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Streamlining V-T Flash: A Simple, Robust and Reliable Algorithm Built on PT-Flash

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Abstract

Volume-Temperature equilibrium calculations (VT-Flash) are essential for simulating confined fluids in reservoir grid-blocks, rigid vessels, and separators. This work presents an approach, robust VT-Flash algorithm that enhances the efficiency and reliability of the indirect PT-Flash method. Two modifications are introduced: first, a nested stability analysis loop provides reliable initial equilibrium constants (k-values) before the equilibrium calculation, overcoming the limitations of Wilson's correlation at high temperatures. Second, three numerical manners (Bisection, Levenberg-Marquardt Algorithm (LMA), and Trust-Region Quasi-Newton (TRQN) methods) are employed to solve the molar volume objective function with improved convergence speed. The results are compared with constant composition expansion (CCE) test data for a synthetic gas condensate and a live oil, yielding R^2 values of 0.926 and 0.983, respectively, and cross-validated with the Helmholtz free energy minimization approach, showing very good agreement (R^2> 0.9999). Comparative analysis demonstrates that all three proposed mathematical methods reduce the number of iterations and elapsed time by up to 70% and 92% relative to the

reference method, introduced by Cisomandi et al. [1], while maintaining almost constant iterations across a wide temperature range, also in high temperatures. The approach produces smooth, physically consistent isochoric lines, phase envelopes, and three-dimensional pressure-temperature-volume surfaces. The Bisection method offers the lowest computational cost but requires a predefined operational pressure range; LMA and TRQN eliminate this need by initializing it with the ideal gas law. The proposed framework thus provides a simple, accurate, and robust PT-based VT-Flash tool suitable for diverse fluid systems and operating conditions.

Keywords:

Volume-Temperature equilibrium calculation (VT-Flash), PT-Flash, Bisection method, Levenberg-Marquardt algorithm, Trust-Region Quasi-Newton method

1. Introduction

Flash calculation is considered one of the most vital computational tools for phase behavior, introduced by Michelson, the PT-Flash algorithm based on Gibbs free energy minimization [2-4], which is known as the most widely used type of flash calculation. In addition, there are other types of flashes such as PH-Flash, PS-Flash, UV-Flash, HS-Flash, and VT-Flash, whose calculation basis is different from each other, and each is used depending on the existing conditions [5].

Among the types of flashes mentioned, VT-Flash is also known as a widely used flash calculation. In VT-Flash, a fluid is considered at a fixed volume (for example, a rigid vessel, a reservoir grid-block with a known pore volume, or a batch reactor) and a fixed temperature, and as a result

of the flash calculations, the fluid pressure is calculated [6-9]. VT-Flash applications are also considered in petroleum engineering and in underground storage, as well as determining the liquid level within separators of surface production units [1]. Given that in VT-Flash, the volume and temperature are specified and the pressure parameter is unknown, it is necessary to use Helmholtz free energy minimization to perform flash calculations, which was proposed by Michelsen [5]. Other authors continued to develop more sophisticated methods and improve the VT-Flash calculation algorithm based on the Helmholtz free energy minimization, although this approach has many computational and optimization complexities [6, 10-15]. In addition, some researchers also developed isochoric-isothermal equilibrium calculations for confined fluids, such as nanopores, based on the Helmholtz free energy minimization [7, 8, 16-22].

Due to the very high computational cost of VT-Flash based on the Helmholtz free energy minimization, especially for multicomponent mixtures, Michelsen [4, 23] proposed an approach for indirect VT-Flash calculation, that the VT-Flash problem is solved through a nested approach rather than a direct Helmholtz free energy minimization. A well-established PT-Flash calculation runs in an inner loop, while an outer loop adjusts the pressure until the volume constraint or the given specification is satisfied. This strategy avoids reformulating the equilibrium equations in volume-based variables. Cisomandi et al. (2018) [1] also proposed a simple algorithm for VT-Flash calculation based on adaptation of the classic successive substitution method for PT-Flash. Instead of the conventional nested approach that relies on repeated PT-Flash calculations to converge on the system pressure, this work proposes a direct VT-Flash formulation. The inner iterations for solving phase volume roots, which are intrinsic to PT-Flash, are avoided by reformulating the problem so that the two-phase equilibrium reduces to satisfying pressure equality

between the phases. Furthermore, Lu et al. [24] combined the approach presented by Cisomandi et al. with the algorithm presented by Pan et al. [25] to perform VT-multiphase flash calculations. The main goal of this paper is to improve and enhance performance and reduce the computational costs of PT-based VT-Flash calculations. For this purpose, the objective function is defined based on the molar volume, and in each iteration, its convergence process to zero with a specific tolerance must be evaluated. It is observed that in the approach proposed by Cisomandi et al. [1], the initial guess for the equilibrium constants is provided by the Wilson equation, and then the Rachford-Rice equation [26] is solved with respect to the initial guesses of k-values. Given that the k-values calculated by the Wilson equation only give values close to the actual values at low temperatures and have a high deviation from reality at high temperatures, it is likely that the Rachford-Rice equation does not have a solution in the first iteration stage in the range 0 and 1, and therefore, it is not possible to perform VT-Flash calculations. Even if the Rachford-Rice equation has a solution, due to the very large deviation at high temperatures, the number of iterations required to achieve convergence will increase significantly. In addition, the convergence speed can be increased by using an efficient and robust mathematical algorithm to solve the objective function. According to the explanations given, in this paper, two modifications are proposed to improve the approach introduced by Cisomandi et al.; First, adding a nested loop to obtain a suitable initial guesses of the k-values initial for PT-Flash calculations, and second, using three methods, Bisection, LMA (Levenberg–Marquardt Algorithm), and TRQN (Trust-Region Quasi-Newton method), to increase the convergence speed of the defined objective function. Therefore, the advantages of the approach proposed in this article over the Cisomandi et al. approach include providing reliable initial guesses of the k-value, as well as increasing the convergence speed and reducing computational costs. The results obtained also confirm the improved performance of the

approach proposed in this article, which will be examined and evaluated in detail in the rest of the article.

The general structure of the article is as follows: In the second section, the collected phase equilibrium equations as well as the definition of the objective function are presented. Also, three methods, Bisection, LMA, and TRQN, are expressed in order to solve the objective function in the form of a combined algorithm with phase equilibrium calculations. In the third section, the results of the proposed approach for VT-Flash are compared with the experimental results of two fluid samples (live oil and gas condensate). A cross-validation is also carried out between the results of the proposed approach and the results obtained from VT-Flash based Helmholtz free energy minimization. In the fourth section, various calculations and analyses are performed to investigate and prove the desired performance of the introduced approach for the two fluids used in this article, and the results and discussion are presented. Finally, in the fifth section, there is a general conclusion from the studies conducted in this article.

2. Model Specification

2.1.PT Flash Calculation

According to Michelsen (1982) [2], if two phases of liquid and vapor are in the thermodynamic equilibrium, the fugacity of each component in two phases must be equal to each other, so, he write this equilibrium as:

$$\ln(K_i) + \ln(\Phi_i^V) - \ln(\Phi_i^L) = 0 \quad , \quad i = 1,2,3,...,nc \tag{1}$$

where, K_i is the equilibrium ratio (k-value) for ith component, Φ_i^V and Φ_i^L are the fugacity coefficient of ith component in vapor and liquid phases, respectively, and nc is the number of

components in the feed. By writing the overall material balance for the feed, the classical Rashford-Rice equation [26] is obtained:

$$\sum_{i=1}^{nc} \frac{z_i (K_i - 1)}{1 - \beta \left(1 + K_i\right)} = 0 \tag{2}$$

where, z_i is the overall mole fraction for each component, and β is the gas phase mole fraction. The mole fraction of each component in two phases also can be calculated as:

$$y_i = \frac{z_i K_i}{1 - \beta(1 - K_i)} \tag{3}$$

$$x_i = \frac{z_i}{1 - \beta(1 - K_i)} \tag{4}$$

The Eqs. (1) and (2) must be solved in a nested loop, with Eq. (1) being solved in the outer loop and Eq. (2) in the inner loop. Eq. (2) is solved for gas mole fraction, β, using a numerical method, such as bisection or Newton-Raphson method. In the outer loop, a nonlinear system of equations consisting of nc equations for each component must be solved for updating k-values in each iteration. For this purpose, the Quasi-Newton successive substitution (QNSS) method is used to increase convergence speed [27]. The QNSS method for calculating the Eq. (1) using is given in Appendix A. To start the nested loop, an initial guess is needed for the gas mole fraction (if using open numerical methods) and the equilibrium ratios of the fluid components. The mole fraction of gas is usually taken to be 0.5. But for an initial guess of equilibrium ratios, using Wilson's equation is not sufficient [28]. For this purpose, fluid stability analysis (STA) is used before performing PT-flash calculations [3, 29]. STA helps to both determine the need for fluid splitting using PT-flash calculations and, if an unstable (two-phase) fluid is detected, the calculated values for equilibrium

ratios can be used as a good initial guess in flash calculations. For this purpose, the initial fluid composition is considered as the feed and a trial composition as the second phase, and Eq. (1) is rewritten as:

$$\ln(X_i)+\ln(z_i)+\ln(\Phi_i^X)-\ln(\Phi_i^z)=0 \quad , \quad i=1,2,3,...,nc \tag{5}$$

where, X_i is the trial phase composition, Φ_i^X and Φ_i^z are the fugacity coefficient of trial and feed composition, respectively. The trial phase also is calculated as:

$$X_i = z_i K_i \tag{6}$$

To ensure stability analysis, various values of equilibrium ratios are considered as initial guesses, which are [25, 30]:

$$K_i = \left\{ \frac{1}{K_i^{Wilson}}, K_i^{Wilson}, \frac{1}{\sqrt[3]{K_i^{Wilson}}}, \sqrt[3]{K_i^{Wilson}}, K_i^{pure-j} \right\}, \quad i=1,2,3,...,nc \tag{7}$$

The Wilson's equation for calculating the ideal k-factor is:

$$K_i^{Wilson} = \frac{P_{c,i}}{P}\exp\left[5.3711(1+\omega_i)\left(1-\frac{T_{c,i}}{T}\right)\right] \quad , \quad i=1,2,3,...,nc \tag{8}$$

where, $P_{c,i}, T_{c,i}, \omega_i$ are the critical pressure, critical temperature, and acentric factor of *i*th component, respectively. The pure k-factor also can be determined as:

$$K_j^{pure-j} = \frac{0.9}{z_i} and K_{i\neq j}^{pure-j} = \frac{0.1}{(nc-1)z_i} \quad , \quad i=1,2,3,...,nc \tag{9}$$

For assessing the stability of the fluid, the tangent plane distance (TPD) is calculated as:

$$TPD = -\ln\left[\sum_{i=1}^{nc} X_i^k\right] \tag{10}$$

If the calculated *TPD* is larger than or equal to -1×10^{-8} [31], the feed is temporarily stable, and the set of k-values must be analyzed. Otherwise, it is deemed as unstable and no more k-value is need for surveying. It should be noted that in this study, the Peng-Robinson (PR-78) equation of state [32] has been used for phase equilibrium calculations.

2.2. VT-Flash Algorithms based on PT-Flash

The main purpose of this section is to develop a simple model based on the PT flash calculation. According to Michelsen [5], the PT flash is based on the free Gibbs energy minimization. On the other hand, the VT-flash can be performed by minimizing free Helmholtz energy. For this goal, a system with Nc component mixture has been considered with the specified temperature (T^*) and specified molar volume (v^*), So, the pressure of the system can be expressed as:

$$P = P\left(T^*, v^*, \hat{z}\right) \tag{11}$$

where, $\hat{z}$ is the mole fraction vector of each component. If the trial pressure is known for the system, the trial molar volume of the system at specified temperature and trial pressure can be given by:

$$v_{trial} = v\left(P_{trial}, T^*, \hat{z}, \hat{\beta}_{\alpha-1}\right) \tag{12}$$

In Eq. (12), because the system can be multiple phases, the trial molar volume is a function of molar fraction of each existing phase. If the system has α phases, $\hat{\beta}$ is the mole fraction vector of $\alpha-1$ phases. It is obvious that if the trial pressure is equal to the actual pressure, the trial volume

can be approached to the specified volume. According to this fact, an objective function can be formed as:

$$F(P) = v\left(P_{trial}, T^*, \hat{z}, \hat{\beta}_{\alpha-1}\right) - v^* \tag{13}$$

For obtaining the root of the objective function in Eq. (13), PT flash calculation in trial pressure and specified temperature can be implemented in an efficient iterative calculation. To examine the variation range of the defined objective function, Fluid#1 was considered (its composition is presented in Table 1.), and the values of the objective function were calculated at different volumes and temperature ranges, as shown in Figure 1. The results of this graph show that the objective function is continuous over the entire pressure range and at different molar volumes and just has one root; therefore, its root can be determined using numerical mathematical methods.

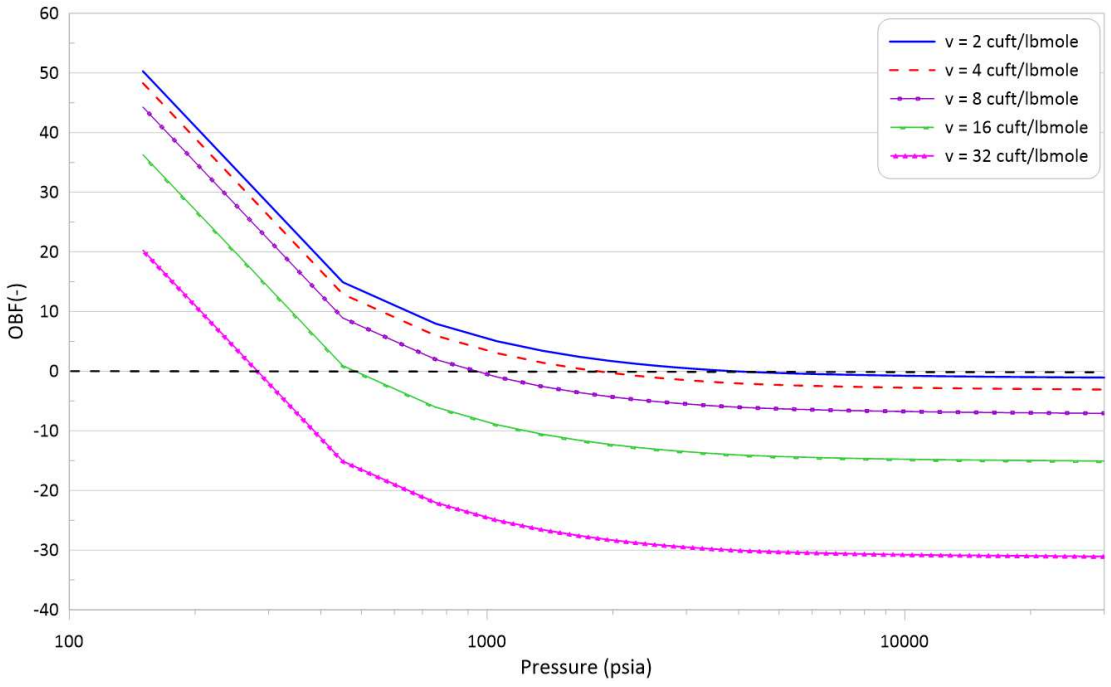


Figure 1: Variation of the objective function with pressure for different molar volumes, illustrating that their roots coincide (a unique root) within the interval, for the synthetic gas condensate from Gozalpour et al. (2003) [33].

To calculate the root of the objective function, the bracket or open method can be used [34]. In this study, three numerical methods were used, which will be explained below.

2.2.1. Bisection method

In solving the objective function using the bisection method, it should be noted that at a given temperature and molar volume, the pressure value must be within a specific range for operational purposes. Therefore, a pressure interval can be selected that is also operationally meaningful and Eq. (13) will be solved using the bisection method. The bisection method is reliable and always converges to a root, does not require derivative of the objective function, and has predictable calculation costs. But on the other hand, it always needs an operational pressure interval for convergence. The flowchart of the implemented bisection method in this study has been shown in Figure 2. In order to increase the convergence speed of the bisection method, the calculation of the average of the beginning and end of the pressure interval is performed by weighted averaging:

$$\bar{P} = avg(P_{\min}, P_{\max}) = \frac{1}{P_{\max} - P_{\min}} \left[\left| F(P_{\min}) \right| P_{\min} + \left| F(P_{\max}) \right| P_{\max} \right] \tag{14}$$

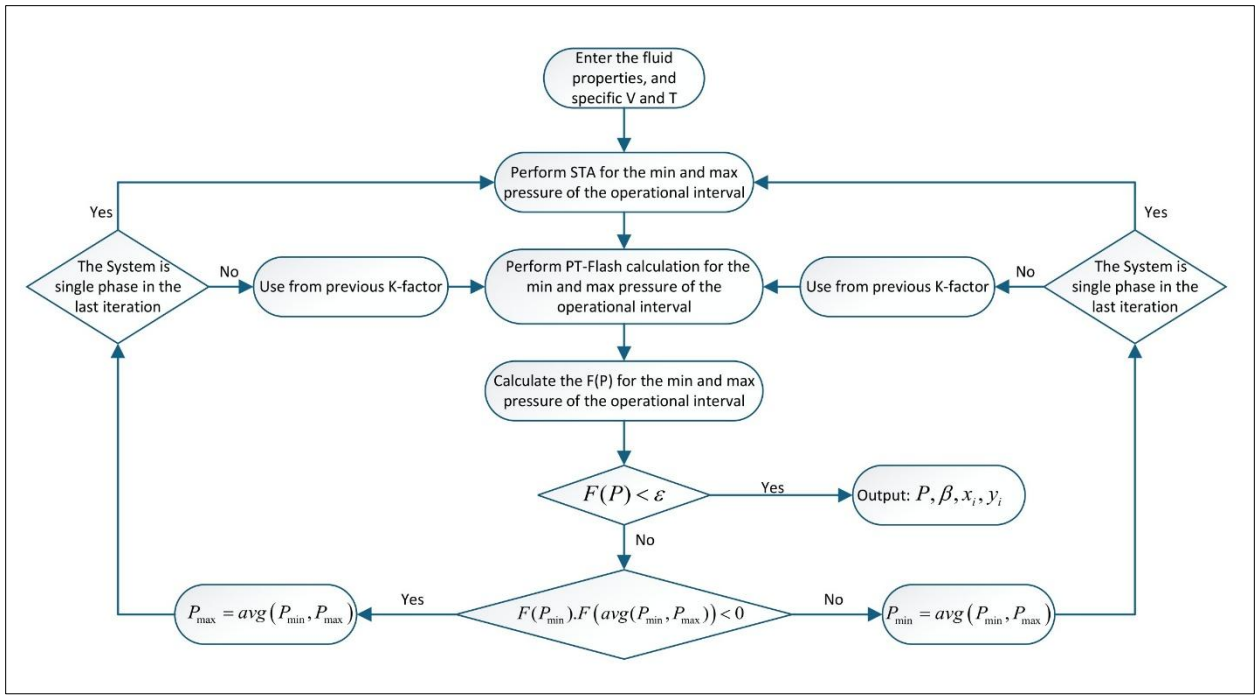


Figure 2: Flowchart for performing PT based VT-Flash, using the bisection method.

2.2.2. Levenberg–Marquardt Algorithm (LMA)

The Levenberg-Marquardt algorithm (LMA) [35, 36] was employed for minimization. This iterative algorithm solves nonlinear least-squares problems by adaptively blending the Gauss–Newton update (which ensures fast convergence near a minimum) with a steepest-descent direction (which guarantees progress when far from the solution). In this study, the LMA has been implemented for obtaining the root of the objective function. The algorithm begins by reading fluid properties (composition and other needed properties), the specified molar volume, v^*, and temperature, T^*. An initial pressure, $P_{initial}$, is estimated using the ideal gas equation of state:

$$P_{initial} = \frac{RT^*}{v^*} \tag{15}$$

The damping parameter, λ, also is initialized to 1.0. A stability analysis is performed at initial pressure to determine whether the system is single-phase or multiphase. If the previous iteration (if any) indicated a single-phase state, the algorithm attempts to reuse the K-factors from the prior calculation to accelerate convergence; otherwise, a full PT-flash calculation is carried out at the initial pressure. From the PT-flash results, the objective function, $F(P)$, is evaluated. If the absolute value of objective function is less than an acceptable tolerance, convergence is achieved, and the algorithm outputs the current pressure, gas mole fraction, and phase compositions. If convergence is not met, a pressure correction step is computed:

$$dP = -\frac{F(P_{initial}).F'(P_{initial})}{\left[F'(P_{initial})\right]^2 + \lambda} \tag{16}$$

The derivative of the objective function is estimated numerically as backward approach. dP is a modified Newton step where λ acts as a Levenberg–Marquardt damping factor to prevent large, unstable updates when the derivative is small or the residual is noisy. The new pressure can be calculated as:

$$P_{new} = P_{initial} + dP \tag{17}$$

To adjust λ for the next iteration, the algorithm compares the actual reduction in the squared residual:

$$\Delta S_{actual} = F^2(P_{initial}) - F^2(P_{new}) \tag{18}$$

with the predicted reduction:

$$\Delta S_{pred} = dP\left[dP\lambda - F(P_{initial}).F'(P_{initial})\right] \tag{19}$$

If the predicted reduction is less than or equal to zero, the step prediction is invalid, and the efficiency factor is set to zero. Otherwise:

$$\eta = \frac{\Delta S_{actual}}{\Delta S_{pred}} \tag{20}$$

If efficiency factor, η, is less than or equal to zero, the step cannot be considered successful and λ must be updated as $\lambda_{new} = \lambda.\eta$, and the modified Newton step should be calculated again. On the other hand, the initial pressure can be updated, and also the new damping parameter is calculated as:

$$\lambda_{new} = \lambda.\max\left[\frac{1}{\tau}, 1-\left(2\eta-1\right)^3\right] \tag{21}$$

where τ is a safety factor (typically >1) and constant, ensuring damping parameter does not drop too quickly. This iterative calculation must be performed until the acceptable convergence. The flowchart summary of the used LMA in this study is presented in Figure 3. The advantages of the LMA method include not requiring a confidence interval for convergence and using an ideal initial guess to start the calculations. But on the other hand, the need to calculate the derivative using numerical methods can increase the cost of the solution.

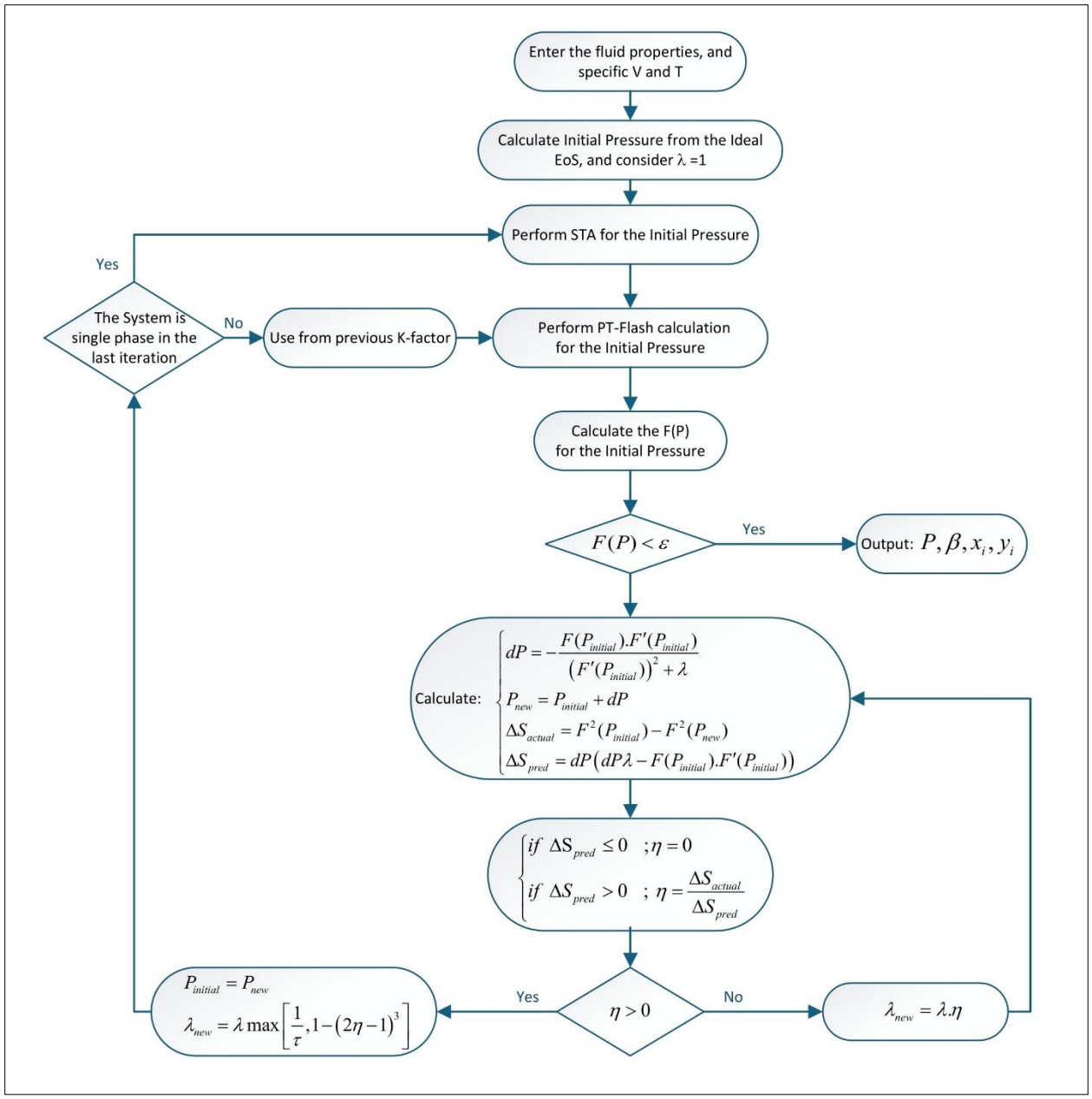


Figure 3: Flowchart for performing PT based VT-Flash, using the LMA.

2.2.3. Trust-Region Quasi-Newton method (TRQN)

Although the LMA is faster than the bisection method, it can lead to a decrease in the desired convergence speed due to the need to calculate the derivative of the objective function. For this

purpose, the use of a Quasi-Newton, with a trust region [37], called in this study as TRQN method, is recommended because it does not require calculating the derivative of the objective function. In this method, after initialization, like the LMA, an initial pressure $P_{initial,1}$ is also computed from the ideal gas equation of state, and the damping parameter λ is set to 1.0. A stability analysis is performed for both pressure points. If the system was single-phase in the previous iteration, K-factors from the prior step are reused; otherwise, a full PT-flash calculation is carried out at each pressure. The objective function is evaluated for both points. If the objective function is less than a specific tolerance, the current pressure is the answer. In this method, a second pressure point is calculated as:

$$P_{initial,2} = P_{initial,1} + dP_{initial}.P_{initial,1} \tag{22}$$

where $dP_{initial}$ is a small relative pressure step. By calculating the objective function for both initial pressure, and comparison between them, yields:

$$\begin{cases} if \left|F(P_{initial,1})\right| < \left|F(P_{initial,2})\right|, & P = P_{initial,1}, G = F(P_{initial,1}), P_{prev} = P_{initial,2}, G_{prev} = F(P_{initial,2}) \\ f \left|F(P_{initial,1})\right| \geq \left|F(P_{initial,2})\right|, & P = P_{initial,2}, G = F(P_{initial,2}), P_{prev} = P_{initial,1}, G_{prev} = F(P_{initial,1}) \end{cases} \tag{23}$$

This ensures that the direction is always based on the point with the smaller residual. A finite-difference slope is calculated:

$$s = \frac{G - G_{prev}}{P - P_{prev}} \tag{24}$$

Therefore, the new pressure is obtained using an LMA-like formula:

$$P_{new} = P - \frac{Gs}{s^2 + \lambda} \tag{25}$$

When λ is small, this approximates a Newton step using the slope, when λ is large, the step is damped, enhancing stability. The predicted reduction in the squared residual is computed as:

$$\pi = \frac{G^2 s^2}{s^2 + \lambda} - \frac{1}{2} \frac{G^2 s^4}{\left(s^2 + \lambda\right)^2} \tag{26}$$

Then, if parameter π is less than or equal to zero, the ϑ is considered as zero, otherwise:

$$\vartheta = \frac{F^2(P) - F^2(P_{new})}{2\pi} \tag{27}$$

If the square value of objective function of new calculated pressure is larger than the objective function of the last pressure, the predicted reduction must be calculated again by updating the damping parameter, equal to $\min\left(4\lambda, \lambda_{\max}\right)$, if not, the values of P, P_{prev}, G and G_{prev} is updating by considering new pressure calculation. For the next iteration calculation, ϑ control the damping parameter as:

$$\lambda_{new} = \begin{cases} \max\left(\lambda / 3, \lambda_{\min}\right) & \vartheta > 0.75 \\ \lambda & 0.25 < \vartheta < 0.75 \\ \min\left(2\lambda, \lambda_{\max}\right) & \vartheta < 0.25 \end{cases} \tag{28}$$

This iterative calculation must be performed until the acceptable convergence. The flowchart summary of the used TRQN in this study is presented in Figure 4.

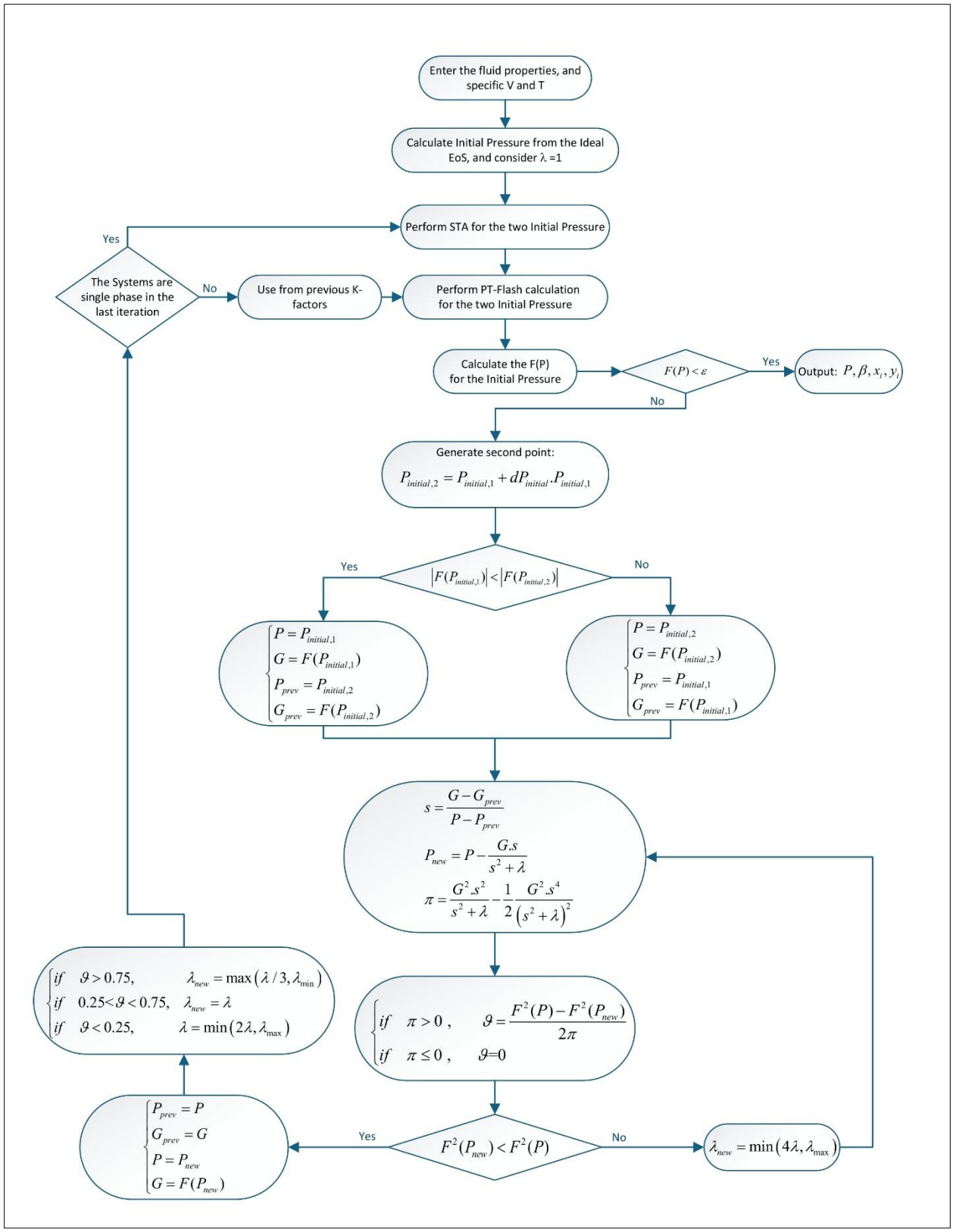


Figure 4: Flowchart for performing PT based VT-Flash, using the TRQN.

3. Verification and Cross-validation

In this section, the results of the three proposed methods are compared with both experimental data and the results of Michelson's proposed method. It should be noted that the results of all three proposed methods are the same and differ only in the number of iterations and the elapsed time.

At first, to verify the accuracy of the proposed VT-Flash algorithm's calculation, its results were first compared with laboratory data. Two sets of laboratory data were collected from previous studies, corresponding to the Fluid#1 and the Fluid#2. The selected laboratory data for Fluid#1[33] and Fluid#2 [38] are constant composition expansion (CCE) test data in both single-phase and two-phase conditions for a synthetic gas condensate and a live oil, respectively, and thus, the accuracy of the results has been examined in both phases. The data from these experiments include the pressure and total volume of the fluid at constant temperature. In order to perform the simulation, first, the amount moles of oil under test were measured and based on that, the molar volume of each point was determined. Therefore, in the experiment data, the temperature and calculated molar volumes are considered as inputs to the VT-Flash algorithm. The calculation output, which is pressure, is compared with the experimental pressure at each stage. For Fluid#1 and Fluid#2, this comparison has been presented in Figure 5 and Figure 6, respectively. According to these figures, it can be seen that the VT-Fash results are in very good agreement with the relevant laboratory data, and their R-squire is calculated to be about 0.926 and 0.983 for Fluid#1 and Fluid#2, respectively.

Second, Also, the results of the VT-Flash algorithm presented in this article (based on PT-flash) have been compared with the VT-Flash results presented by Michelson [5] (based on Helmholtz free energy minimization). For performing this cross-validation, at a constant molar-volume,

pressure of the system has been calculated at 100 random temperatures. The pressure results have been normalized using the following formula:

$$P_{normalized} = \frac{P - P_{\min}}{P_{\max} - P_{\min}} \tag{29}$$

The results of this cross-validation for both fluids are presented in Figure 7, which shows that a very high agreement (with R^2=0.99999 and R^2=0.99999 for Fluid#1 and Fluid#2, respectively) is observed between the two flash calculation approaches. So, it can be deduced that the introduced PT-based VT-Flash can obtain reliable results, like the VT-Flash based on the Helmholtz free energy optimization.

According to the validation with experimental data and cross-validation performed with the Michelson method, the results obtained from the three methods proposed in this article can be considered valid.

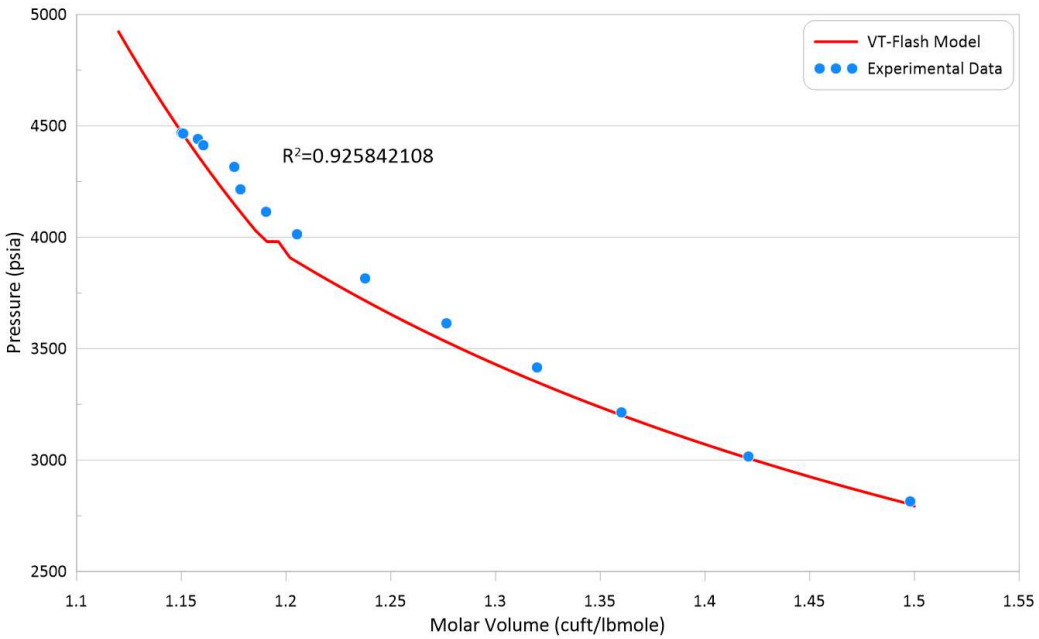


Figure 5: Comparison of VT-Flash results with CCE test laboratory data of the Fluid#1, a synthetic gas condensate in the experimental study by Gozalpour et al. (2003) [33].

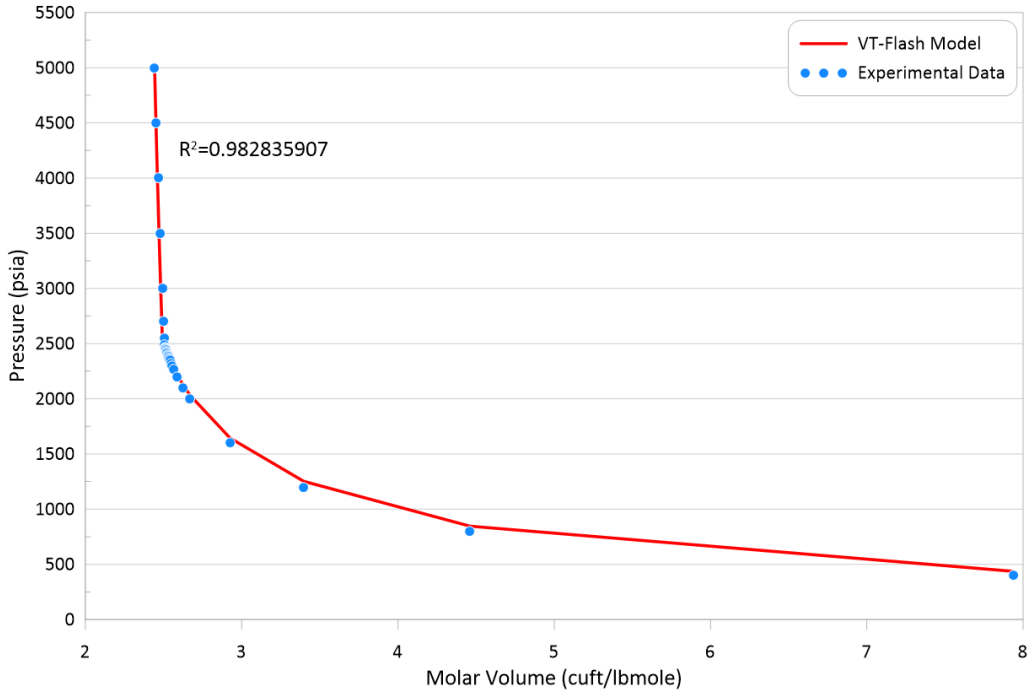


Figure 6: Comparison of VT-Flash results with CCE test laboratory data of the Fluid#2, a live oil sample in the experimental study by Safaei et al. (2023) [38].

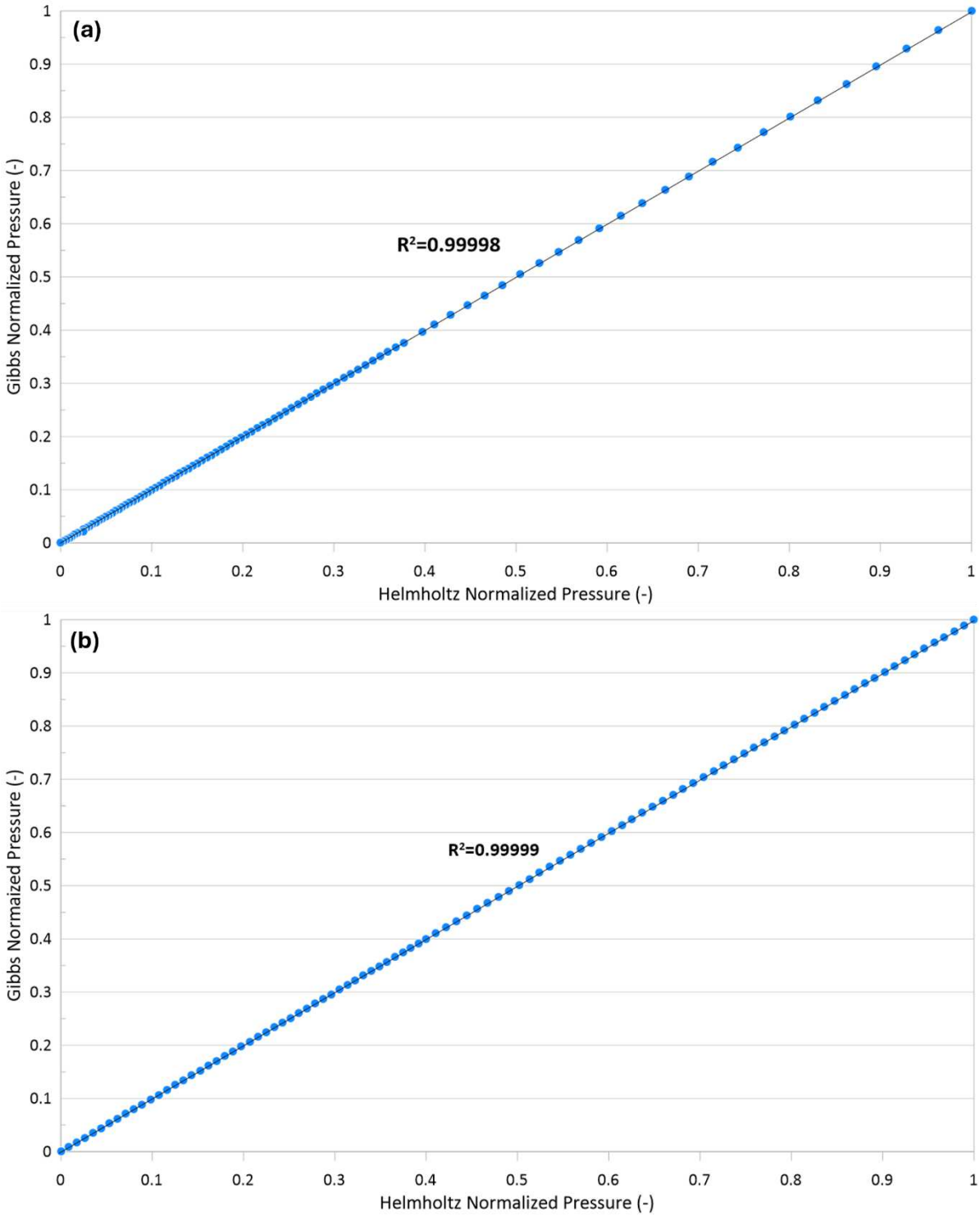


Figure 7: Cross-validation between the results from PT based VT-Flash (Gibbs normalized pressure) and the VT-Flash based on the Helmholtz free energy minimization (Helmholtz

normalized pressure) introduced by Michelsen [5], a) cross validation for Fluid#1, and b) cross validation for Fluid#2.

4. Results and Discussion

In the third section, the results of the proposed approach in this paper were cross-validated with experimental results and also with VT-Flash results based on Helmholtz free energy minimization, which shows acceptable agreement. In this section, the performance of the introduced approach will be investigated for the two fluids introduced in Table 1. The results of all three proposed methods are equal to each other with respect to the tolerance defined for convergence and differ only in the computational cost. Computational cost is divided into two parts: the number of iterations and the elapsed time of the calculations. To examine the number of iterations, the three methods proposed in this paper are compared with each other and also with the method presented by Cismandi et al. [1], as can be seen in Figure 8. This figure shows the number of iterations in term of temperature for all methods, for 1.6 cuft/lbmole isochore. Overall, the results show that the number of iterations in the three proposed methods is much less than the approach proposed by Cisomandi et al. Also, in the Cisomandi et al. approach, the number of calculations increases with increasing temperature. However, in the three methods proposed, the number of iterations remains almost constant within the temperature range. In addition, the number of iterations was the least for the Bisection method and the most for the TRQN method, although the number of iterations in the Bisection and LMA methods were approximately in the same range. For qualitative comparison of the number of iterations, their averages in the specified temperature range (from 100 points) are presented in Table 2. In this table, the average elapsed time is also presented for

the four methods. It can be seen that the elapsed time for the three methods proposed in this article is significantly reduced compared to the Cisomandi et al. approach. On the other hand, it can be seen that the TRQN method, despite the higher number of iterations, takes less elapsed time than the LMA method. This means that the calculations in each loop are more optimized and each loop is performed in a shorter time interval. However, the Bisection method requires less iterations and elapsed time than both methods in this case. In general, it can be concluded that all three methods proposed in this article have significantly reduced the number of iterations and elapsed time compared to the Cisomandi et al. approach.

Table 1: The composition of used fluids in this study.

Components	Mole %	
	Fluid#1 [33]	Fluid#2 [38]
CO_2	/	0.1504
N_2	/	0.1273
C1	82.20	33.8984
C2	/	8.4226
C3	8.80	8.6910
i-C4	/	1.9773
n-C4	/	2.8119
i-C5	/	0.9752
n-C5	5.00	1.1580
C6	/	1.7783
C7	/	2.1529
C8	/	4.3934

C9	/	2.2126
C10	2.00	1.5804
C11	/	1.0410
C16	2.00	/
C12+	/	28.6284
		C12+ properties: Molecular Weight: 370 g/mol Specific Gravity: 0.948

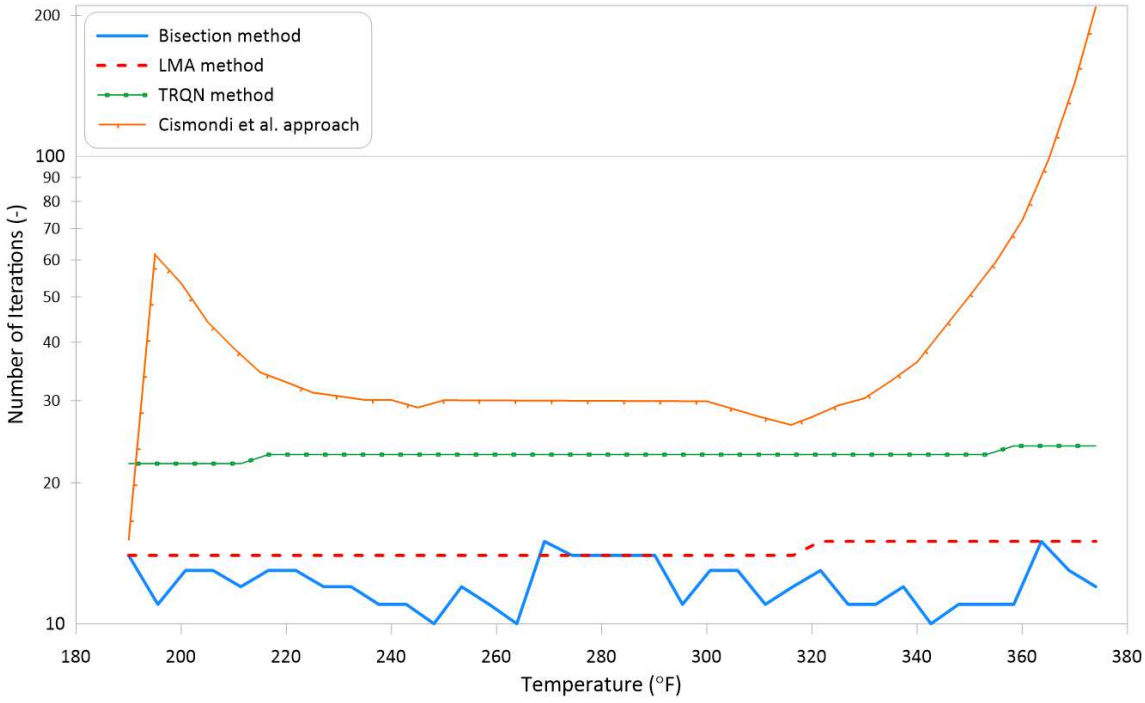


Figure 8: Comparison between the three proposed methods with each other and also with the method presented by Cismondi et al. [1] from the point of view of the number of iterations at different temperatures.

Table 2: Comparison of both number of iterations and elapsed time of all methods for 1.6 cuft/lbmole isochore and the temperature range of 190-375 °F, for Fluid#1.

Methods	**Average number of iterations (-)**	**Average Elapsed time (sec)**
Cismondi et al.	44	1.2891
Bisection	13	0.1018
LMA	14	0.2938
TRQN	23	0.1686

In order to investigate the sensitivity analysis of the computational cost with molar volume, the number of iterations as well as the elapsed time for Fluid#1 at a temperature of 300 °F were calculated in terms of molar volume, as shown in Figure 9. It is observed that with increasing molar volume, both the number of iterations and the elapsed time have a decreasing trend. This is while both parameters have almost the same trend with temperature and do not change noticeably. Such behavior has also been observed for other fluids.

By comparing the performance of the three proposed methods, it can be said that the convergence speed and computational cost for the Bisection method are lower than the other two methods. But, to begin, it requires defining an operating pressure range. While the two LMA and TRQN methods, although slower than the bisection method, do not require defining the operating pressure range and calculating the initial guess using the ideal gas equation of state. In fact, by defining the two aforementioned methods, the dependence of the PT based VT-Flash on the definition of the

operating pressure range has been eliminated. Finally, the advantages and disadvantages of PT based VT-Flash calculation approaches are summarized in Table 3.

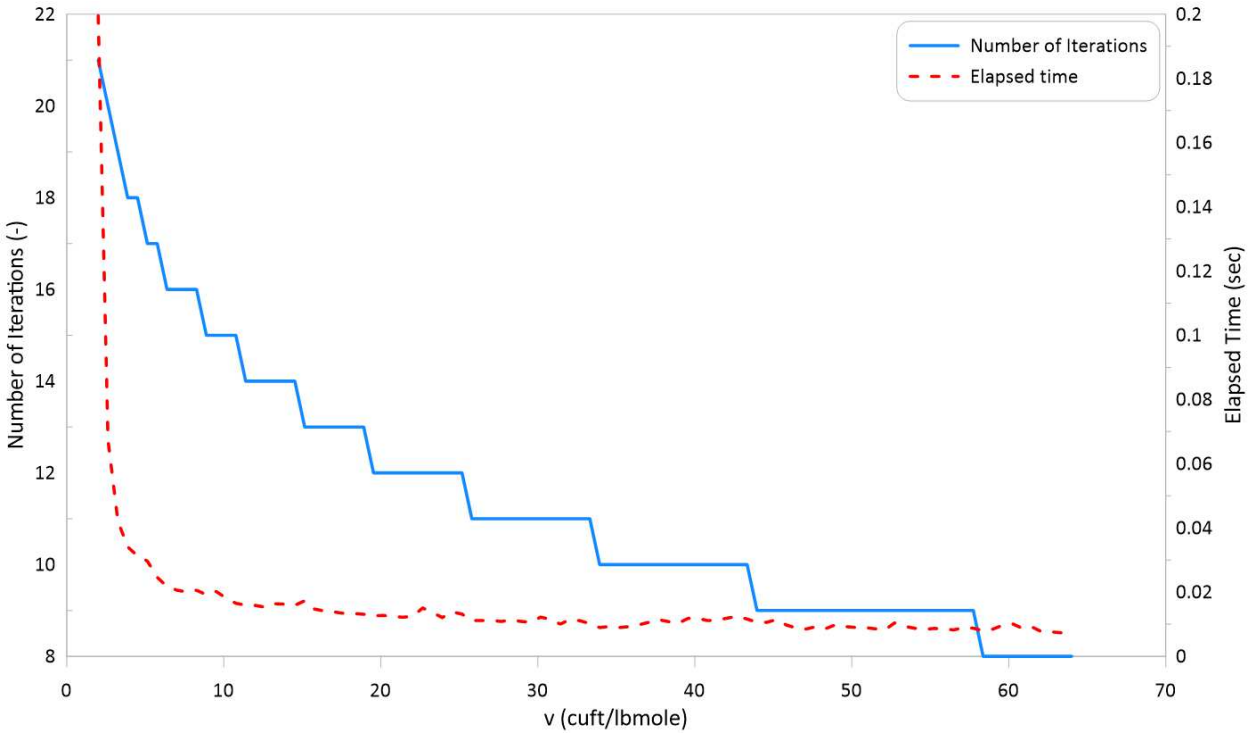


Figure 9: Sensitivity analysis of the number of iterations and elapsed time in term of molar volume.

Table 3: A summary of the advantages and disadvantages of the three methods proposed.

Proposed Methods	**Advantage**	**Disadvantage**
Bisection method	- Simplicity - No need to calculate the derivative of functions - Predictable computing costs	- Need to define the operational pressure range

	- Optimal convergence speed at high temperatures	
LMA method	- No need to define the operational pressure range - Optimal convergence speed at high temperatures - Calculating an initial guess with the ideal gas equation	- Need to calculate the derivative of functions numerically - Slower speed compared to the bisection method
TRQN method	- No need to define the operational pressure range - Need to calculate the derivative of functions numerically - Calculating an initial guess with the ideal gas equation	- Slower speed compared to the bisection method

In Figure 10, seven isochores are plotted along with the phase envelope (which has been constructed using the Michelsen's algorithm [39]) for Fluid#1. The construction of the isochore lines is performed without any prior assessment of the feed phase stability (i.e., whether it resides in a single-phase or two-phase region). The smooth, continuous nature of these paths across the phase envelope demonstrates that the proposed framework autonomously and reliably executes VT-flash calculations, seamlessly transitioning between thermodynamic states without relying on priori stability information. From the point of view of fluid physics, at constant volume, the pressure of fluid increases with increasing temperature, which is clearly seen in Figure 10. On the

other hand, at high molar volumes, the slope of isochores is much lower than at their small values. This is due to the very small distance between fluid molecules in smaller molar volumes, which causes a greater increase in pressure due to temperature. Also, obviously, as the temperature increases, the mole gas mole fraction must also increase, for which purpose, the graph of gas mole fraction versus temperature is plotted in Figure 11. In this figure, for 1.5 cuft/lbmole isochore, the gas mole fraction variation is much greater than for other isochores. Because for the minimum isochore, the high pressure-temperature slope causes the isochore line to have a more vertical intersection with the quality lines of the two-phase region. Another notable point observed in Figure 11 is that the 8 cuft/lbmole isochore line reaches a value of 1 at a higher temperature than the other isocurves. This issue is justified according to Figure 10, which shows that 8 cuft/lbmole isochore enters the single-phase region at higher temperatures than other isocurves.

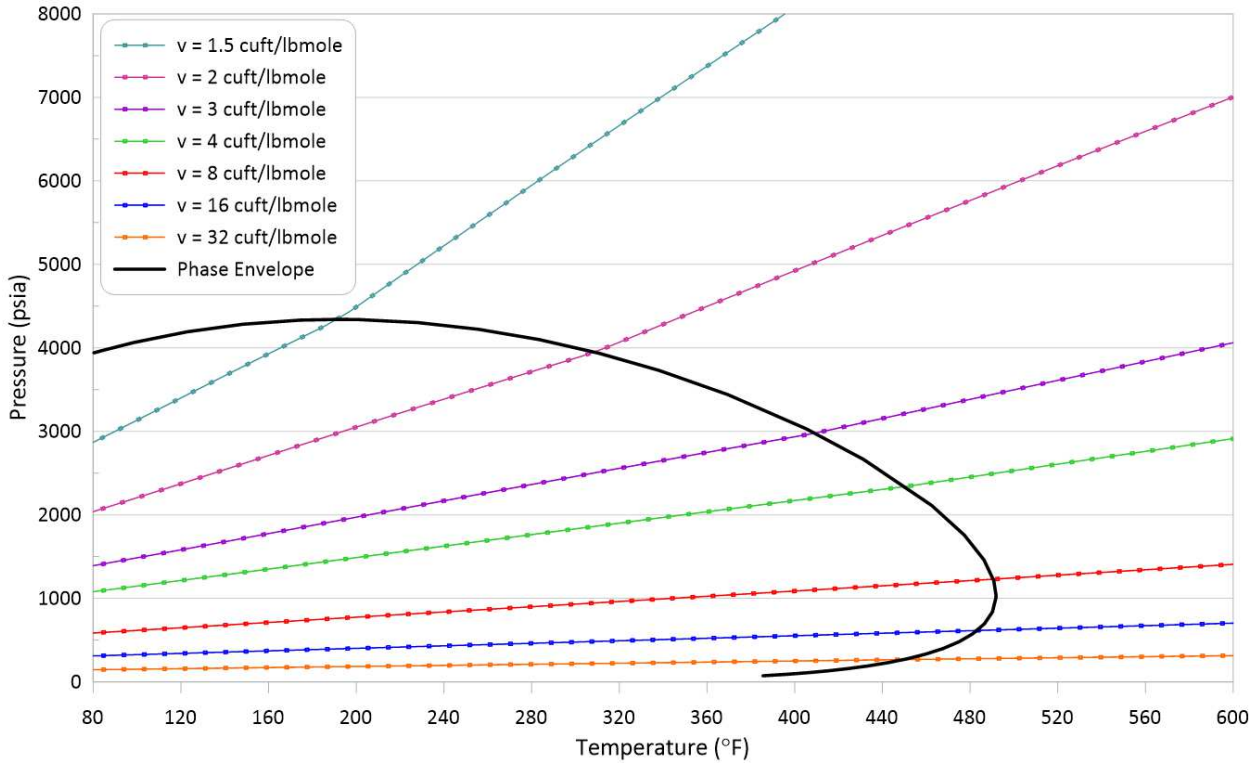


Figure 10: Pressure versus temperature at different isochores for Fluid#1. The diagram of each isochore has been generated using the proposed approach and the phase envelope has been constructed using the Michelson's algorithm [39].

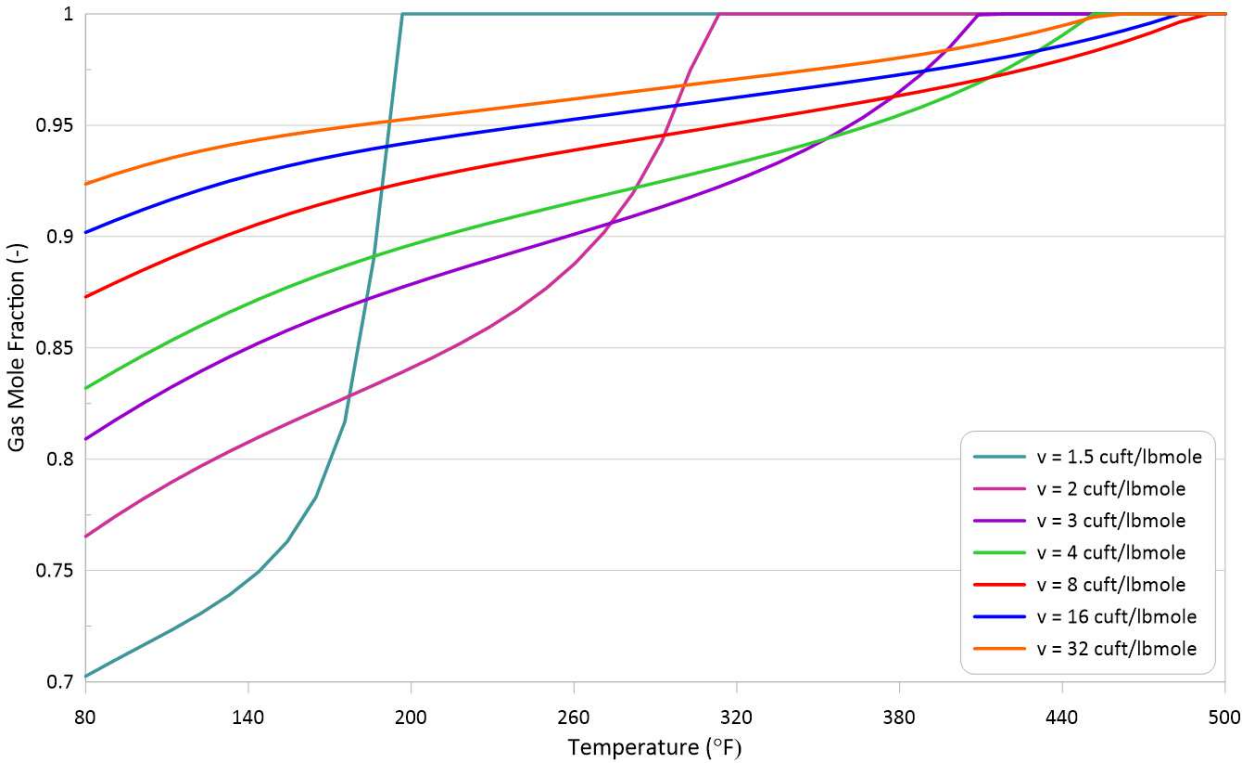


Figure 11: Gas mole fraction in term of temperature at different isochores, for Fluid#1 in the two-phase region.

The gas mole fraction also has a direct relationship with pressure, the graph of which is presented in terms of pressure in Figure 12, for different isochores. This figure shows that smaller molar volume volumes (1.5 cuft/lbmole) require substantially elevated pressures to achieve a given phase transition compared to large specific volumes (32 cuft/lbmole). The progressive shift of the curves toward lower pressures as molar volume increases is quantitatively consistent with the equation of

state, providing further evidence that the PT-based VT-Flash routine correctly enforces the material balance constraints inherent to the volume specification.

It is also possible to simultaneously display pressure at specific molar volume-temperature points in a three-dimensional graph, as presented in Figure 13. The curved surface perfectly depicts the fundamental thermodynamic properties of a real fluid. Notably, it illustrates the asymmetry between liquid and vapor behavior. In the high-temperature, low-volume region, the material exhibits extremely low compressibility. Here, a minor increase in temperature causes a massive, steep rise in pressure, as the molecular thermal agitation is heavily constrained within a small specific volume. On the other hand, at higher molar volumes, the fluid behaves closer to an ideal gas. The pressure gradient with respect to temperature is much milder, as the molecules have abundant free volume to expand into.

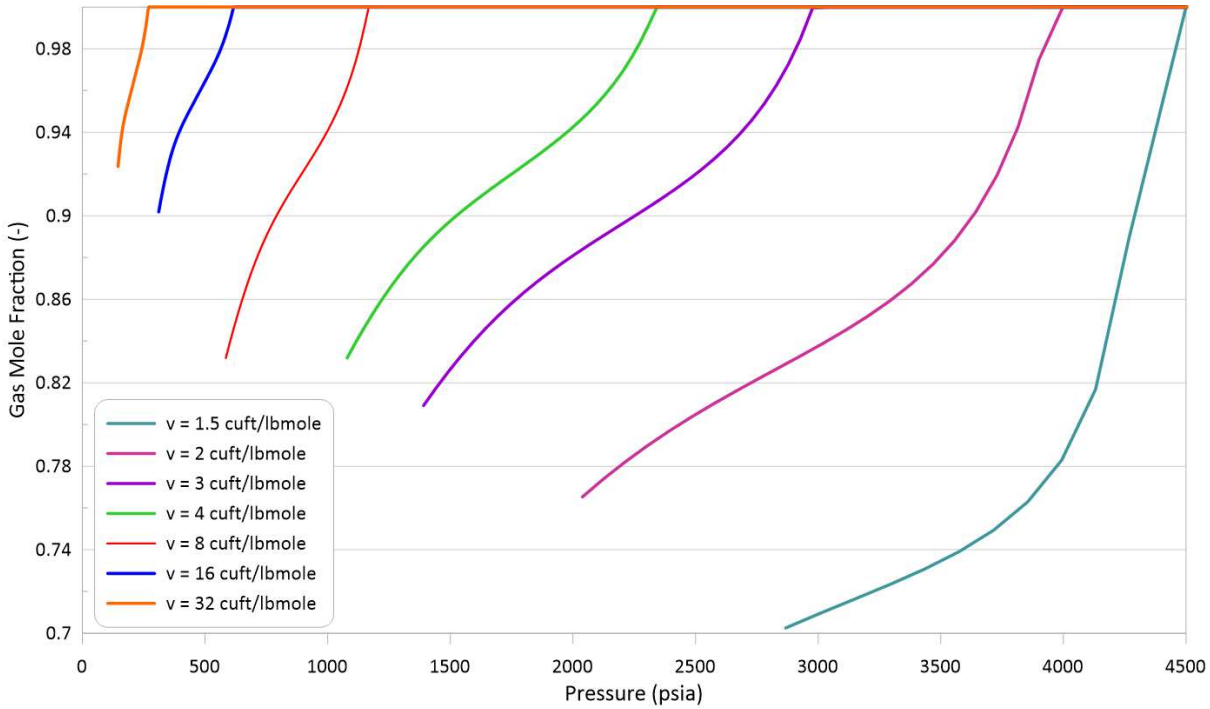


Figure 12: Gas mole fraction in term of pressure at different isochores, for Fluid#1 in the two-phase region.

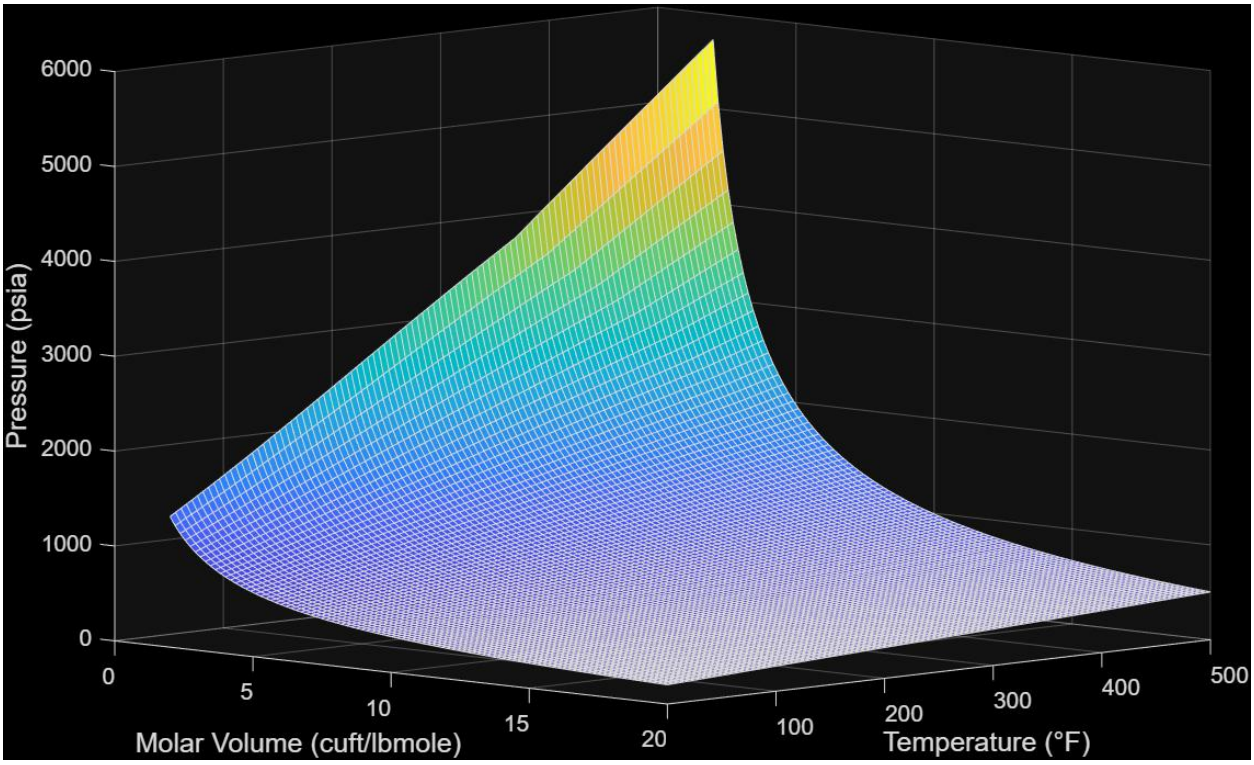


Figure 13: Pressure as a result of VT-Flash in term of specified molar volume-temperature points, for Fluid#1.

Figure 14 shows also a comprehensive 3D visualization of gas mole fraction in term of specified molar volume-temperature for Fluid#1. The 3D plot reveals a distinct depression at low temperatures and low molar volumes. Physically, this corresponds to a dense, liquid-like mixture where the fluid has the lowest gas mole fraction within the investigated domain. As the molar volume increases (reducing the system's density) or as the temperature rises, the gas mole fraction increases monotonically, eventually flattening into a plateau where the system converges to a

single gas phase. This shape is consistent with the equation of state, where proximity to the dense liquid phase suppresses vaporization. According to the explanations given, Figure 13 and Figure 14 are consistent with fluid physics, indicating meaningful results of VT-Flash.

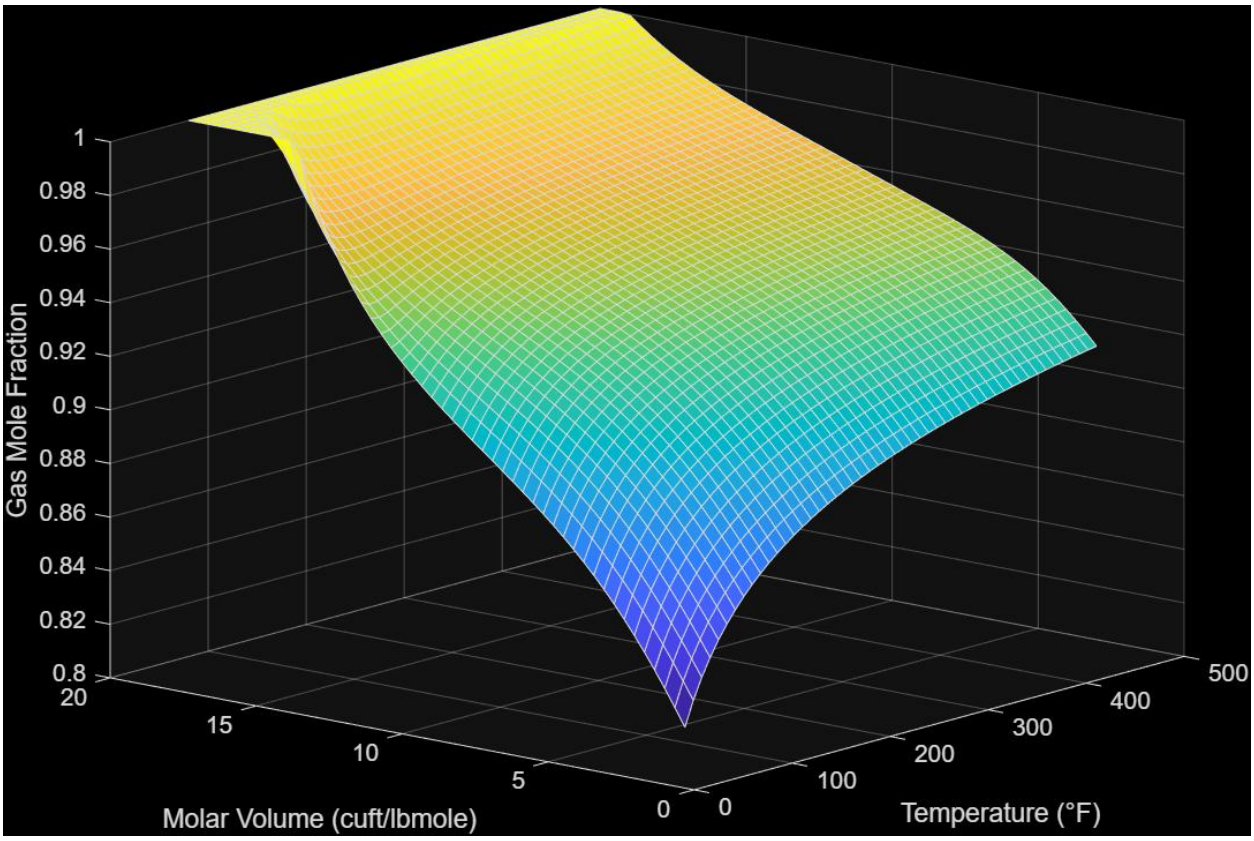


Figure 14: Gas mole fraction as a result of VT-Flash in term of specified molar volume-temperature points, for Fluid#1.

Fluid#1 was a synthetic gas condensate sample that was investigated using the proposed approach in this paper. However, it is necessary to evaluate the proposed method for a live reservoir oil sample as well. In Section 3, the results from PT-based VT-Flash were compared with the experimental data of Fluid#2, and an acceptable agreement was observed. Here, the generation of isochore lines for fluid#2 is also fulfilled using VT-Flash, as seen in Figure 15. In this figure, the

process of pressure-temperature changes of each isochores is similar to the changes of Fluid#1, which is shown in Figure 10. But for the live oil fluid (Fluid#2), it is observed that at the fluid saturation point (phase boundary), a significant change in the isochore slope is observed, which is greater for larger isochores, i.e. v = 3, 4, and 6 cuft/lbmole isochores. Regarding the location of the critical point of the fluid, this is because at the aforementioned molar volumes, considering the constant molar volume, we enter the liquid single-phase region from the two-phase region with increasing temperature and pressure. In the single-phase liquid state, pressure changes with respect to temperature will be more intense than in the two-phase gas-liquid state, where part of the fluid is gas. This is while for isochore 16 cuft/lbmole, at the phase boundary, the two-phase liquid-gas state enters the single-phase gas state, and therefore the change in the slope of the isocurves is negligible.

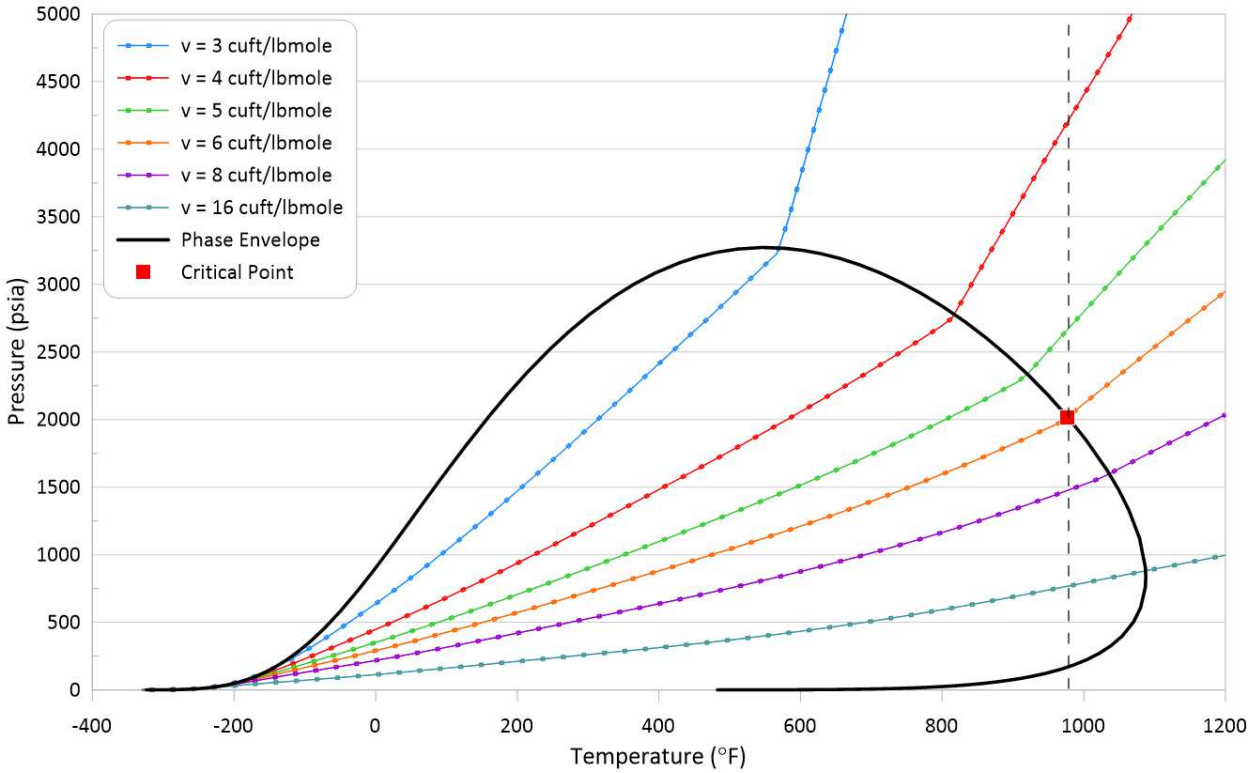


Figure 15: Pressure versus temperature at different isochores for Fluid#2. The diagram of each isochore has been generated using the proposed approach and the phase envelope has been constructed using the Michelson's algorithm [39].

The mole fraction of the gas phase has also been examined for the isochores drawn in Figure 15, as can be seen in Figure 16. It is observed that for small isochores (3,4, and 5 cuft/lbmole), the gas mole fraction first increases and then decreases with increasing temperature. This means that evaporation occurred first and then condensation, which is due to the high slope of the pressure-temperature curve with small isochores, and by intersecting the quality lines in the vertical direction, it shows the retrograde condensation by pressure decreasing. The notable point of small isochores is that in the single-phase liquid region, with increasing temperature, a phase change

occurs suddenly, and the liquid phase turns into gas phase. Because according to Figure 15, it crosses the critical temperature line, which determines the boundary between the liquid and gas phases and the single-phase regions. Although it is better to say that it enters the supercritical region from the liquid phase. On the other hand, for larger isochores (6, 8, and 16 cuft/lbmole), due to the low slope of the pressure-temperature curve, the retrograde processes do not occur and as the temperature increases, the process is always evaporation.

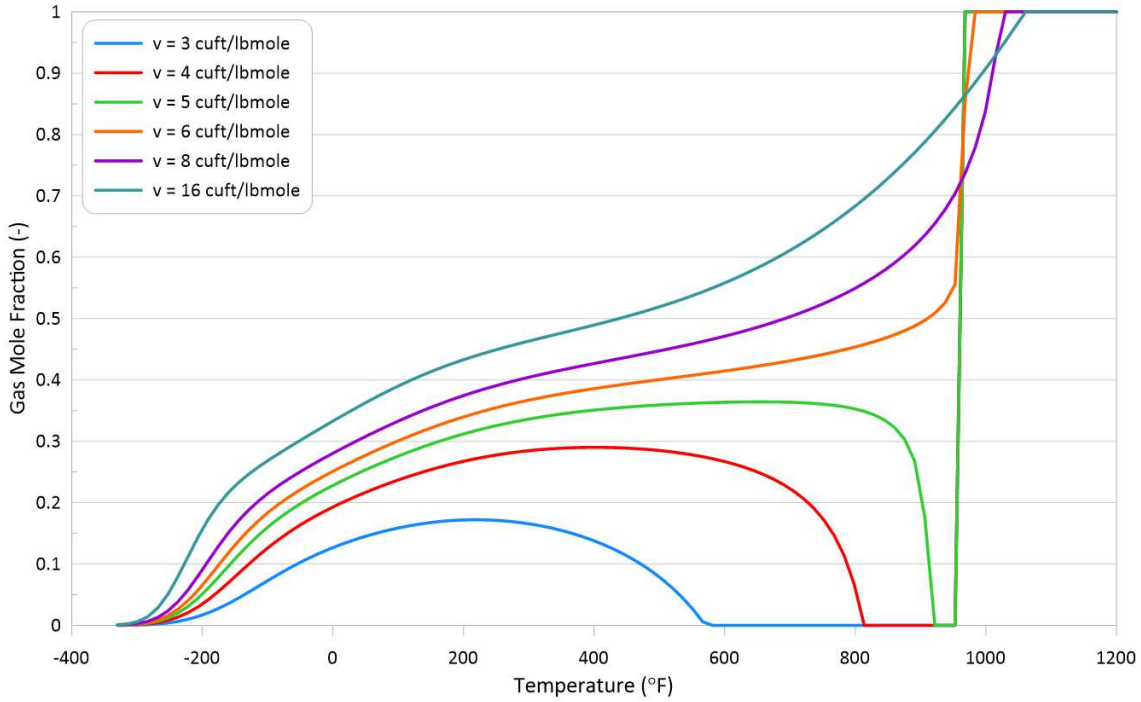


Figure 16: Gas mole fraction in term of temperature at different isochores, for Fluid#2.

To further validate the physical consistency of the proposed VT-Flash algorithm, Figure 17 presents a 3D thermodynamic surface (PVT plot) of the reservoir fluid, mapping pressure as a function of temperature and molar volume across the full operational envelope. As illustrated, the surface shows that at low molar volumes (approximately below 10 cuft/lbmole), the fluid exhibits a steep, near-linear pressure by increasing temperature. Conversely, at higher molar volumes, the

pressure shows the vapor phase behaviors. The smooth and continuous rendering of this figure, devoid of numerical artifacts or discontinuities, confirms that the proposed algorithm robustly handles the underlying non-linear root-finding problems across all combinations of volume, temperature, and pressure, avoiding the singularities that plague conventional flash solvers in these high-gradient transition zones.

Figure 18 shows also a comprehensive 3D visualization of gas mole fraction in term of specified molar volume-temperature for Fluid#2, just in the two-phase region. Unlike the steeply rising PVT curve, this phase-composition surface displays a comparatively smooth topographic gradient, wherein the vapor fraction increases in a continuous, predictable trend as both temperature and molar volume increase. A notable physical feature is the soft curvature at low molar volumes, which illustrates the non-linear effect of temperature on vaporization when the fluid is confined to a dense, high-pressure state; under these constraints, thermal expansion does not translate linearly into vapor generation. The continuity of the 3D graph of gas mole fraction and pressure indicates the reliability of the PT VT-Flash computational algorithm over a range of relevant parameters.

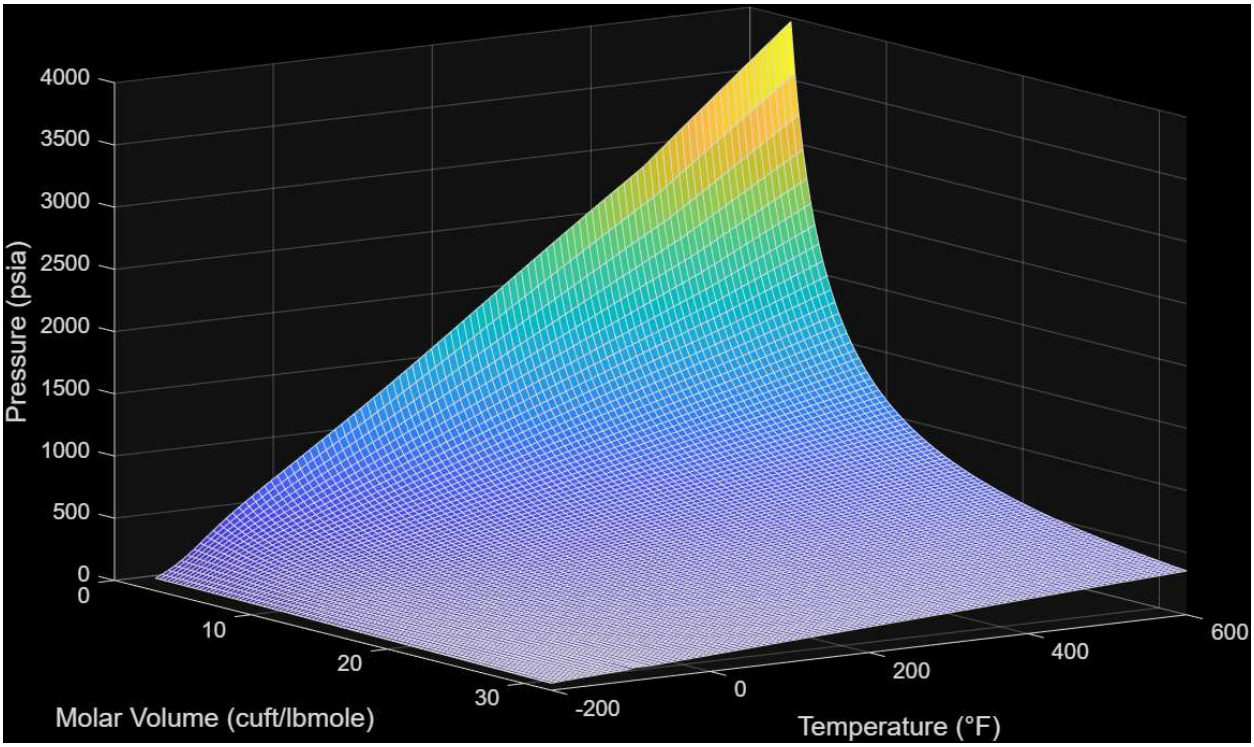


Figure 17: Pressure as a result of VT-Flash in term of specified molar volume-temperature points, for Fluid#2.

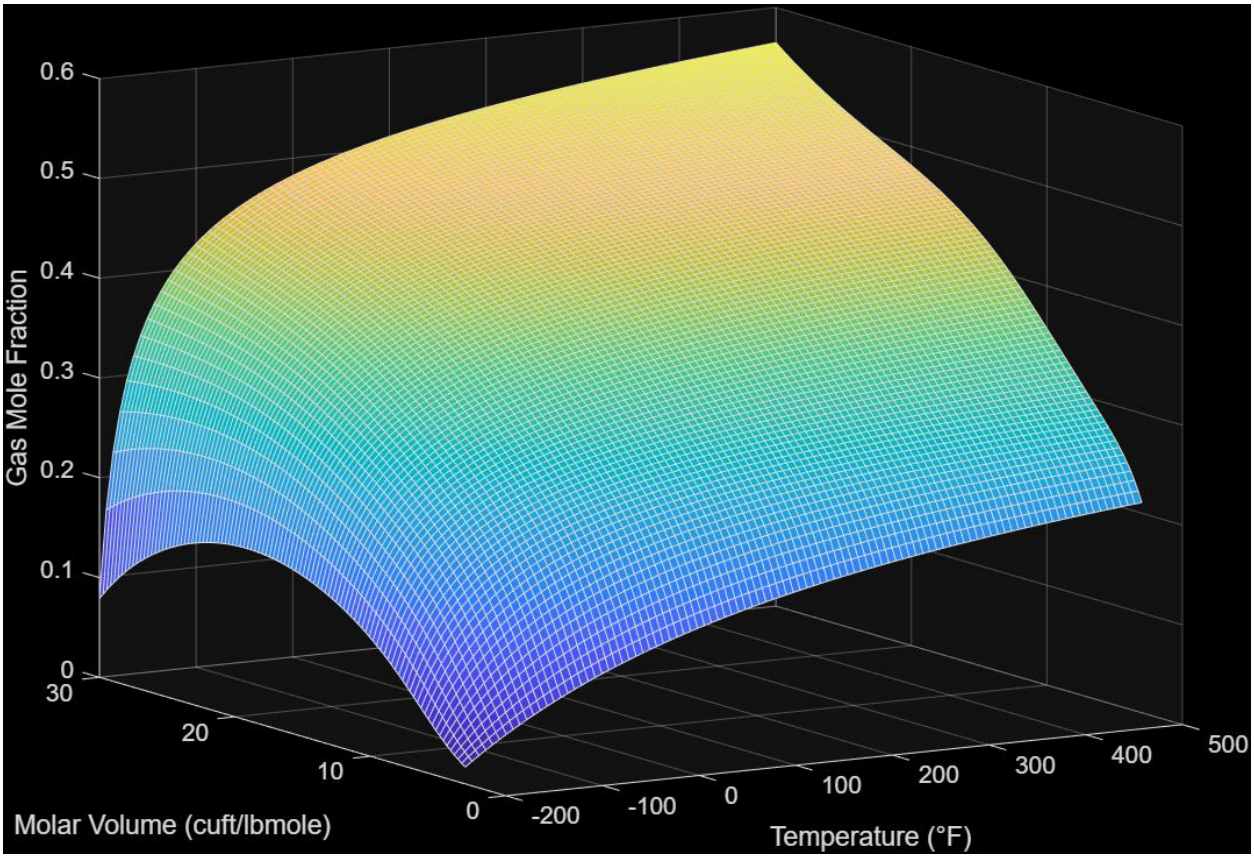


Figure 18: Gas mole fraction as a result of VT-Flash in term of specified molar volume-temperature points, for Fluid#2.

5. Conclusions

In this paper, a PT based VT-Flash calculation approach was proposed that is capable of being reliable for a variety of fluids and under different conditions. For this purpose, an objective function was defined based on molar volume and its root was calculated using three computational methods: Bisection, LMA, and TRQN. Also, the VT Flash computational algorithm based on all three methods is presented. According to the results obtained from this study, the following conclusions can be drawn:

- VT flash calculations were performed using the proposed approach for two fluids: synthetic condensate gas (Fluid#1) and live oil (Fluid#2). Comparison of the results obtained with experimental data (CCE test) shows good agreement, the R^2 is about 0.9258 and 0.9828 for Fluid#1 and Fluid#2, respectively. Also, the results at 100 random points were compared with the results from the VT-Flash proposed by Michelsen (based on Helmholtz free energy minimization), and a very high agreement was seen for both fluids, the R^2 is about 0.99998 and 0.99999 for Fluid#1 and Fluid#2, respectively. Therefore, it will be reliable both from the point of view of predicting the real state (laboratory) and in comparison with Michelsen's method [5] for VT-Flash.
- Comparing the three developed methods of Bisection, LMA, and TRQN for solving the objective function with the approach presented by Cisomandi et al. [1] shows that, in general, both the number of iteration calculations and elapsed time for all three methods is less than the Cisomandi et al. approach. On the other hand, due to Cisomandi's use of Wilson's equation for the k-value as an initial guess and the deviation of the values calculated by it from the actual values at high temperatures, the number of iteration calculations increases significantly as the temperature increases. However, the number of iteration calculations for all three methods proposed in this article is almost constant with temperature changes and does not change significantly. It can be concluded that the three methods proposed in this paper have significantly reduced the computational cost compared to the method proposed by Cisomandi et al. approach. For example, for Fluid#1, the number of iterations and elapsed time in the Bisection method were reduced by an average of about 70.45% and 92.10%, respectively, compared to the Cisomandi et al. approach.

- Among the three methods proposed in this study, it is observed that the Bisection method has a lower computational cost than the other two methods, both in terms of the number of iterations and the elapsed time. But in this method, it is necessary to consider an operating range for the pressure as an initial guess to start the calculations. While the other two methods, LMA and TRQN, require an initial guess for the pressure, which is calculated automatically using the ideal gas equation of state in their algorithms.
- Using the approach proposed in this paper for PT-based VT-Flash calculations for two fluids, live oil and gas condensate, shows that its performance is desirable and it is capable of producing acceptable results in a wide range of temperature and molar volume. This, along with the acceptable cross-validation results with the results of the Michelson's method (based on Helmholtz free energy minimization), makes the approach proposed in this paper a suitable, simple, and robust tool for performing VT-Flash calculations for various fluids and different conditions.

From the point of view of the accuracy and correctness of the results of the approach proposed in this article, this approach can be used with high confidence instead of VT-Flash based on the Helmholtz free energy minimization, due to its simplicity of use and calculations. However, considering the proposed algorithm, it is necessary to significantly reduce the computational cost by improving it, which can be considered and carried out as future works.

Appendix A: Quasi-Newton successive substitution (QNSS)

In order to solve the system of nonlinear equations in stability analysis and PT-flash calculations, the above method has been used due to its advantages. The most important advantages of this method include the absence of the need to calculate any analytical derivatives, as well as the very high convergence speed. If Eq. (1) and (5) are considered equal to a function like ψ for each component, yields:

$$\psi = \left[\psi_1, \psi_2, \psi_3, ..., \psi_{nc}\right]^T = 0 \tag{A-1}$$

Also, considering the initial values as a function of ξ, it gives:

$$\xi = \left[\xi_1, \xi_2, \xi_3, ..., \xi_{nc}\right]^T \tag{A-2}$$

where, ξ_i in Eq. (1) and in Eq. (5) are equal to $\ln(K_i)$ and $\ln(X_i)$, respectively. The new value of ξ must be updated in each iteration calculation as:

$$\xi^{j+1} = \xi^j + \Delta\xi^j \tag{A-3}$$

The step value, $\Delta\xi$, in the QNSS method can be estimated by:

$$\Delta\xi^j = -\delta^j \psi^j \quad , \quad \delta^j = \left|\frac{\Delta\xi^{j-1}\psi^{j-1}}{\Delta\xi^{j-1}\Delta\psi^{j-1}}\right|\delta^{j-1} \tag{A-4}$$

where, j is the iterator number. Also, it can be noted that δ^0 is considered as 1.0. in each iteration calculation, some limitation must be applied for ensuring convergence and not step-jumping. These are applied as:

$$|\delta| \leq 30 \quad , \quad |\Delta\xi| \leq 6 \tag{A-5}$$

The QNSS method is restarted at every specified number of iterations. Generally, this specified number has the same magnitude as the total number of components.

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Competing interests

The authors declare no competing interests.

Data availability

The datasets generated and/or analyzed during the current study are not publicly available but are available from the corresponding author on reasonable request.

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