, I. Recovery Rate of Vapor Extraction in Heavy Oil Reservoirs – Experimental, Statistical, and Modeling Studies. *Industrial & Engineering Chemistry Research*, 2014; 53(41), 16091-16106.
- [32] Ferreira C. Gene expression programming: a new adaptive algorithm for solving problems. *Complex Syst.*, 2001; 13(2): 87-129.
- [33] Ferreira C. *Gene Expression Programming: Mathematical Modeling by an Artificial Intelligence*. 2nd ed. ed. 2006, Berlin/New York: Springer-Verlag.
- [34] Gharagheizi F, Ilani-Kashkouli P, Farahani N, Mohammadi AH. Gene expression programming strategy for estimation of flash point temperature of non-electrolyte organic compounds,. *Fluid Phase Equilibria*, 2012; 329: 71- 77.
- [35] Zhang X, Pedrosa N, and Moorwood T. Modeling Asphaltene Phase Behavior: Comparison of Methods for Flow Assurance Studies. *Energy & Fuels*, 2012; 26: 2611-2620.
- [36] de Boer RB, Leerlooyer K, Eigner MRP, van Bergen ARD. Screening of Crude Oils for Asphalt Precipitation: Theory, Practice, and the Selection of Inhibitors. *SPE Production & Facilities*, 1995. SPE 24987,; 55-61.
- [37] Sako T, Wu AH, and Prausnitz JM. Modelling of high-pressure phase equilibrium using the Sako-Wu-Prausnitz equation of state I. Pure-components and heavy n-alkanes solutions. *Fluid Phase Equilibrium*, 1999;163(1):61-77.
- [38] Yarranton HW, Alboudwarej H, Jakher R. Investigation of Asphaltene Association with Vapor Pressure Osmometry and Interfacial Tension Measurements. *Ind. Eng. Chem. Res.*, 2000; 39: 2916-2924.
- [39] Akbarzadeh K, Alboudwarej H, Svrcek WY, Yarranton HW. A generalized regular solution model for asphaltene precipitation from n-alkane diluted heavy oils and bitumens. *Fluid Phase Equilibria*, 2005; 232: 159-170.

To whom correspondence should be addressed: Dr. Mohammad Shadadeh, Research Institute of Petroleum Industry, Tehran, Iran, mohamad.shadadeh@gmail.com; shadadehm@ripi.ir