

A new simple and efficient flash algorithm for T-v specifications

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ABSTRACT

Flash calculations have innumerable applications. Fast and robust algorithms for the (*T-P*) variant have spread since the early 80's, when Michelsen proposed an efficient successive-substitution algorithm for this specification, the most common and important one in practice. Specification of volume instead of pressure, along with temperature (*T-v*), for a fluid of known composition, can also be very important in many applications, including storage tanks, fluid mechanics and flow where phase equilibrium is important such as in oil reservoir. Some recommendations on how to solve indirectly this problem can be found in the literature, as well as a few studies proposing different formulations and sophisticated methods for minimizing the Helmholtz energy. Nevertheless, there has not been so far an efficient algorithm developed specifically for the *T-v* specification, that could be considered equivalent to the "Michelsen *T-P* flash".

In this work, we propose a new algorithm for *T-v* flash calculations, which is based on results from adapting the classic successive substitution method for a *T-P* flash, with equivalent simplicity, and therefore making it very attractive for engineering calculations, especially when speed may be important. Complementary aspects like initialization of variables and application to liquid-liquid separation are also discussed. Based on the new developed algorithm and the use of equations of state, the isochoric behaviors of different multicomponent mixtures are analyzed, including a natural gas, a synthetic gas condensate, and a CO₂-hydrocarbon mixture, considering both vapor-liquid and liquid-liquid separations. The effect of temperature on storage tanks is illustrated based on isochores, and it is also shown how these calculations can help in the search of convenient conditions for separating the condensable fraction from a natural gas.

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1. Introduction

Flash calculations play a major role in the application of chemical engineering thermodynamics, both in the upstream and downstream industries. In the early 80's, Michelsen proposed an efficient successive-substitution algorithm for the temperature and pressure specification (*T-P*) [1,2], which is the most common and routinely applied in practice. At present, such type of algorithm is implemented probably in most commercial simulators, as well as in a diversity of codes developed in academia, involving flash calculations.

The specification of volume instead of pressure, along with temperature (*T-v*), for a fluid of known composition, can also be

very important in many applications. These applications can be as diverse as storage tanks and simulation of flow in a reservoir, when considering the latter as an interconnected net of cavities with fixed volumes. Fields containing large amount of acid gases like CO₂ and Hydrogen sulfide are more common in more recent oil discoveries. To minimize production cost and reduce the environmental damage in such fields, a procedure that has been gaining strength is to capture these acid gases underground by using hollow fiber membrane. The gas permeates through the membrane and can be reinjected into the reservoir for an EOR Project purpose or storage. A challenge related to this process is to calculate the pressure and the gas composition in the hollow fiber membrane, that is to perform a *T-v* flash calculation [3]. Another useful application of *T-v* flashes is the calculation of liquid level in separator and desalting column where the total volume is specified.

The objective of a *T-v* flash calculation is to determine

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whether a phase is stable at specified volume, temperature, and mole numbers. In the case of phase split (unstable monophasic conditions), a calculation procedure is performed to find the resulting pressure, and each phase quantity, composition and molar volume.

Michelsen's practical recommendation, for this as well as for other alternative specifications, has been to run the well-known and well-behaved T - P flash on an inner loop, while adjusting the pressure on an outer loop, until matching the specification [2] [4]. Other authors have recently proposed and implemented new specific and more sophisticated methods, based on minimizing the Helmholtz free energy at specified T - v conditions, through complex optimization approaches [5–7]. Mikyska and Firoozabadi [8] proposed also a T - v flash algorithm based on new defined thermodynamic functions and modified variables, which are not the typical ones for equation of state calculations. Related but more complex problems and phenomena, including systems subject to gravitational fields [9] and multiple adsorbed and bulk phases [10] were also formulated as minimizations of the total Helmholtz free energy. These types of minimization approaches have generally been tested and demonstrated just for binary systems, while their application to multicomponent mixtures can be computationally very expensive.

So far, there was no T - v equivalent for the "Michelsen T - P flash". This is, an algorithm designed specifically for T - v specifications, which is efficient and convenient to be implemented in process simulators and, if possible, formulated in similar terms to the well known T - P flash.

In this work, we propose such type of new algorithm for T - v flash calculations, based on an adaptation of the classic successive substitution method for T - P flash, with equivalent simplicity, and therefore making it very attractive for engineering calculations, especially when speed may be important. In comparison to the common strategy of solving a T - P flash in an inner loop, the algorithm we propose here is designed to solve one direct T - v flash instead of several or many T - P flashes. And the inner iterative calculations for finding the volume roots in the two phases –characteristic of T - P flashes—are naturally replaced by an equivalent problem, involving the pressure equality between the two phases.

2. Problem formulation

Given one mole of a fluid with specified overall composition \mathbf{z} , at temperature T and molar volume v , we need to find –according to a specified equation of state and sets of parameters—which are the values for:

- The resulting equilibrium pressure P
- Molar volumes for the two phases, e.g. liquid and vapor, in equilibrium: v^L and v^V .
- Compositions (molar fractions) of the liquid \mathbf{x} and vapor \mathbf{y} .
- The vaporized fraction β

If we consider the pressure P just as a function of the independent variables temperature, composition and the corresponding molar volume in each phase, then for a system with C components we have $2C + 3$ unknowns.

The list of equations includes the following $2C + 1$ equations in common with the T - P flash case:

$$\Phi_i^L x_i = \Phi_i^V y_i \text{ (equilibrium conditions; } i = 1, 2 \& C) \quad (1)$$

$$y_i \beta + x_i (1 - \beta) = z_i \text{ (component material balance; } i = 1, 2 \& C) \quad (2)$$

$$\sum_{i=1}^C (y_i - x_i) = 0 \text{ (global material balance)} \quad (3)$$

And then the following two extra equations:

$$P(y, T, v^V) = P(x, T, v^L) \text{ (pressure equality)} \quad (4)$$

$$\beta v^V + (1 - \beta)v^L = v \text{ (volume distribution)} \quad (5)$$

Which providing a total of $2C + 3$ equations, matches the number of unknowns.

We need to remark that, in the context of T - v specification where the system pressure is an unknown, and having each phase molar volumes as independent variables, then when trying any numerical guess each phase will have in principle a different pressure. That is why the necessity of Eq. (4) as a restriction to be fulfilled. Once the calculation has converged, both phases will have the same pressure, and its value will be the resulting flash pressure.

If we rearrange the formulation in terms of K factors, then the first $2C$ reduce to the following C equations:

$$\ln K_i - \ln \Phi_i^L + \ln \Phi_i^V = 0 \text{ (equilibrium conditions; } i = 1, 2 \& C) \quad (6)$$

while Eq. (3) becomes the classic Rachford-Rice equation [11]:

$$\sum_{i=1}^C \frac{z_i (K_i - 1)}{1 - \beta + \beta K_i} = 0 \quad (7)$$

This leads to $C+3$ equations (Eqs. (4)–(7)) in $C+3$ unknowns: the C K_i 's, β , v^L and v^V . Note that, given a set of K_i values, Eq. (7) can be solved for β and then –solving the component material balances–mole fractions are obtained through

$$x_i = \frac{z_i}{1 - \beta + \beta K_i} \quad (8)$$

$$y_i = x_i K_i \quad (9)$$

The question is now how to solve the system of equations (4)–(7) and how to initialize the $C+3$ independent variables, for a given specification of \mathbf{z} , T and v or, if preferred, \mathbf{n} , T and V .

Based on the experience with Michelsen's successive substitution (SS) strategy for the T - P flash, and in order to get the most from this type of mature codes, we propose an adaptation which is explained as follows. While the SS algorithm for the T - P flash problem can be summarized in the scheme presented in Fig. 1, the proposed approach for solving the T - v flash consists in following essentially the same procedure, and solving the two extra equations (4) and (5) every time that new mole fractions are obtained for the two phases, as it is indicated in Fig. 2. But how? Such problem is discussed in the next section.

Before, we just want to clarify something in relation with the number of equations and independent variables, which implies a decision that, in a way, is always arbitrary. The molar volumes of the two phases v^L and v^V , together with the corresponding equations (Eqs. (4) and (5) in this work) are of course valid in the context of a T - P flash and could also be accounted, to give a total of $C+3$ equations in $C+3$ unknowns. Nevertheless, they are computed in internal loops and therefore have not been traditionally and explicitly

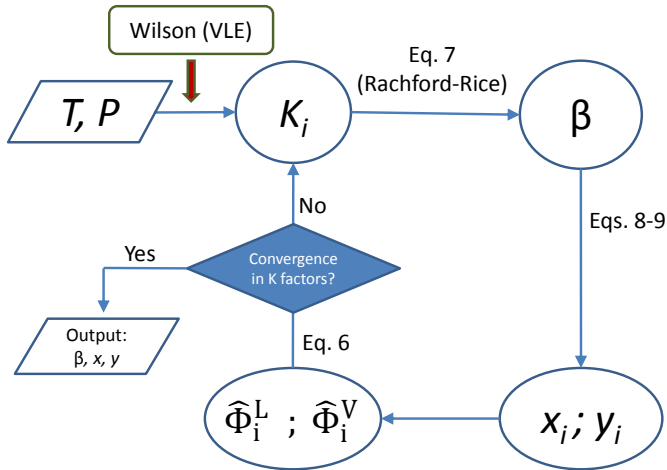


Fig. 1. Schematic representation of Michelsen's successive substitution strategy for solving the T - P Flash problem. Equations are referenced as numbered in this work.

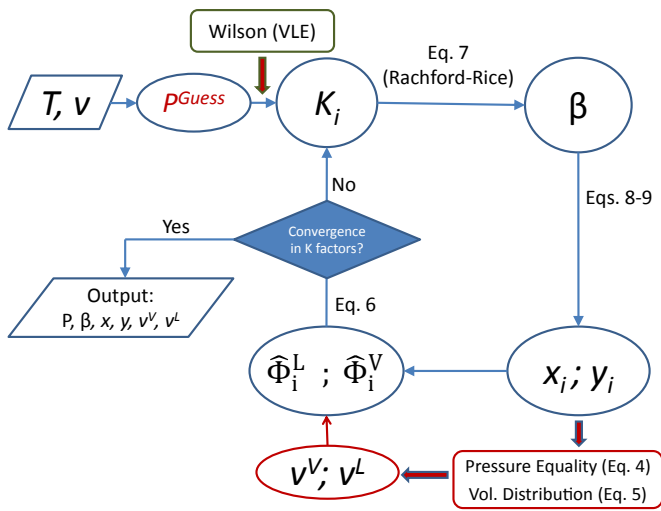


Fig. 2. Schematic representation of the successive substitution strategy proposed and implemented in this work for solving the T - v Flash problem.

recognized as variables in the T - P flash. This changes in the context of a T - v flash, given the specification of the overall molar volume present in Eq. (5). Then, accounting for these variables and equations becomes a must instead of an option.

2.1. Solving the two extra equations for the phases molar volumes

Based on the volume distribution restriction (Eq. (5)) we can put v^V in terms of v^L as follows:

$$v^V = \frac{v - (1 - \beta)v^L}{\beta}; \quad \text{with} \quad \left(\frac{\partial v^V}{\partial v^L}\right) = -\frac{(1 - \beta)}{\beta} < 0 \quad (10)$$

Then, replacing v^V , Eq. (4) becomes an equation with only one unknown, which is v^L :

$$F = P^V(v^L) - P^L(v^L) = 0 \quad (11)$$

The corresponding derivative being $\frac{dF}{dv^L} = \left(\frac{\partial P^V}{\partial v^L}\right)_{y,T} \left(\frac{\partial v^V}{\partial v^L}\right) - \left(\frac{\partial P^L}{\partial v^L}\right)_{x,T}$

Given that both terms are always positive (as long as both v^V and v^L are located in mechanically stable branches of the isotherm), the derivative of F is monotonically increasing. Then, Eq. (11) can be conveniently solved by the Newton method to find v^L , and therefore also v^V through Eq. (10). As illustrated in Fig. 3, the search range for v^L goes from the co-volume of the mixture to the local minimum pressure in the isotherm, while a reasonable and generalized initial guess can be 1.5 times the co-volume.

2.2. Initialization of pressure and K factors

The other specific point to be considered, of course, is that we do not have pressure as an input in the T - v flash. Therefore, in order to start the procedure represented in Fig. 2, we need to guess the pressure somehow. A reasonable default option is to use the one-fluid pressure predicted by the equation of state for the specified temperature and volume. Fig. 4 illustrates how this pressure is usually close to the converged value for the flash calculation and, naturally, tends to be the same as we approach the saturation limits given by the phase envelope.

But we have to remark here that the proximity of the guess pressure value with respect to the solution value will not necessarily be enough, since what really matters for a good initialization of the procedure are the K factors. In absence of a better alternative, the classic Wilson K -factors are used for VLE:

$$K_i = \left(\frac{P_{c,i}}{P}\right) \exp\left[5.373 \cdot (1 + \omega_i) \cdot \left(1 - \frac{T_{c,i}}{T}\right)\right] \quad (12)$$

Although this will work in most cases, they can be a bad estimation or even fail in the proximity of a retrograde dew point and also in some cases at low temperatures, in the proximity of a three-phase region. Therefore, when a series of flashes is to be calculated, for example along an isochore, we recommend using the Wilson K factors just to initialize the first point, but then use the converged K values from the previous point. Or even better, an extrapolation as a function of temperature based on the last two converged points. Fig. 5 shows, for the case of a series of flashes with decreasing pressure along an isochore, how the number of iterations is reduced by implementing these alternatives.

We need to remark here that, although the numbers of

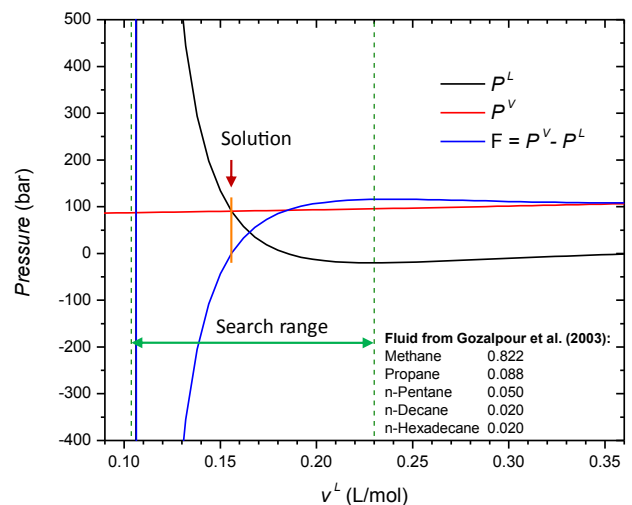


Fig. 3. Example illustrating the resolution of Eq. (11) for v^L . As well as for Fig. 6 and 7 in section 3, the fluid corresponds to the synthetic gas condensate in the experimental study by Gozalpour et al. (2003) [12].

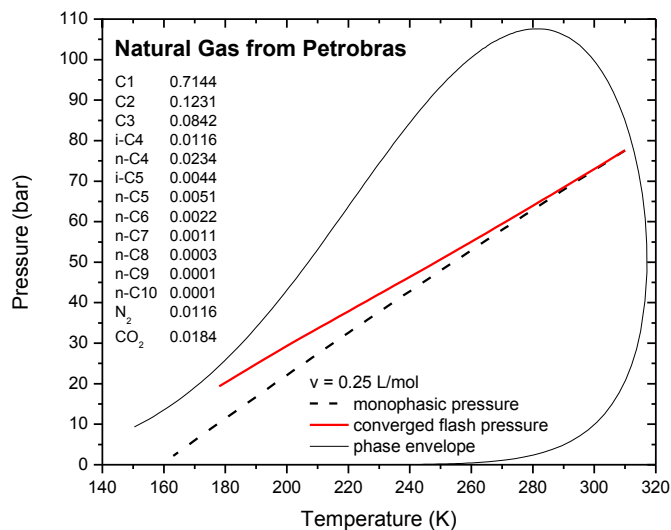


Fig. 4. Difference between the one-fluid pressure used as initialization and the converged flash pressure, along an isochore for a 14-component natural gas. Calculations performed with the RKPR EoS [13,14]. As well as for Fig. 10–12 in section 3, the fluid corresponds to a natural gas denoted as NKT, reported by dos Santos et al. [15]. Composition is given in mole fractions.

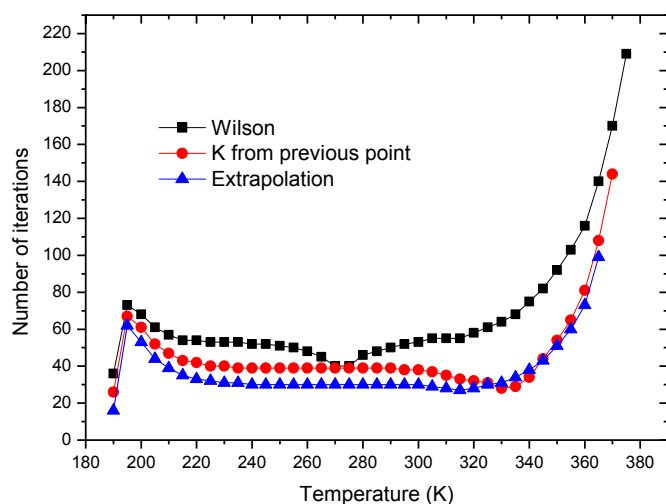


Fig. 5. Effect of different initializations for the K factors on the number of iterations required to solve the T - v flash, along the isochore of 0.10 L/mol for a 5-component synthetic gas condensate (Gozalpour et al., 2003, see Figs. 6 and 7). The sequence of specified temperature was defined by a decreasing step of 5 K.

iterations in the higher temperature range may appear to be high even for the extrapolation case, this is commonly observed with successive substitution procedures for T - P flash calculations when deviation from ideality is pronounced in both phases. And, as Michelsen has pointed out, this occurs normally at high pressures, in particular in retrograde or near-critical regions [2] as it is the case in Fig. 5 (the pressure range and proximity to the phase envelope can be observed in Fig. 6).

For LLE conditions, and in absence of nearby converged points, the Wilson K factors may still work in some cases. Otherwise, the initial guess for K values will have to be based on specific knowledge of the system, either in the form of single typical values or correlations. When such type of information is not available, initialization can proceed as follows. If there is one component identified as responsible for the second liquid phase, e.g. water in a

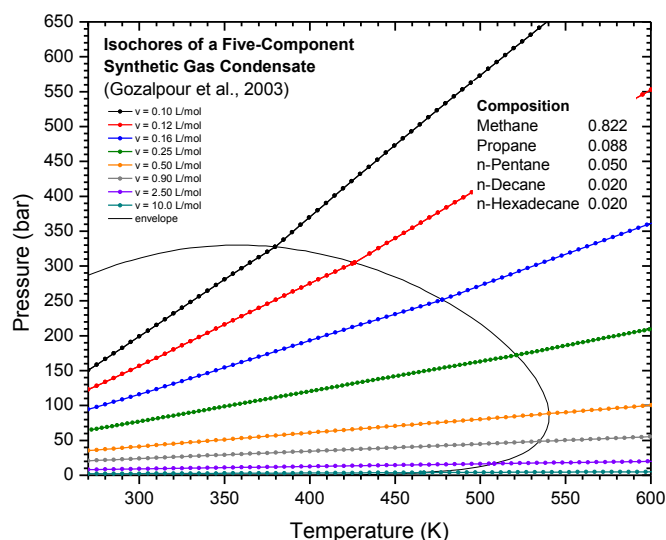


Fig. 6. Eight different isochors calculated with the RKPR EoS [13,14] for a 5-component synthetic gas condensate (mole fractions indicated). The segments inside the phase envelope were constructed as sequences of T - v flashes.

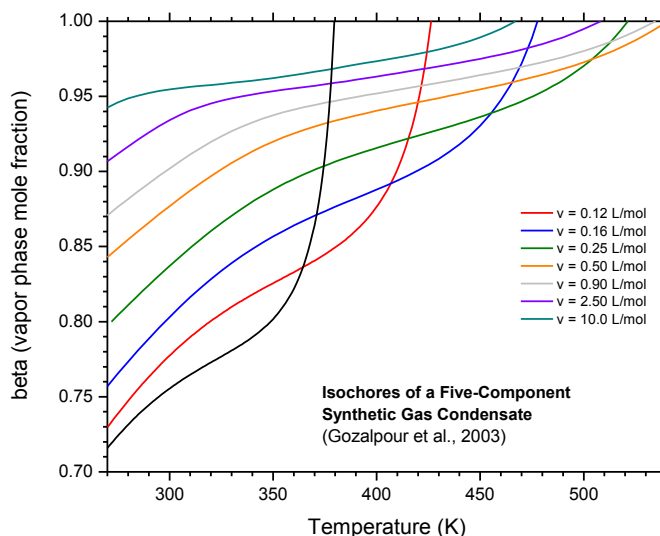


Fig. 7. Calculated vapor phase fraction curves corresponding to two-phase sections of the isochors presented in Fig. 6 for a 5-component synthetic gas condensate. Note that, although the notation in section 2 seems to refer only to vapor-liquid separations, the proposed procedure is equally applicable to liquid-liquid equilibrium, provided reasonable initializations are available. To illustrate that, Figs. 8 and 9 present different isochors for a CO₂ + hydrocarbon fluid showing a continuous transition from VLE to LLE behavior, where the initialization for each point resulted from the previous points at higher temperatures, as discussed in section 2.2. The isochors were organized in two sets: one corresponding to relatively low molar volumes, showing LLE behavior in the two-phase region (upper part of Fig. 8), and the other involving higher molar volumes and VLE behavior (lower part).

hydrocarbon mixture, one of the liquid phases can be initially considered to be that component pure, and the corresponding K factors are obtained as ratios between fugacity coefficients at infinite dilution in that component and fugacity coefficients in a mixture of the specified composition.

3. Results and discussion

The approach described in the previous section has been

implemented and systematically tested. Some details and recommendations were provided in the previous section. Here we present some case studies in order to illustrate some applications. The phase envelopes presented together with isochores in some pressure-temperature diagrams for selected fluids were calculated with our own algorithm, based on Michelsen's method for tracing two-phase boundaries [2,16].

Fig. 6 shows eight different isochors calculated for a synthetic gas condensate fluid [12], together with the corresponding phase envelope. Predictions correspond to the RKPR EoS [13] with predictive correlations of interaction parameters recently published [14]. The calculation of each isochore considered a series of T - v specifications inside the two-phase region as well as another sequence of points in the monophasic region, having previously identified the saturation point for the specified molar volume. In practical terms, each isochore tells us, for example, how the pressure would evolve, or behave, during the heating, or temperature increase, of a fixed volume vessel with a given charge of the specified fluid. The corresponding vapor phase fraction curves in the two-phase region are presented in Fig. 7.

This is also a good example to show that, the same as for the classic T - P flash, obtained two-phase distributions may not be stable for some systems at specific regions in the thermodynamic space. The non-stable condition of those points could be detected based on different stability analysis approaches or, simpler, based on their position with respect to a three-phase boundary when available, as it is shown in Fig. 8. Such boundary was calculated and included in Fig. 8, establishing a limit for the stability of solutions to the T - v two-phase flash problem: all points with temperatures falling below the intersection between the isochore and this boundary need to be discarded, although they are included in Fig. 8 for illustrative purposes.

In order to facilitate a proper interpretation, note that, for multicomponent fluids like this, there will be a region in the T - P space corresponding to three-phase equilibrium. The boundaries for this region -included in Fig. 8- were calculated following a method described elsewhere [17]. However, given the similarity among four of the five components, which is responsible for a quasi-binary phase behavior, the three-phase region is very narrow in this case, reducing almost to a line. It is interesting to see that the

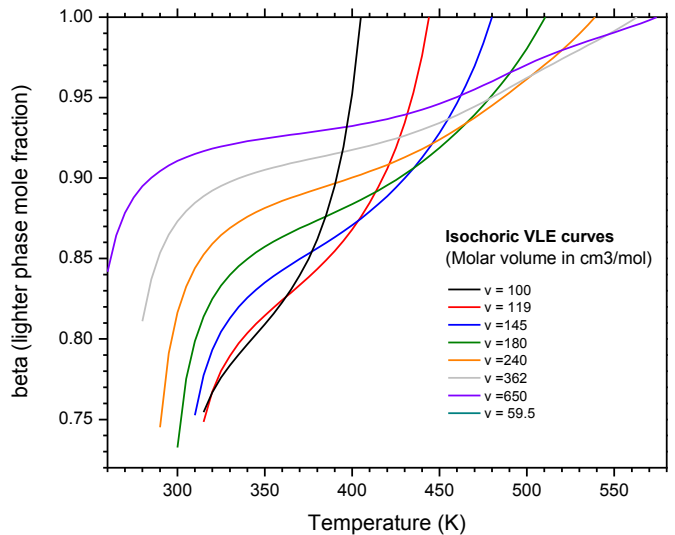
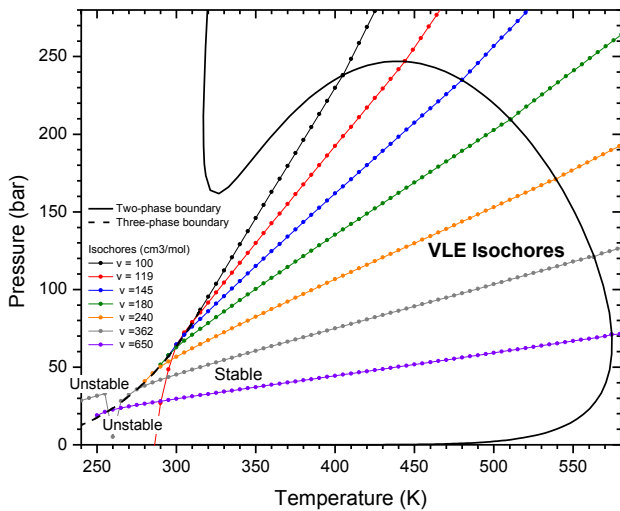
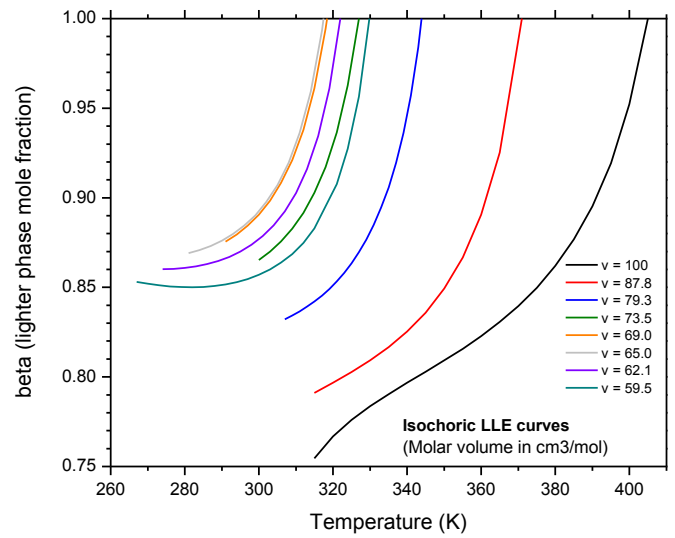
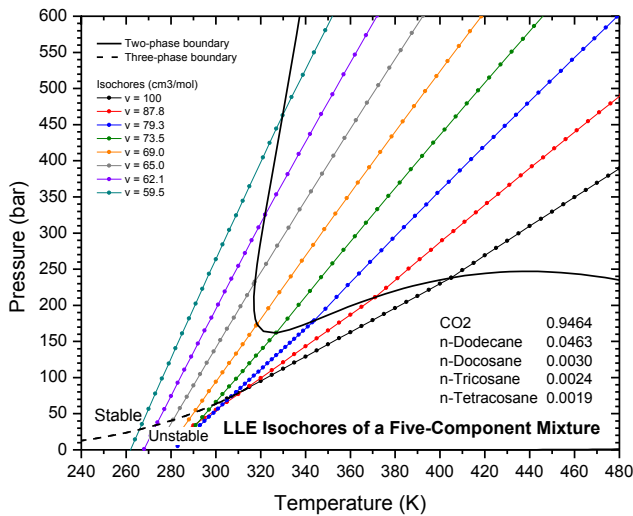


Fig. 8. Different isochors of LLE type (upper part) and VLE type (lower part) calculated with the PR EoS [19] for a 5-component CO₂ + hydrocarbon mixture (mole fractions indicated). Segments inside the phase envelope were constructed as sequences of T - V flashes. k_{ij} (CO₂ -alkane) = 0.09.

Fig. 9. Calculated beta vs temperature curves, corresponding to stable two-phase sections of the isochores presented in Fig. 8 for a 5-component CO₂ + hydrocarbon mixture.

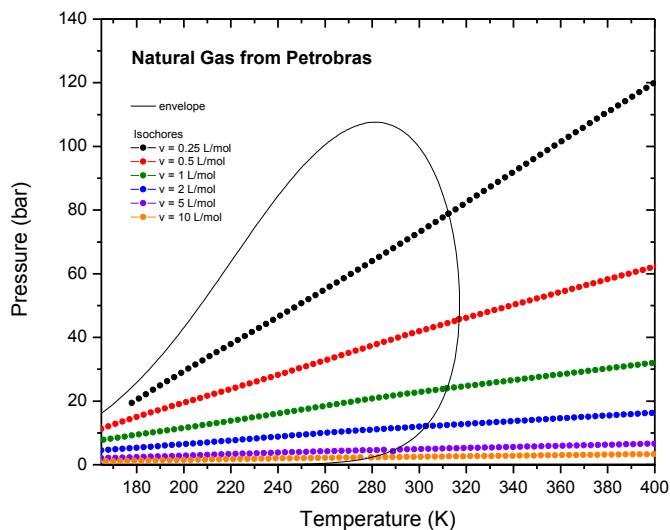


Fig. 10. Six different isochors calculated with the PR EoS for a 14-component natural gas (composition given in Fig. 4). Segments inside the phase envelope were constructed as sequences of T-V flashes.

behavior of the different two-phase isochores around the three-phase “line” is completely analogous to the well-known behavior of a pure substance isochores with respect to the vapor pressure curve (see for example Fig. 3.3 in the classic textbook by Smith et al. [18]). Indeed, this similarity allowed us to classify as of LLE type those isochores leaving the three-phase region towards higher pressures and as of VLE type those isochores departing to the lower pressure region. To complete the analogy, note that the isochore corresponding to $v = 100 \text{ cm}^3/\text{mol}$ is the one departing from the three-phase region at the highest temperature and pressure, and could therefore be considered as the critical isochore. That is why, as the limiting one, it has been included in both sets. Now, coming back to the unstable solutions represented by the last points with lowest temperature at some isochores, it should be clear that the stable solution for each of those T-v specifications will be a three-phase separation, with a pressure falling inside the three-phase region or line.

Although an equivalent implementation and discussion for multiphase cases are beyond the scope of this work, note that the

extension to higher numbers of phases would be possible through the addition of $C + 2$ variables per each extra phase, involving a new set of K factors plus the phase fraction and phase molar volume, and the corresponding $C+2$ equations: the new set of equilibrium conditions plus a new material balance and pressure equality.

Fig. 9 presents the phase fraction curves corresponding to the two sets of isochores in Fig. 8. It is interesting to note that, according to the model, condensation –or formation of the hydrocarbon richer liquid phase– would reach minimum values for isochores somewhere between 65 and $69 \text{ cm}^3/\text{mol}$, while both lower and higher volumes would lead to more condensation, based on an isochoric cooling process. Accordingly, maximum condensation can be reached for the transition isochore of $100 \text{ cm}^3/\text{mol}$. Note also that the qualitative behavior of the VLE set in Fig. 9 is essentially the same as the one observed in Fig. 7 for the synthetic gas condensate fluid.

Finally, the case of a 14-components natural gas is presented in Figs. 10–12. As for the synthetic gas condensate fluid in Figs. 6–7, calculations correspond to the RKPR EoS [13,14]. Fig. 10 confirms, once again, that the change of the isochoric slope from the two-phase to the monophasic region is not that important at dew points, and it is even hard to detect in the higher temperature or lower pressure regions. Diagrams like the ones presented in Figs. 11 and 12, showing phase fractions and $C5+$ compositions in both phases along the isochores respectively, can be important when searching for appropriate conditions for separating the heavier condensable fractions of a natural gas. It becomes clear that higher loadings of storage or separation tanks –which imply lower specific volumes– will produce larger fractions of condensed phase during cooling. But, on the other hand, they will lead to lower contents of the heavier fractions in those condensed phases. Therefore, any optimum design, either considering a single or several stages to achieve the desired separation, will depend on the fluid composition and process specifications.

In relation to speed or computing time, Table 1 shows the times required for computing some selected biphasic isochores for the fluids previously discussed. The times reported are the mean values between two different runs for the same case and method. Each run covered a number of 6–48 flashes, separated by steps of 5 K. In some cases, the temperature range was limited by convergence problems with the indirect, T-P flash-based alternative. In all cases an important reduction in computing time was observed. Except for

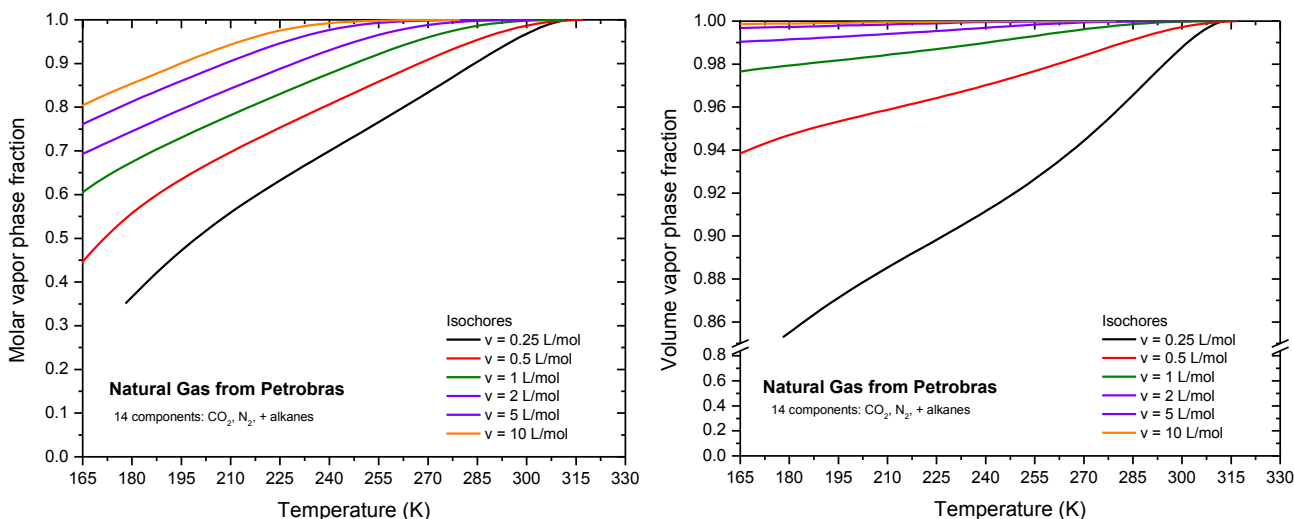


Fig. 11. Calculated Molar and Volume vapor phase fractions along different isochors, for the natural gas in Fig. 10.

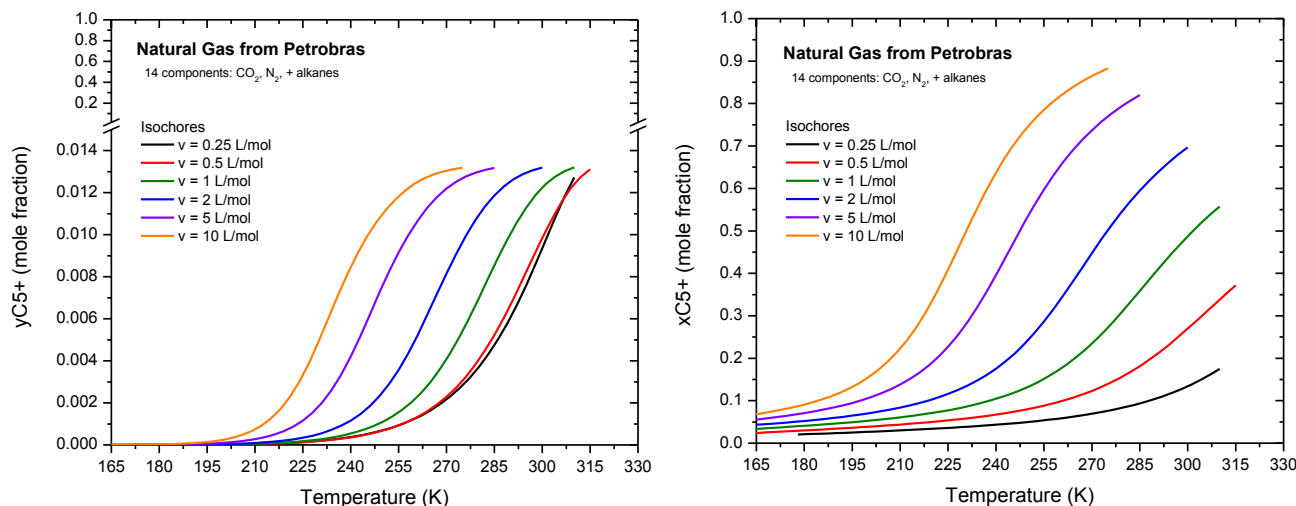


Fig. 12. Calculated C5+ fractions in vapor and liquid phases along the isochores for the natural gas in Fig. 10.

Table 1

Comparison of computing times^a with the indirect (based on T - P flashes) and the direct T - v Flash proposed in this work.

Case	Figure	Isochore (L/mol)	T range (K)	Total time (s) Indirect Flash	Total time (s) Direct Flash
5-Component Gas Condensate – RKPR	6	0.10 0.25	240–375 280–515	1.2891 0.3516	0.2188 0.0703
CO ₂ + Hydrocarbons - PR	8	0.069 0.24	290–315 305–535	0.3125 0.5234	0.1250 0.0859
14-Component natural gas – PR	10	0.25 2.00	185–310 150–300	0.5313 0.2656	0.0703 0.0547

^a Calculations were run offline on a PC with Intel Core i7 Processor.

one particular isochore where the direct T - v flash proposed here required 40% of the time required by the indirect alternative, in all other cases the required time was very low, ranging between 13% and 21% of the time required by the indirect method.

4. Conclusions

A new simple and efficient algorithm, equivalent to and based on the Michelsen successive substitution “ T - P Flash” has been proposed and implemented for the case of temperature-volume (T - v) specifications.

Its use has been illustrated for the calculation of two-phase isochores, and the corresponding isochoric liquid dropout curves, for different multicomponent mixtures, including a synthetic gas condensate, a CO₂ + hydrocarbon fluid and a natural gas. These isochores allow simulating the heating or cooling effects, for example on storage tanks pressure. It was also illustrated, for the case of the natural gas, how these calculations can provide useful information for the design of separation processes aiming at tuning the composition before transport to prevent condensation. An interesting finding that arose from the CO₂ + hydrocarbon fluid is that biphasic isochores of a mixture can organize around a three-phase region in the same way as monophasic isochores of a pure compound do around the vapor pressure curve.

In terms of speed, and based on comparisons made for some isochores of the three fluids studied, the proposed algorithm normally requires around 20% or less of the time required by an indirect T - v flash based on nested T - P flashes, which has been probably the most frequently implemented strategy so far, in the thermodynamic community.

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Nomenclature

Abbreviations

EOR	Enhanced Oil Recovery
EoS	Equation of State
LLE	Liquid-Liquid Equilibrium
PR	Peng-Robinson equation of state
RKPR	Generalized Redlich-Kwong-Peng-Robinson equation of state
SS	Successive substitution
VLE	Vapor-Liquid Equilibrium

Roman letters

C	Number of components in the system
i	Component index
K_i	Equilibrium ratio or ‘K factor’ of component i , defined as y_i/x_i
n	Number of moles vector
P	Pressure
T	Temperature

v	Molar volume (overall or phase-specific, see superscripts)
V	Total volume
x_i, y_i, z_i	Mole fractions of component i in the liquid, vapor and overall composition respectively
$\mathbf{x}, \mathbf{y}, \mathbf{z}$	Liquid, vapor and overall mole fraction vectors

Greek letters

β	Molar vapor (or lighter liquid) fraction
$\hat{\Phi}_i^L$	Fugacity coefficient of component i in the liquid phase
$\hat{\Phi}_i^V$	Fugacity coefficient of component i in the vapor or lighter phase

Super/subscripts

L	Liquid phase
V	Vapor or lighter phase
I	component index

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