Application of Simulated Annealing Technique to Non-Linear Optimization of PC-SAFT for Petroleum Reservoir Fluids

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Abstract
Equations of state should be tuned to reservoir conditions by PVT tests for phase behavior modeling. This tuning is achievable via an optimization method. In this work, simulated annealing algorithm is applied as a global optimization method to parameter optimization for PC-SAFT from the statistical associating fluid theory incorporating hard chain as reference fluid. The optimization parameters are determined by minimizing the calculated phase behavior of a synthetic petroleum mixture and real petroleum fluids from Iranian oil and gas reservoirs, based on their PVT-tests. We examined several tests, assumed to be representative of reservoir processes, such as differential liberation and constant composition expansion for oil samples and constant volume depletion for gas condensate sample. In petroleum systems, new petroleum fraction characterizing correlations were developed and validated according to PVT data and other equations of state. The results showed a high degree of accuracy for these newly developed correlations. It is observed that for the synthetic mixture and real reservoir fluids, considering the parameters obtained using the annealing technique, the solutions are theoretically justifiable. For real samples of petroleum fluid, the results are acceptables such results provide a measure of confidence that the annealing method does converge to the global minimum in the majority of the studied systems.

Key words: Petroleum Fluids, EOS Tuning, PVT-Test, Non-linear Parameter Optimization, Simulated Annealing, PC-SAFT

Introduction

Reservoir fluid phase behavior modeling and tuning to reservoir condition play an important role in reservoir study. Cubic equations of state have traditionally been used to model phase behavior in the oil industry because they provide good results and are mathematically simple. The SRK (Soave-Redlich-Kwong) and the PR (Peng-Robinson) equations are the most popular cubic equations currently used in research, simulations, and optimizations in which thermodynamic and VLE properties are required. These two equations have been considered for all types of calculations from simple estimations of pure-fluid volumetric properties and vapor pressures to descriptions of complex multi-component systems [1-3]. Soave-Redlich-Kwong achieved several goals in developing a new two-parameter equation of state cubic in volume. The parameters are expressible in terms of critical pressure, critical temperature and Acentric factor (P_C, T_C and ω). The model results in an improved performance in the vicinity of the critical point, particularly for calculations of Z_C and vapor pressure. SRK is able to predict the vapor pressure more accurately than other equations of state.

With the advent of molecular simulation coupled with statistical physics, new approaches have been investigated for equations of state [4]. Statistical Associating Fluid Theory is a statistical mechanical equation of state developed from Wertheim's first-order perturbation theory [5]. It is similar to group contribution theories in that the fluid of interest is initially considered to be a mixture of independent segments. The theory, proposed by Chapman, predicts the change in free energy both upon bonding these segments to form chains and on the further association of the chain-like molecules [6,7]. In this work, PC-SAFT equations of state from SAFT family is used

to describe phase behavior of petroleum fractions [8].

Any equation of state ultimately relies on a number of intermolecular parameters (binary interaction parameter), which must be obtained by direct comparison with experimental data [9-11]. In the case of petroleum reservoir fluids, there are other sources of uncertainties such as petroleum fraction characterization and conditions in which reservoir fluids exists. The optimum values of these parameters are obtained by fitting the calculations to available experimental data using a suitable parameter optimization method. An advantage of modern equations over cubic equations of state is that fewer experimental data points may be needed to obtain a full description of the phase behavior of a system, especially in the case of mixtures. Traditionally, gradient based optimization methods are used to tune equations of sates, which may lead to unsatisfied results. Stochastic optimization refers to an optimization process of a function in which randomness is present [12]. Examples of various stochastic optimization methods are greedy search, stochastic programming, and genetic algorithm and simulated annealing. A general optimization process involves a series of trials and errors [13]. The function to be optimized is termed objective function. In a typical modeling task, where the aim is to produce a realization that matches a target, their differences define the objective function to be minimized. Starting from an initial guess, a number of realizations are generated, each of which corresponds to a new objective function value. The generation is repeated until the minimum value of objective function is established. The generation procedure is essential for an optimization since it determines speed of the optimization process and whether or not the objective function can be optimized.

One of the simplest forms of stochastic optimization methods is greedy algorithm or exhaustive search. As the name suggests, iterations are carried out in a very random manner. For each of iterations, a new realization is computed from previous one. If there is a decrease in values of the objective functions, the new realization becomes the base for next iterations. However, this is very time consuming and has the risk of trapping in local minimums. In global optimization methods such as simulated annealing, if objective function is decreased, the set of optimization parameters is kept unconditionally, otherwise a probability function is assigned to it. This decreases the chance of trapping in local minimum with lower amounts of iterations [12].

In this work, a global optimization algorithm is applied for tuning of equation of state for petroleum reservoir fluid phase behavior modeling. The optimization parameters are determined by minimizing the calculated phase behavior of a synthetic petroleum mixture and real petroleum fluids from Iranian oil and gas reservoirs, based on their PVT-tests. We carried out several tests, assumed to be representative of reservoir processes, such as differential liberation and constant composition expansion for oil samples and constant volume depletion for gas condensate sample. In petroleum systems, new petroleum fraction characterizing correlations were developed and validated according to PVT data and other equations of state. The results of simulated annealing were compared with the experimental data. Finally, a brief discussion of the method and the results are presented.

Equation of State Model

Traditionally, a cubic equation of state is used for phase behavior modeling of petroleum fluids. The SRK (Soave-Redlich-Kwong) and the PR (Peng-Robinson) equations are the most popular cubic equations currently used in research, simulations, and optimizations in which thermodynamic and VLE properties are required. These two equations have been considered for all types of calculations from simple estimations of pure-fluid volumetric properties and vapor pressures to descriptions of complex multi-component systems [1-3]. Statistical Associating Fluid Theory is a statistical mechanical equation of state developed from Wertheim's first-order perturbation theory [5]. In this work, PC-SAFT equations of state from SAFT family is used to describe phase behavior of petroleum fractions [8]. This equation of state is developed by Gross and Sadowski for non-associating fluids [8]. It assumes a modified square-well potential. PC-SAFT describes the residual Helmholtz free energy (A_{res}) of a mixture of non-associating fluids as shown in Figure 1.
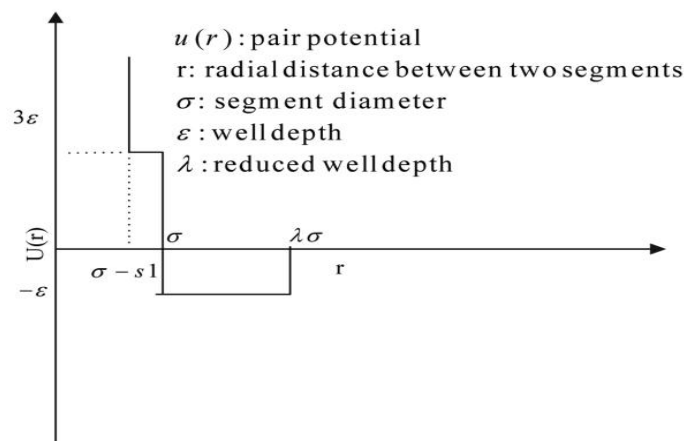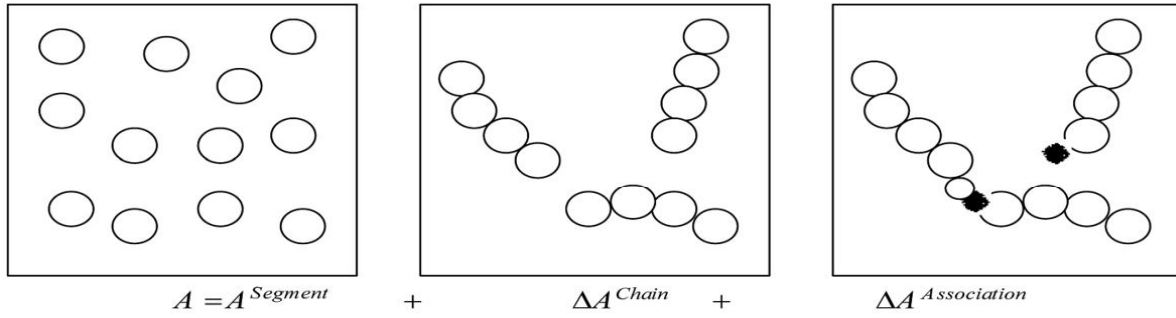

Figure 1- Modified Square-Well Interaction Potential Used in PC-SAFT Equation of State

$$A = A^{Segment} \quad + \quad \Delta A^{Chain} \quad + \quad \Delta A^{Association}$$

Figure 2- The free energy is the sum of the independent segment free energy and the change in free energy due to chain formation and association

It describes the residual Helmholtz free energy (A_{res}) of a mixture of non-associating fluids, which is shown schematically in Figure 2.

$$\frac{A^{res}}{RT} = \frac{A^{seg}}{RT} + \frac{A^{chain}}{RT} = m\left(\frac{A^{hs}_0}{RT} + \frac{A^{disp}_0}{RT}\right) + \frac{A^{chain}}{RT} \quad (1)$$

Where

$$\frac{A^{chain}}{RT} = \sum x_i(1-m_i)\,ln g_{ii}^{hs}(d_{ii}) \quad (2)$$

In which radial distribution function is:

$$g_{ij}^{hs}(d_{ij}) = \frac{1}{1-\zeta_3} + \frac{3d_{ii}d_{jj}}{d_{ii}+d_{jj}}\left(\frac{\zeta_2}{(1-\zeta_3)^2}\right) + 2\left[\frac{d_{ii}d_{jj}}{d_{ii}+d_{jj}}\right]^2\left(\frac{\zeta_2^2}{(1-\zeta_3)^3}\right) \quad (3)$$

And packing fraction density is:

$$\zeta_n = \frac{\pi}{6}\rho\sum x_i m_i\,d_i^{\,n} \quad , \ n\,\epsilon\,\{0,1,2,3\} \quad (4)$$

Temperature dependent diameter:

$$d_i(T) = \sigma_i\left[1 - 0.12Exp\left(\frac{-3\varepsilon_i}{KT}\right)\right] \quad (5)$$

The dispersion contribution to Helmholtz free energy is:

$$\frac{A^{disp}_0}{RT} = \frac{A_1}{RT} + \frac{A_2}{RT} \quad (6)$$

In that:

$$\frac{A_1}{kTN} = -2\pi\rho m^2\left(\frac{\varepsilon}{kT}\right)\sigma^3\int_1^\infty \tilde{u}(x)g^{hc}\left(m;x\frac{\sigma}{d}\right)x^2 dx \quad (7)$$

And:

$$\frac{A_2}{kTN} = -\pi\rho m\left(1 + Z^{hc} + \rho\frac{\partial Z^{hc}}{\partial\rho}\right)m^2\left(\frac{\varepsilon}{kT}\right)^2$$
$$\sigma^3\frac{\partial}{\partial\rho}\left[\rho\int_1^\infty \tilde{u}(x)^2 g^{hc}\left(m;x\frac{\sigma}{d}\right)x^2 dx\right] \quad (8)$$

The summation for compressibility of hard chain is:

$$\left(1 + Z^{hc} + \rho\frac{\partial Z^{hc}}{\partial\rho}\right) = 1 + m\frac{8\eta-2\eta^2}{(1-\eta)^4} +$$
$$(1-m)\frac{20\eta-27\eta^2+12\eta^3-2\eta^4}{[(1-\eta)(2-\eta)]^2} \quad (9)$$

And in the extension to the mixture we have the following relations:

$$\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j) \quad (10)$$

And:

$$\varepsilon_{ij} = \frac{1}{2}\left(\sqrt{\varepsilon_i\varepsilon_j}\right)\left(1 - k_{ij}\right) \quad (11)$$

In the above equations, ρ is the density number, η is the packing fraction (same as ζ_3), σ is the temperature independent segment diameter, d_{ij} is the temperature dependent segment diameter, ε/k is the segment energy, x_i is the mole fraction of species i, and k_{ij} is the binary interaction parameter between species i and j. I_1 and I_1 are functions of the system packing fraction and average segment number and can be found in the work by Gross and Sadowski [8]. The SAFT association term is not used in this work because of our assumption that there is no association in reservoir fluids. SAFT has been successfully used to predict the phase behavior of fluids where molecular size and shape interactions dominate. As seen in the above equations, SAFT requires three parameters for each pure component: the number of segments per molecule (m), the molecular segment diameter (σ), and the segment energy (ε/k). An important feature of SAFT is that the correlations of pure component parameters with molecular weight can be made for hydrocarbon and polynuclear aromatics. As a result, appropriate correlations are needed to characterize petroleum fraction and heavy oil plus fraction. SAFT has been successfully used to predict the phase behavior of fluids where molecular size and shape interactions dominate. For instance, it accurately describes the phase behavior of high molecular weight and the vapor liquid equilibrium of long-chain, short-chain hydrocarbon mixtures.

Phase Behavior Analysis

In this work, the SRK and PC-SAFT equation of state were used for phase behavior calculations such as computing saturation pressure and simulation of PVT test such as DL (differential simulation), CCE (constant composition expansion) and CVD (constant volume depletion). For PVT test, we need flash calculation algorithm. The successive substitution approach was used [9,10]. To plot PT diagram, we require saturation pressure, which can be calculated by Gibbs free energy analysis. Using Gibbs free energy analysis, phase stability analysis can be formulated by calculating the distance between Gibbs free energy surface and the tangent plane, called the tangent plane distance (TPD). Stability analysis is to locate the minimum of the TPD at all compositions. It is further suggested that checking the positivity at stationary points is sufficient [14-16]. Here, equations for calculating the saturation pressure of a homogeneous phase were developed using the tangent plane criterion for stability. At a given pressure P and temperature T, a mixture of composition **Z** is stable if and only if the tangent plane to the Gibbs free energy surface at **Z** always lies below the Gibbs free energy surface. This can be mathematically

expressed as follows:

$$D_Z(y, P, T) = RT \sum y_i ln \left[\frac{f_i(y, P, T)}{f_i(Z, P, T)} \right] \geq 0 \qquad (12)$$

For all **y,** the function $D_Z(y, P, T)$ is the distance from the Gibbs free energy surface to the tangent plane at **Z**, evaluated at a composition y and the given pressure P and temperature T, and f_i is the fugacity of component i. It is also more convenient to work with the dimensionless distance D_Z^* defined as follows

$$D_Z^*(y, P, T) = D_Z(y, P, T)/RT \qquad (13)$$

As proposed by (Michelsen M., 1982), to test the stability of mixture **Z**, it is sufficient to check the values of D_Z^* at all the minimum points y of D_Z^*. The stationary points y of D_Z^* satisfy the following equation

$$g_i = \ln K_i + \ln \phi_i(y, P, T) - \ln \phi_i(Z, P, T) \quad i = 1, \dots, n_c \quad (14)$$

Where ϕ_i denotes the fugacity coefficient of component I calculated using PC-SAFT EOS [4]. Composition y is found from the equations:

$$Y_i = K_i Z_i \qquad i = 1, \dots, n_c \qquad (15)$$

And

$$y_i = \frac{Y_i}{\sum_{j=1}^{n} Y_j} \qquad i = 1, \dots, n_c \qquad (16)$$

At a stationary point, when $g_i = 0$ as required by equation (19).

$$D_Z^*(y, P, T) = -ln \left(\sum_{i=1}^{n_c} Y_i \right) \qquad (17)$$

Since D_Z^* must be positive for the mixture **Z** to be stable, it is necessary that the

$$\sum_{i=1}^{n_c} Y_i \leq 1 \qquad (18)$$

When two phases are in equilibrium, the plane drawn tangent to the Gibbs free energy surface at one of the compositions is also a tangent to the Gibbs free energy at the second composition. If the first composition is **Z** and the second **y**, intersection of the tangent plane at **Z**

with the Gibbs free energy at **y** requires that the distance be zero; i.e.

$$D_Z^*(y, P, T) = 0 \qquad (19)$$

Combining eqns. (17) and (19) results in the following equation

$$\sum_{i=1}^{n_c} Y_i = 1 \qquad (20)$$

Obviously, all sets of equations are strongly nonlinear and are required to be iteratively solved using iterative methods such as Newton-Raphson.

Simulated annealing

Kirkpatrick introduced simulated annealing to complex problems in combinatorial optimization [12]. Since then, this has been used in a variety of problems that involve finding optimum values of a function of a very large number of independent variables. The basic concept of simulated annealing originates from physical process of metallurgical annealing. An annealing process occurs when a metal in a heat bath is initially at high temperature and is slowly cooled. At first, all particles are randomly distributed in a quasi-liquid state. As temperature drops, particles arrange themselves in a lowenergy ground state (i.e. at or very close to the global minimum of energy), forming crystals. If the cooling process is too rapid, equilibrium conditions are not always maintained. Crystals are not formed and the total energy of the system is not at minimum in this case. Crystallizing can be viewd as a combinatorial optimization problem to arrange the atoms in a material to minimize the total potential energy. Crystallizing is often performed with a cooling procedure called annealing. The theoretical modeling of this process applicable to arbitrary combinatorial spaces is called simulated annealing. The flow diagram of simulated annealing used in this work is shown in Figure 3.
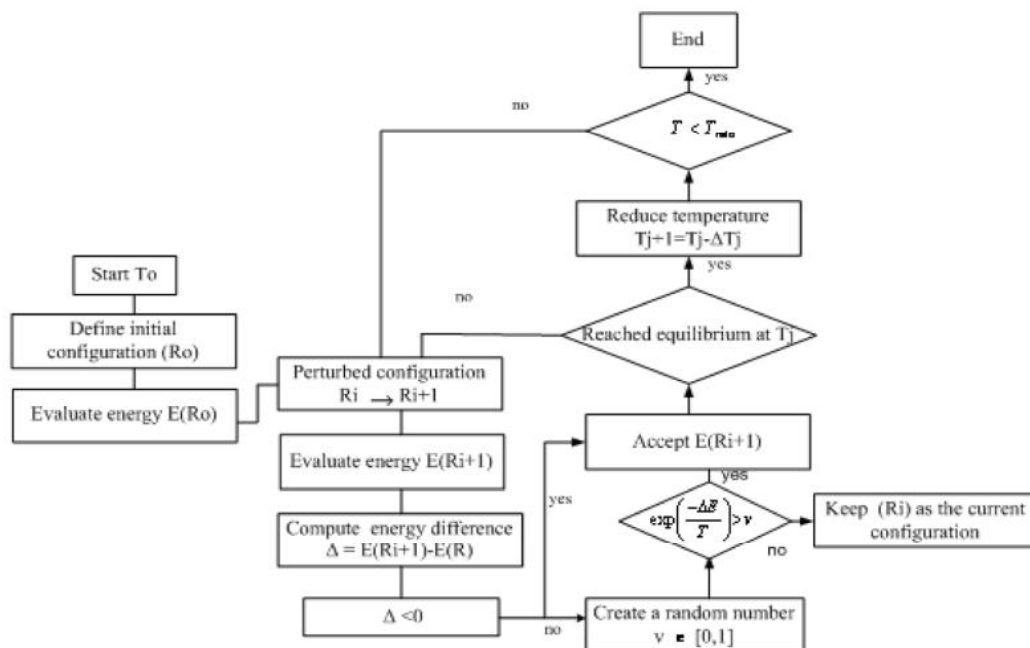

Figure 3- Flow Diagram of Simulated Annealing Applying Metropolis algorithm

Herault noticed that SA took a long time to find an optimal solution [17]. To remedy this, he created an algorithm called rescaled simulated annealing (RSA). The only thing that Herault changed about SA is the Metropolis Criterion. In this flow diagram, the Metropolis algorithm is applied to help program to be transformed out of local minimum applying random number generation process [18]. If energy (objective function) is decreased, the set of optimization parameters is kept unconditionally. Otherwise, a Boltzman probability function is assigned to it as in equation 21.

$$P(accept) = \begin{cases} \Delta E < 0 & Unconditionally\ accepted \\ \Delta E < 0 & accepted\ with\ probability\ P = Exp\left(\frac{-\Delta E}{T}\right) \end{cases} \quad (21)$$

Then, a random number is generated within metropolis algorithm. If the probability of the set of parameters is greater than random number, it will be accepted as the next iteration. The following linear schedule is simple and yet effective, where α is a reduction factor or learning rate parameter:

$$T_{new} = \alpha T_{old} \quad (22)$$

It has been proved that by carefully controlling the rate of cooling of the temperature, SA can find the global optimum. However, this requires infinite time. Fast annealing and very fast simulated re-annealing (*VFSR*) or adaptive simulated annealing (*ASA*) are each in turn exponentially faster and overcome this problem.

The SA algorithm does not require or deduce derivative information. It merely needs to be supplied with an objective function for each trial solution it generates. Thus, the evaluation of the problem functions is essentially a "black box" operation as far as the optimization algorithm is concerned. Obviously, in the interests of overall computational efficiency, it is important that the problem function evaluations be efficiently performed; especially as in many applications, these function evaluations are by far the most computationally intensive activity. Some thought needs to be given to the handling of constraints when using the SA algorithm. In many cases, the routine can simply be programmed to reject any proposed changes, which result in constraint violation, so that a search of feasible space only is executed. This is the case for negative interaction coefficients. It is also valid about plus fraction properties. Phase behavior of petroleum fluid is strongly dependent on these properties and large changes in these variables may cause the SA to fail.

Results and discussion

A number of different methods for optimizing (tuning) EOS have been developed, which rely on using information about the gradient of the function to guide the direction of search. These methods can perform well on functions with only one peak (uni-modal functions). However, functions with many peaks, (multimodal functions), suffer from the problem that the first peak found will climb, to form the highest peak. Having reached the top of a local maximum, no further progress can be made. This is the main disadvantages of classical methods for non-linear optimization of PVT tests. Using gra-

dient based algorithms, we may have good results for some properties in PVT test, while other properties have considerable deviations from experimental data. Therefore, global optimization approaches such as simulated annealing (SA) are good choices for EOS tuning. In this section, simulated annealing technique is applied to PC-SAFT equations and compared to non-optimized EOS. Experimental PVT data are obtained from a reliable resource by Iranian oil and gas reservoirs. The data include several tests such as constant composition expansion (CCE) and differential liberation (DL). Two types of objective functions have been constructed. The first one was according to minimization of difference between compositions obtained by equations of sate and those experimentally obtained via flash test. In the second, the objective was to minimize the difference between equation of states model and PVT tests. Several sets of parameters were selected.

Petroleum Fraction Characterization

Pure component parameters for PC-SAFT equation of state can be found in Table 1. An important feature of SAFT is that correlations of pure component parameters with molecular weight can be made for n-alkanes and polynuclear aromatics. As a result, appropriate correlations are needed to characterize petroleum fraction and heavy oil plus fraction. In fact, the main advantage of SAFT based equations is that the SAFT parameters are well-behaved and suggest predictable trends with macroscopic properties. Based on this fact, Huang and Radosz proposed correlations of SAFT parameters in terms of the average molecular weight for poorly characterized oil fractions [7].

Table 1- Pure Component Parameter for PC-SAFT Equation of Sate [6]

Component	Molecular Weight	Diameter [Å]	Energy Parameter
Nitrogen	28.01	1.205	3.313
Carbon dioxide	44.01	2.073	2.785
Methane	16.043	1	3.704
Ethane	30.07	1.607	3.521
Propane	44.096	2.002	3.618
n-Butane	58.123	2.332	3.709
n-Pentane	72.146	2.69	3.773
n-Hexane	86.177	3.058	3.798
n-Nonane	128.25	4.208	3.845
n-Decane	142.285	4.663	3.839
n-Dodecane	170.338	5.306	3.896
n-Tetradecane	198.392	5.9	3.94
n-Eicosane	282.553	7.9849	3.987
Isobutane	58.123	2.2616	3.757
Isopentane	72.146	2.562	3.83
Cyclopentane	70.13	2.365	3.711
Benzene	78.114	2.465	3.648
Toluene	92.141	2.815	3.717
Ethylene	28.05	1.593	3.445
Propylene	42.081	1.96	3.536

The correlations are given in terms of the different families, e.g., n-alkanes, polynuclear aromatics, etc. These correlations give poor results. Also, it is not clear exactly what proportion of each fraction belongs to specific family of hydrocarbons. For example for n-alkanes, Gross and Sadowski proposed correlations in terms of molecular weight [8].

These relations are not enough to characterize petroleum fractions, which include several types of hydrocarbon families. A simple solution to this problem is to completely define the composition of fractions and then relate their PC-SAFT parameter to molecular weight for each family. The method used in this work, is plotting PC-SAFT parameters for different types of hydrocarbon and trying to find universal curves by scaling figures of different families into a unit curve introducing normal boiling point into x axis. These curves are shown in Figures 4, 5 and 6. The following relations are therefore obtained from figures in terms of molecular weight and normal boiling point.

$$m = 0.0838MW((237°K)/(T_b°K)) - 2.6552 \qquad (23)$$

$$m\sigma^3 = 5.7712MW((237°K)/(T_b°K)) - 229.92 \qquad (24)$$

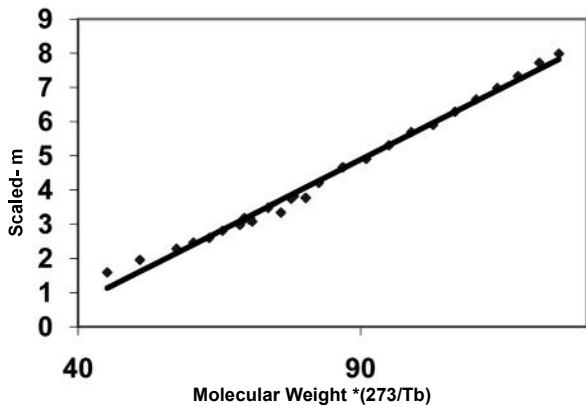$$m(\varepsilon/k) = 21.686MW((237°K)/(T_b°K)) - 702.57 \qquad (25)$$

Figure 4- Universal Curve for Segment Number Verses Molecular Weight Normalized with Normal Boiling Point for n-Alkanes, Alkenes and Benzenes.
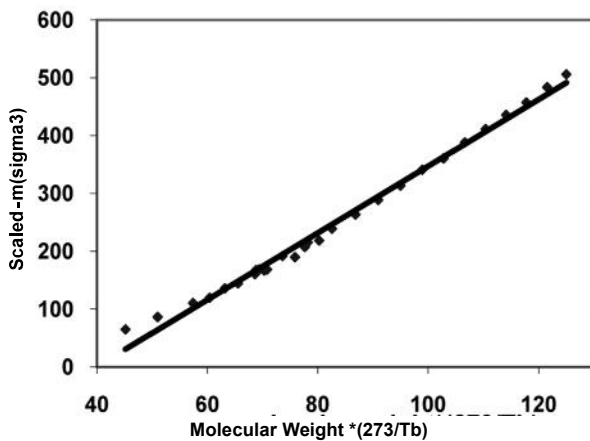

Figure 5- Universal Curve for Segment Diameter Term ($m\sigma^3$) Verses Molecular Weight Normalized with Normal Boiling Point for n-Alkanes, Alkenes and Benzenes.
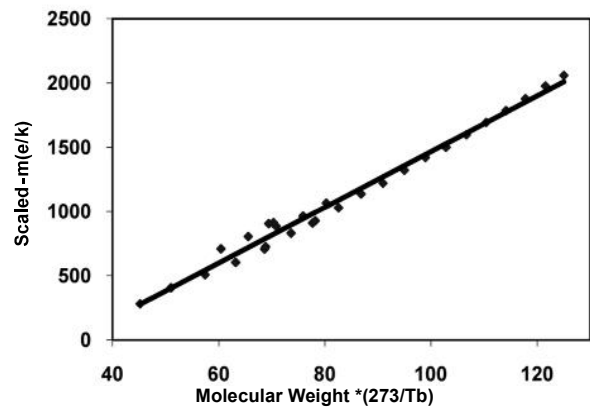

Figure 6- Universal Curve for Energy Term ($m\,\varepsilon/k$) Verses Molecular Weight Normalized with Normal Boiling Point for n-Alkanes, Alkenes and Benzenes.

Optimization using equilibrium condition

The first task in this research was to create a framework for lumping for PVT analysis. This framework facilitates program development by maximizing the code reuse, extendibility, and maintainability. All algorithms are coded by C#. Several subroutines were written for File I/O, PVT analysis and optimization. The first sample is a synthetic hydrocarbon mixture from [11]. For PC-SAFT equation, sample A, all binary interaction parameters were selected with following objective functions:

$$objFunc(k_{ij}) = \sum_{l,g} \sum_{i=1}^{n_{comp}} \left| \frac{z_i^{calc} - z_i^{exp}}{z_i^{exp}} \right| \qquad (26)$$

The algorithm stops when the objective function does not change after a certain number of iterations (convergence attained). It also stops if total number of iterations exceeds a predefined limit (cannot reach optimum value). As it can be observed, allowing higher iteration makes the objective function to be more finally stable. Change in the value of binary interaction parameter is as follows:

$$\begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \rightarrow \begin{bmatrix} 0 & 0.0152 & 0.0356 \\ 0.0152 & 0 & 0.0018 \\ 0.0356 & 0.0018 & 0 \end{bmatrix}$$

As it can be seen from binary interaction coefficient matrix, the quality of optimization was so appropriate that physical meanings of the parameter observed (those with higher molecular weight difference), have higher values. The composition of each phase from experiment, using all of these sets of binary interaction parameters is presented in Table 2.

Table 2- Liquid phase composition with optimization method and no optimization in comparison with experiment-Sample A- PC-SAFT equation

PC-SAFT –simulated annealing	PC-SAFT – zero interaction coefficients	Experiment	Components
0.242	0.2742	0.242	C1
0.1518	0.1469	0.152	n-C4
0.6062	0.5789	0.606	n-C10

PC-SAFT equation of state, can also be optimized in the same way, applying binary interaction coefficient. It can be observed from Table 2 that when there are no uncertainties in the PC-SAFT component parameters, the main source errors are handled by binary interaction parameters, which make it clear that the equation itself, according to stronger theoretical basis, has less deviation from experimental data. Simulated annealing can deal with highly nonlinear models, chaotic and noisy data and many constraints.

It is a robust and general technique. Its main advantages over other local search methods are its flexibility and ability to approach global optimality. The algorithm is quite versatile since it does not rely on any restrictive properties of the model. SA methods are easily "tuned". For any reasonably difficult nonlinear or stochastic system, a given optimization algorithm can be tuned to enhance its performance and since it takes time and effort to become familiar with a given code, the ability to tune a given algorithm for use in more than one problem should be considered an important feature of an algorithm.

Optimization using PVT-Tests

There are several uncertainties associated with fluid phase behavior in reservoir conditions. These unknown uncertainties can be reduced when an equation of state is tuned to PVT-tests, which simulate reservoir, well-bore and surface facilities. In this case, some physical properties of three real petroleum reservoir fluids, samples B, C and D are shown in Tables 3 and 4. For sample B, a black oil mixture, differential liberation test is considered for optimization. This process simulates the volumetric depletion of a reservoir when the differential pressure steps become small. DL consists of a series of flashes at decreasing pressures along an isotherm. At each pressure step, the gas phase is withdrawn and a new flash is carried out at a lower pressure with the remaining liquid phase. After the system has been equilibrated, the gas phase is removed from the cell at constant pressure. The gas volume is measured with a gas-meter and recorded. Once the last pressure has been reached, the cell temperature is reduced to 15 ℃ and the cell pressure to 1 atm. Two important outputs of this test are GOR (gas oil ratio) and oil specific gravity SG in each pressure step. Here, GOR is obtained as the ratio of volume of remaining gas in solution (measured at standard conditions) to the volume of oil plus dissolved gas (measured at a given pressure). PC-SAFT is considered and optimized against experimental data. Several parameters can be selected for non-linear optimization of this test for PCSAFT including binary interaction coefficients and critical properties of lumped plus fractions. Therefore, the following objective function can be written:

$$objFunc\left(k_{ij}, m_{C12+}, \sigma_{C12+}, \frac{\varepsilon}{k_{C12+}}\right) = \quad (27)$$

$$\sum_{\psi=Rs,Bo}\sum_{i=1}^{steps}\left|\frac{\psi_i^{calc}-\psi_i^{exp}}{\psi_i^{exp}}\right|$$

Table 3- Reservoir fluids composition

Components	Mole fraction B-Black oil	Mole fraction C-Heavy oil	Mole fraction D-Gas condensate
N2	0.061	0.660	1.480
CO2	0.051	0.230	0.700
C1	46.848	10.350	94.020
C2	7.558	2.350	1.400
C3	4.627	1.950	0.450
IC4	1.021	1.620	0.200
NC4	2.421	4.000	0.280
IC5	1.358	3.600	0.150
NC5	2.288	2.280	0.160
C6	3.953	2.740	0.210
C7	3.084	2.150	0.210
C8	1.910	2.420	0.150
C9	2.645	2.150	0.140
C10	2.084	3.130	0.120
C11	2.012	2.520	0.100
C12+	18.080	57.850	0.240

Table 4- C12+ Molecular Weight and Specific Gravity.

Specific Gravity	Molecular Weight	Reservoir Fluids
0.884	340.95	B-Black oil
1.047	485	C-Heavy oil
0.92	201.23	D-Gas condensate

In which k_{ij}, m_{C12+}, σ_{C12+} and ε/k_{C12+} are used as optimization parameters. The objective functions for 50 and 200 iterations are represented in Figures 7 and 8.

The comparison of our optimization scheme with extended analysis in simulating DL test on sample B is shown in Figures 9 and 10. As it can be seen from the figures, the optimized (tuned figure) is much closer to the experimental data and nearly matches experimental data for gas oil ratio and oil formation volume factor. It should be noted that simulated annealing transformed optimization out of local optimums. As seen from equation 27, k_{ij}, m_{C12+}, σ_{C12+} and ε/k_{C12+} are selected as optimization parameters and gas oil ratio, oil formation volume factor and specific gravity are the candidate properties for tuning.

The same objective function was used for sample C, a heavy oil mixture. Since SA is meta-heuristic, a lot of choices are required to turn it into an actual algorithm. There is a clear tradeoff between the quality of the solutions and the time required to compute them. The tailoring work required to account for different classes of constraints and to fine-tune the parameters of the algorithm can be rather delicate. The precision of the numbers used in implementation of SA can have a significant effect upon the quality of the outcome. The results obtained for PC-SAFT are presented in Figures 11 and 12.
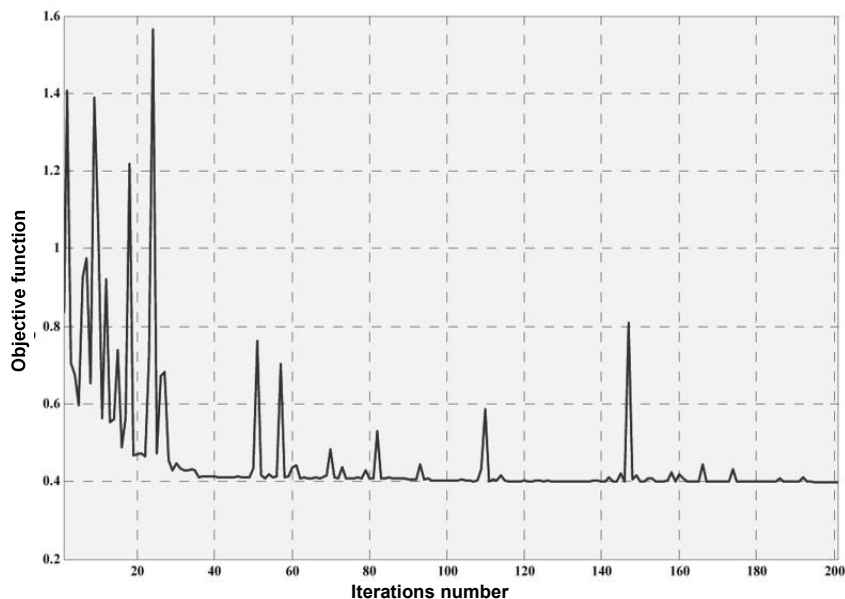
Figure 7- Objective function minimization with simulated annealing optimization of PC-SAFT equation of state-200 Iterations-sample A
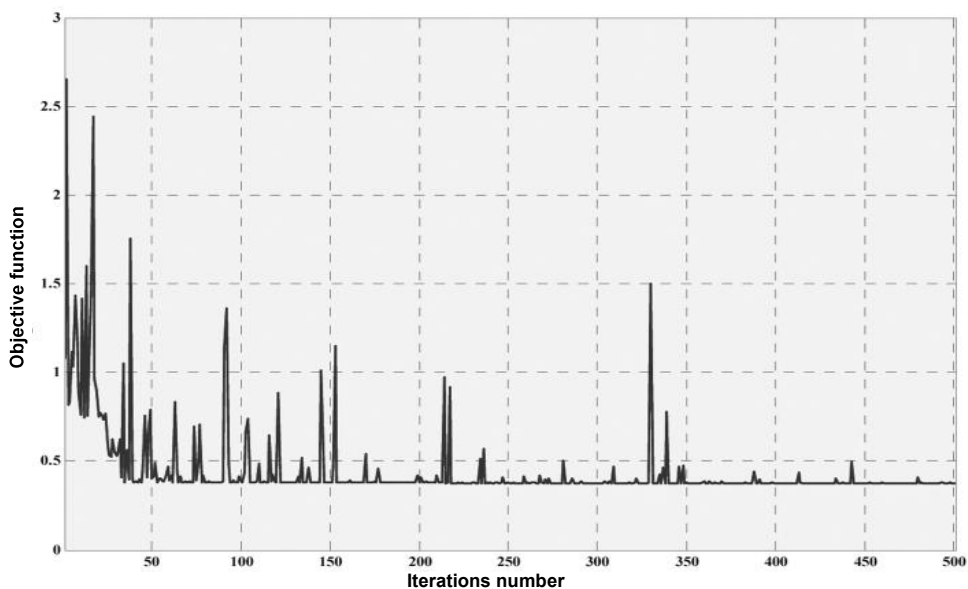

Figure 8- Objective Function Minimization with Simulated Annealing Optimization of PC-SAFT Equation of State-500 Iterations-Sample A
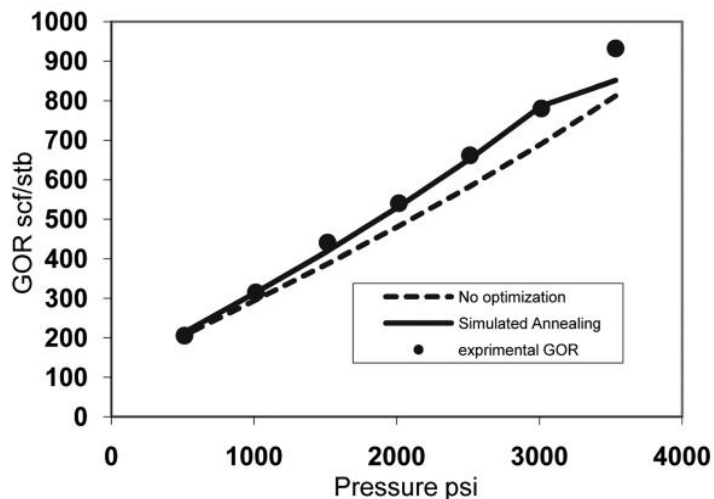

Figure 9- Comparison between simulated annealing and No Optimization for EOS tuning gas oil ratio-sample B – PC SAFT EOS
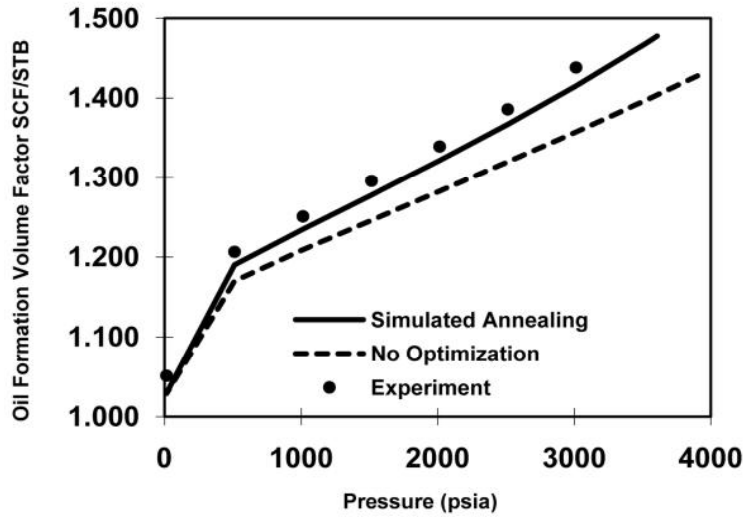
Figure 10- Comparison Between Simulated Annealing and No Optimization for EOS Tuning Oil
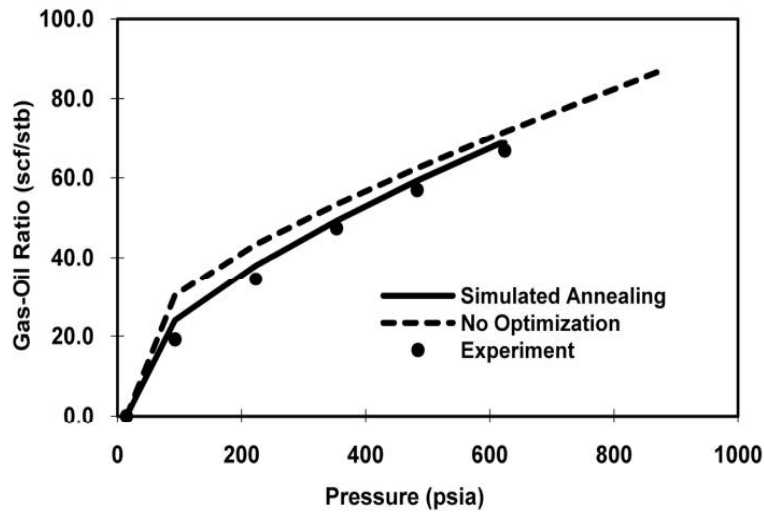Formation Volume Factor -Sample B – PC SAFT EOS.

Figure 11- Comparison Between Simulated Annealing and No Optimization for EOS Tuning Gas Oil ratio-Sample C – PC-SAFT EOS
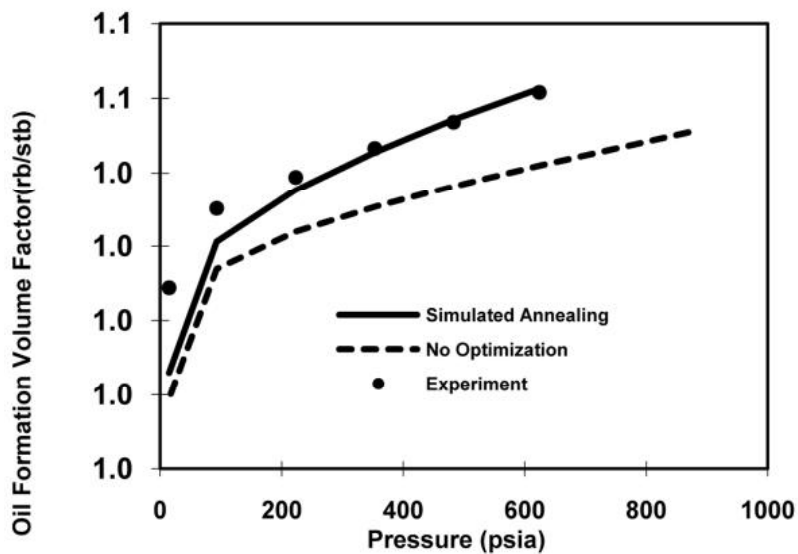
Figure 12- Comparison Between Simulated Annealing and No Optimization for EOS Tuning Gas Oil
Formation Volume Factor - Sample C - PC-SAFT EOS.

Here again the quality of optimization is in good agreement with experimental data. Reproduction of all categories of experimental data is another point to ponder for PC-SAFT with stronger theoretical basis as observed in following figures. For a complex problem, such as tuning of equations of sate, methods such as greedy algorithm (exhaustive search) usually do not produce good results since they could be trapped into a local optimum. Greedy algorithm cannot guide the transformation out of the local to the global optimum due to its total random characteristics. As seen in Figures 11 and 12, unlike simple algorithm such as exhaustive search, advanced global optimization algorithm of simulated annealing accepts all generations with a probability. This mechanism facilitates speed of convergence and avoids being trapped at local optima. The trends in those figures prove this claim.

In the case of gas condensate system, sample D; optimization was carried out for PC-SAFT. Here,

constant volume depletion (CVD) and constant composition (CCE) tests were used. Objective functions in the form of equation 27 were used again, but liquid dropout and cumulative gas produced, in the case of CVD, and relative volume and liquid volume in the case of CCE, were used instead of gas oil ratio, oil formation volume factor and specific gravity. The first PVT test simulated on this sample is constant composition expansion (CCE). CVD test is performed on gas condensates to simulate reservoir depletion performance and compositional variation. The test provides a variety of useful and important information used in reservoir engineering calculations. The pressure is reduced differently in pressure steps, from the saturation pressure to a predetermined level P and liquid condenses. The gas is removed to reach the original volume. Therefore, the liquid is accumulated in each step. The results for CVD, sample D, are shown in Figures 13 and 14.
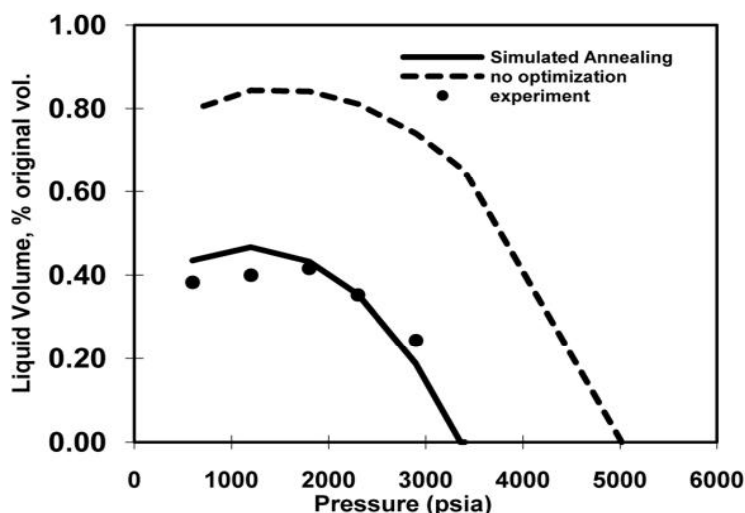

Figure 13- Liquid Dropout of Gas Condensate Fluid- Sample D - in CVD Test at 246 °F Before and After Optimization – PC-SAFT
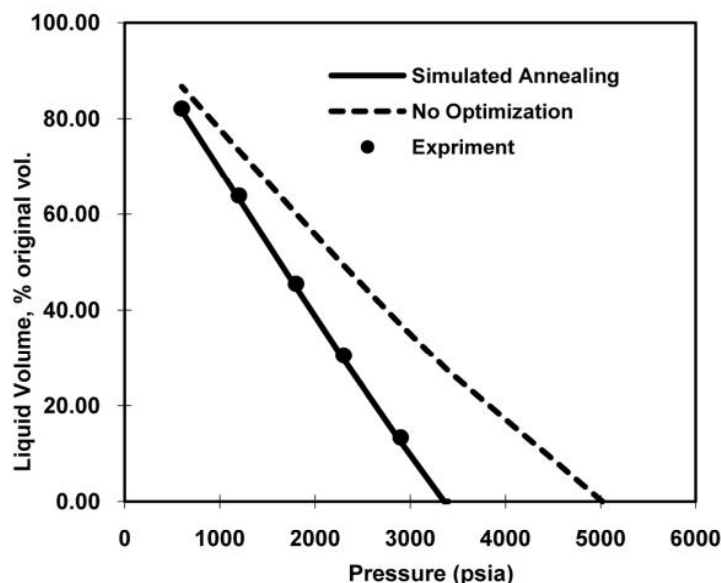

Figure 14- Cumulative Gas produced - Sample D - in CVD Test at 246 °F Before and After Optimization – PC-SAFT

It can be found from these figures that SA optimization is very effective in reproducing liquid dropout and cumulative gas produced during CVD. The produced figures with optimized model follow the trends of experimental data and can be used for future reservoir engineering calculations. In CCE experiment simulation, the reservoir sample is placed under a pressure higher than saturation pressure. Then, the pressure is decreased step by step down to a pressure much lower than saturation pressure. In each step, a flash calculation is performed and the

relative oil volume (ROV) is determined as:

ROV= (total volume at specified pressure)/(total volume at saturation pressure)   (28)

In the case of CCE test, the results are shown schematically in Figure 15. Again, the results show high predictive capabilities of the PC-SAFT to follow the physical trends in the experimental data. The results also represent robust feature of the optimization algorithm used in this study.
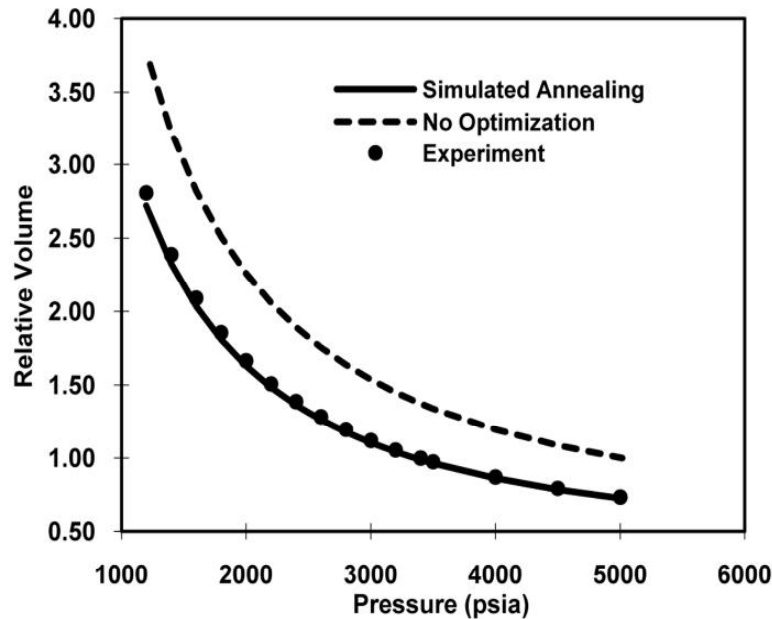

Figure 15- Relative Total Volume - Sample D - in CCE Test at 246 ºF Before and After Optimization – PC-SAFT

Conclusion

Simulated annealing technique has been successfully applied to parameter optimization for PC-SAFT for petroleum reservoir fluids. New correlations were developed and used to characterize petroleum fractions. The applicability of the simulated annealing technique as a global optimization method for thermodynamic models is exploited to ensure effective continuation of the algorithm. Equilibrium conditions and PVT data are used to tune equation of states. In this algorithm, simulated annealing transforms the optimization out of the local optimums.

The results show that optimized EOS is close to experimental PVT data. In the case of equilibrium composition matching, when, there are no uncertainties in the PC-SAFT component parameters, the main source errors is handled by binary interaction parameters, which makes clear that the equation itself, according to stronger theoretical basis, has less deviation from experimental data. It is also concluded that, generally PC-SAFT equation has less uncertainties and reproduces all properties accurately after optimization.

List of Symbols

AAD%	*Average Absolute Deviation Percent*
exp	*Experiment*
MW	*Molecular Weight*
y_i	*Mole fraction*
f_i	*Fugacity*
ϕ_i	*Fugacity Coefficient*
K_i	*Equilibrium Ration*
Max	*Maximum*
Min	*Minimum*
T	*Temprature*
P	*Pressure*
ε/K	*Square Well Potential*
σ	*Segment Diameter*
m	*Segment Length*
R	*Universal Gas Constant*
DL	*Differential Liberation*
CCE	*Constant Composition Expansion*
CVD	*Constant Volume Depletion*
PVT	*Pressure Volume Temperature*
EOS	*Equation of State*
PC SAFT	*Perturbed Hard Chain SAFT*

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