ANALYSIS OF SOME ACCELERATION METHODS FOR ISOTHERMAL FLASH PROBLEM

Mara Jane Neves Lima Freire[1]
Marcelo de Souza Sampaio[2]
João Flávio Vieira de Vasconcellos[3]
Luiz Nélio Henderson[4a]
Department of Mechanical Engineering and Energy - IPRJ
Rio de Janeiro State University – UERJ
P. O. 97.282
28.601-970 – Nova Friburgo – Rio de Janeiro
[1]mjlima@iprj.uerj.br, [2]marcsam@iprj.uerj.br, [3]jflavio@iprj.uerj.br, [4]nelio@iprj.uerj.br

Abstract. *The Successive Substitution Method plays an important role in the Isothermal Flash calculation. The computational problems associated with this method may range from slow rate of convergence to no convergence near the phase boundaries or the critical points. Under certain conditions, apparent convergence may tend to an incorrect solution. Hence, some numerical techniques have been developed to improve the convergence rate in Isothermal Flash calculation. In this work, three of these methods are compared and applied to a wide range of isothermal flash calculations to demonstrate the robustness of these methods.*

Keywords*. Isothermal Flash, Multiphase Equilibrium, Successive Substitution*

1. Introduction

Isothermal flash calculations are of particular importance in petroleum and chemical engineering. Miscible gas floods of oil reservoirs cannot be adequately modeled without a detailed flash phase behavior description. Distillation, adsorption, and extraction are examples of multistage processes in which phase equilibrium calculations at specified values of Pressure (P) and Temperature (T) are required. Process simulators generally require the incorporation of vapor-liquid equilibrium flash. Indeed, flash calculations are the most important aspect of process simulators, therefore these calculations must converge rapidly and must be robust for a wide range of temperatures and pressures and for a broad spectrum of mixtures.

The Successive Substitution Method (SSM) is the most used method and has proved to converge to the optimal in most practical cases (Henley and Seader, 1993). However, a good initial estimation is required to avoid undesired solutions and to enhance convergence. However, the SSM may present either a slow convergence rate or no convergence near the phase boundaries or the critical points. Under certain conditions, apparent convergence may lead to an incorrect solution. The algorithm used for the calculations herein is based on the classical Rachford and Rice (1952) procedure for isothermal flash. The formulation of the isothermal flash problem appears as the minimization of an objective nonlinear function with linear inequality constraints for the conservation of mass and the nonnegativity of phase compositions suggested by Henderson (1993).

The SSM is a very fast methodology, however the rate of convergence becomes increasingly low in the vicinities of critical points. Various attempts have been reported to enhance the rate of SS convergence (Mehra *et alii*, 1982), therefore, it is necessary to change the original algorithm to accelerate it. In the present work, the algorithms suggested by Mehra *et alii* (1983) and by Armijo (1966) are used. Finally, the original SSM, the SSM modified by Mehra *et alii* (1983) and the SSM modified by Armijo (1966) are applied in the solution of the isothermal flash problem and their results are compared.

2. Statement of the Isothermal Flash Problem

We consider here only the isothermal flash, which refers to calculation of the quantities and compositions of the vapor and liquid phases making up a two-phase system in equilibrium, typically a vessel with *T* and *P* values fixed for a given feed $\left(z_1, z_2, \cdots, z_r\right)$

We formulate the isothermal flash model using Callen's (1985) thermodynamic parlance. The equilibrium state is defined as the state of minimum Gibbs free energy among the manifold of states of constant temperature and pressure. For a vapor-liquid system, the total Gibbs free energy is given by

$$G = \sum_{i=1}^{r} n_i^{(v)} \mu_i^{(v)} + \sum_{i=1}^{r} n_i^{(l)} \mu_i^{(l)} \tag{1}$$

where $n_i^{(f)}$, $f = l, v$, represents the numbers of moles of component i in the vapor, $n_i^{(v)}$, or liquid, $n_i^{(l)}$, phase. The chemical potential

---

[a] Author to whom correspondence should be addressed

$$\mu_i^{(f)} = \mu_i^{(f)}\left(n_1^{(f)}, \cdots, n_r^{(f)}\right) \text{ with } i = 1, 2, \cdots, r \text{ and } f = l, v \tag{2}$$

is a homogeneous function of degree zero. By dividing each extensive parameter by the number of moles, $n^{(f)} = \sum_{i=1}^{r} n_i^{(f)}$, the same value for function $\mu_i^{(f)}$ is obtained. Thus, we can write Eq. (2) in terms of intensive parameters as

$$\mu_i^{(f)} = \mu_i^{(f)}\left(n_1^{(f)}, \cdots, n_r^{(f)}\right) = \mu_i^{(f)}\left(\frac{n_1^{(f)}}{n^{(f)}}, \cdots, \frac{n_r^{(f)}}{n^{(f)}}\right) = \mu_i^{(f)}\left(x_1^{(f)}, \cdots, x_r^{(f)}\right) \tag{3}$$

where $x_1^{(f)} = n_1^{(f)} / n^{(f)}$ is the molar fraction of the *i*th component in f phase.

As demonstrated in Henderson *et alii* (2001), if $n = n^{(v)} + n^{(l)}$ is the total number of moles in the mixture, then the total molar Gibbs free energy, $g = G/n$, can be written in the form

$$\begin{aligned} g &= g\left(x_1^{(l)}, \cdots, x_{r-1}^{(l)}, l\right) \\ &= l \sum_{i=1}^{r-1} x_i^{(l)} \left[\left(\mu_i^{(l)} - \mu_i^{(v)}\right) - \left(\mu_r^{(l)} - \mu_r^{(v)}\right)\right] + l\left(\mu_r^{(l)} - \mu_r^{(v)}\right) + \sum_{i=1}^{r} z_i \mu_i^{(v)} \end{aligned} \tag{4}$$

where $\mu_i^{(l)}$ and $\mu_i^{(v)}$ have the functional forms described as

$$\mu_i^{(l)} = \mu_i^{(l)}\left(x_1^{(l)}, \cdots, x_{r-1}^{(l)}\right) \text{ with } i = 1, 2, \cdots, r \tag{5}$$

$$\mu_i^{(v)} = \mu_i^{(v)}\left(x_1^{(v)}, \cdots, x_{r-1}^{(v)}, l\right) \text{ with } i = 1, 2, \cdots, r \tag{6}$$

and $l = n^{(l)} / n$ is the molar fraction of the liquid phase. The chemical potential of the *i*th component can be expressed, with constant *T*, by

$$\mu_i^{(f)} = RT\left[\ln\left(\phi_i^{(f)}\right) + \ln\left(Px_i^{(f)}\right)\right] \tag{7}$$

where R is the universal gas constant, $\phi_i^{(f)}$ is the fugacity coefficient of the *i*th component in phase. In order to model the liquid and vapor phases, the Peng-Robinson (1976) cubic equation of state and the classical mixing rules were utilized.

According to the Gibbs free energy minimum principle, at the equilibrium state the values of the intensive parameters of a system are those that minimize the total molar Gibbs free energy of the system under the same specified values of temperature and pressure.

Therefore, the equilibrium state of a two-phase system undergoing a process at constant temperature and pressure can be stated as follows:

Given T, P and z_i, $i = 1, 2, \cdots, r$, find the values of $x_1^{(l)}, \cdots, x_{r-1}^{(l)}$ and l that minimize

$$g\left(x_1^{(l)}, \cdots, x_{r-1}^{(l)}, l\right) = l \sum_{i=1}^{r-1} x_i^{(l)} \left[\left(\mu_i^{(l)} - \mu_i^{(v)}\right) - \left(\mu_r^{(l)} - \mu_r^{(v)}\right)\right] + l\left(\mu_r^{(l)} - \mu_r^{(v)}\right) + \sum_{i=1}^{r} z_i \mu_i^{(v)} \tag{8}$$

subject to

$$\begin{aligned} &0 < l < 1 \\ &0 < x_i^{(l)} < 1, \text{ for } i = 1, 2, \cdots, r-1 \\ &\sum_{i}^{r-1} x_i^{(l)} < 1 \end{aligned} \tag{9}$$

where $\mu_i^{(l)} = \mu_i^{(l)}\left(x_1^{(l)}, \cdots, x_{r-1}^{(l)}\right)$ and $\mu_i^{(v)} = \mu_i^{(v)}\left(x_1^{(v)}, \cdots, x_{r-1}^{(v)}, l\right)$.

The variables $x_r^{(l)}$, v (the molar fraction of the vapor phase), and $x_i^{(v)}$ are calculated respectively from

$$x_r^{(f)} = 1 - \sum_{i=1}^{r-1} x_i^{(f)} \text{ with } f = l, v \tag{10}$$

$$v = 1 - l \tag{11}$$

$$v x_i^{(v)} = z_i - l x_i^{(l)} \tag{12}$$

at each step of the iterative process until a minimum of g is achieved. A similar discussion yields the formulation of the isothermal flash problem in intensive variables of the vapor phase.

3. The Successive Substitution Method

The successive substitution procedure used in the flash problem herein was proposed by Rachford-Rice (1952) and will be described briefly in this section.

Step 1: The initial value for K_i is estimated using a correlation proposed by Wilson (1969),

$$K_i = \frac{\exp\left[5.37\left(1+\omega_i\right)\left(1-\frac{1}{T_{r_i}}\right)\right]}{P_{r_i}} \tag{13}$$

where $P_{r_i} = P/P_{c_i}$ is the reduced pressure and $T_{r_i} = T/T_{c_i}$ is the reduced temperature of the ith component. ω_i is the accentric factor of each component.

Step 2: Solve the Rachford-Rice (1952) equation to obtain v

$$h(v) = \sum_{i=1}^{r} \frac{z_i\left(K_i - 1\right)}{1 + v\left(K_i - 1\right)} = 0 \tag{14}$$

Step 3: Calculate $x_i^{(l)}$, $i = 1, \cdots, r$, using the equation (15).

$$x_i^{(l)} = \frac{z_i}{1 + v\left(K_i - 1\right)} \tag{15}$$

Step 4: Calculate $x_i^{(v)}$, $i = 1, \cdots, r$, using the equation (16)

$$x_i^{(v)} = \frac{K_i z_i}{1 + v\left(K_i - 1\right)} = K_i x_i^{(l)} \tag{16}$$

Step 5: $\mu_i^{(l)}$ and $\mu_i^{(v)}$ should be calculated using the Peng and Robinson (1976) equation

Step 6: Calculate $\phi_i^{(f)}$, $f = l, v$, using the Eq. (7)

Step 7: Calculate $f_i^{(f)}$, $f = l, v$, using the Eq.(17)

$$\ln\left(f_i^{(f)}\right) = \ln\left(\phi_i^{(f)}\right) + \ln\left(x_i^{(f)} P\right) \tag{17}$$

Step 8: Uptade the K_i factor,

$$K_i = \left(\frac{x_i^{(v)}}{x_i^{(l)}}\right)\left(\frac{f_i^{(l)}}{f_i^{(v)}}\right) \tag{18}$$

Step 9: Investigate the convergence, given by

$$F_i = \frac{x_i^{(l)}}{x_i^{(v)}} \cdot K_i \tag{19}$$

If $|F_i - 1| < \varepsilon$ for $i = 1, \ldots, r$ then the convergence is reached. Otherwise, return to step 2. For all cases presented herein $\varepsilon = 1 \times 10^{-7}$.

In this work, we used the cubic equation of state of Peng-Robinson (1976), because the cubic equation is smaller degree polynomial equation capable to represent behavior simultaneously the balance liquid-vapor.

4. The Mehra Algorithm

Mehra, Heidmann and Aziz (1983) developed some algorithms to accelerate method SSM. Their method is based on a relaxation parameter which is calculated as follows

$$\lambda \cong \left[\frac{g_{k-1}^T H_{k-1}^{-1} g_{k-1}}{g_{k-1}^T H_{k-1}^{-T} \left(g_{k-1} - g_k \right)} \right] \cdot \lambda_{k-1} \text{ and } \lambda_1 = 1 \tag{20}$$

where $g = \nabla G \left(N_1^{(v)}, N_2^{(v)}, \ldots, N_r^{(v)} \right)$ is the gradient of the Gibbs function and each element of $H = \nabla^2 G$ is given for

$$H_{ij} = \frac{1}{lv} \left[\delta_{ij} \frac{z_i}{\left(x_i^{(l)} x_i^{(v)} \right)} - 1 \right] \tag{21}$$

where δ_{ij} is the delta of Kronocker. Each component of the inverse matrix H is calculated using the next equation

$$H_{ij}^{-1} = vl \left(\frac{x_i^{(l)} x_i^{(v)}}{z_i} \right) \cdot \left[\delta_{ij} + \frac{\left(\frac{x_i^{(l)} x_i^{(v)}}{z_i} \right)}{S} \right] \tag{22}$$

where

$$S = 1 - \sum_{i=1}^{r} \left(\frac{x_i^{(l)} x_i^{(v)}}{z_i} \right) \tag{23}$$

To use this algorithm with the SSM ones should calculate the λ value, Eq. (20), and should use the next equation as a substitute of Eq. (18).

$$K_i = \left(K_i \right)_{(k-1)}^{1-\lambda_k} \left(\frac{\phi_i^{(l)}}{\phi_i^{(v)}} \right)^{\lambda_k} \tag{24}$$

Only positive values of λ are expected. Absolute value of λ must be used if Eq. (20) results in negative lambda. The relaxation parameter is set equal one. i. e., $\lambda = 1$, when $|\lambda_k \cdot g_k| > 6$, in this case, the algorithm suggested by Mehra et alii (1982) is similar to the SSM without acceleration.

5. The Armijo Condition

The Armijo condition is a classical procedure in the optimization methods. It allows adjustment of the step to guarantee progress towards the solution of the nonlinear problem at each iteration.

$$f\left(x_n + \lambda_n \cdot d_n \right) - f\left(x_n \right) \le \alpha \cdot \lambda_n \cdot \left(\nabla f\left(x_n \right)^T \cdot d_n \right) \text{ with } 0 < \alpha < 1 \tag{25}$$

Algorithm Model with Lineal Search (Inexact) of Armijo:

```
Parameters $\alpha$, $\beta \in (0,1)$, $k^* \in Z$ and $s \in \{0,1\}$.
Data $x_0 \in IR^n$.
Step 1: Do $n = 0$.
Step 2: If $\nabla f(x_n) = 0$, stop. Else, calculate a direction of descent $d_n$.
Step 3: Do $K^* = \{k \in Z / k \geq k^*\}$ and calculate the size of the step
        $\lambda_n = \beta^k = \max\{\beta^k / f(x_n + \beta^k d_n) - f(x_n) \leq \beta^k \cdot \alpha \cdot \nabla f(x_n)^T d_n\}$
Step 4: Do $x_{n+1} = x_n + \lambda_n \cdot d_n$, $n = n+1$. And return to the step 2.
```

4. Results

In order to evaluate the two proposed methods (SSM-Mehra and SSM-Armijo), two mixtures of acyclic alkanes (Tables 1 and 2) are used

Table 1 – Global composition for the mixture I used to evaluate all algorithms

Mixture I	
Element	Global composition (z_i)
Methane (CH_4)	0.669
n-butane (nC_4H_{10})	0.272
n-decane $(nC_{10}H_{22})$	0.029

Table 2 – Global composition for the mixture II used to evaluate all algorithms

Mixture II	
Element	Global composition (z_i)
Ethane (C_2H_6)	0.39842
Propane (C_3H_6)	0.29313
n-butane (nC_4H_{10})	0.20006
n-pentane (nC_5H_{12})	0.07143
n-hexane (nC_6H_{14})	0.03696

The mixture I was suggested by Henderson (1996), and its critical point is in the immediate vicinity of the pressure of 17,500 $[kPa]$ and the temperature of 343.15 $[K]$. The methane global composition is kept fixed and the n-butene and the n-decane is changed to move this mixture to near the critical point.

Table 3 shows the number of iterations and molar volume, v, for each global composition for mixture I. They are obtained from three different approaches presented in this work. It can be seen that the lowest number of iteration is reached by using the Mehra *et alii* (1983) algorithm. Furthermore, near the critical point, the number of iterations is very different between this method and the others. Similar behavior is observed in more than twenty different mixtures tested as can be seen in Lima (2003). The convergence behavior of these methods can be observed in Figure 1 and 2, where the convergence rate is plotted for each method analyzed herein.

Figure 1 – Convergence rate versus iteration for the Mixture I

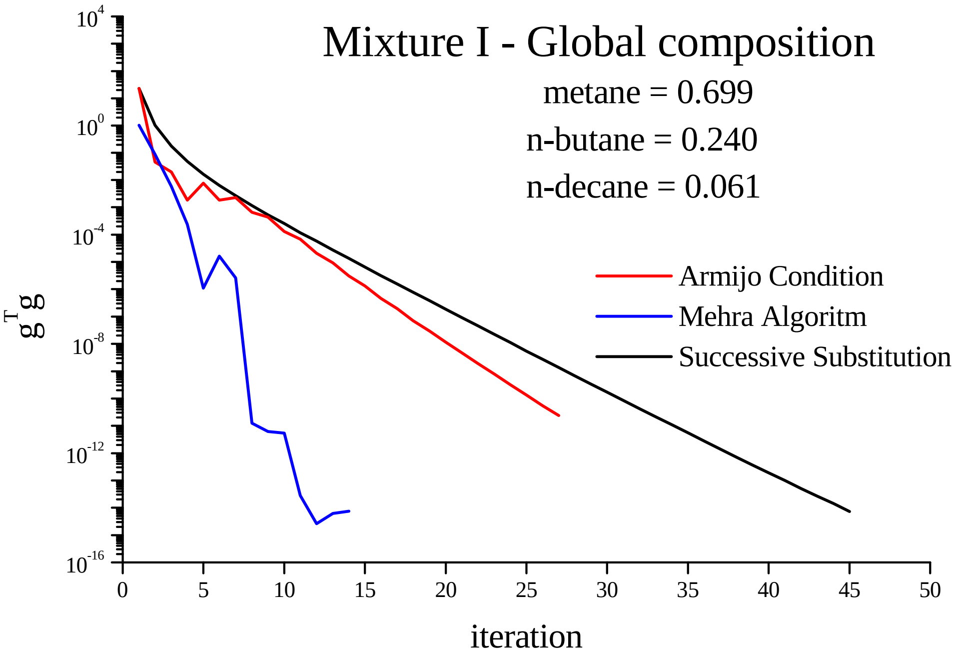
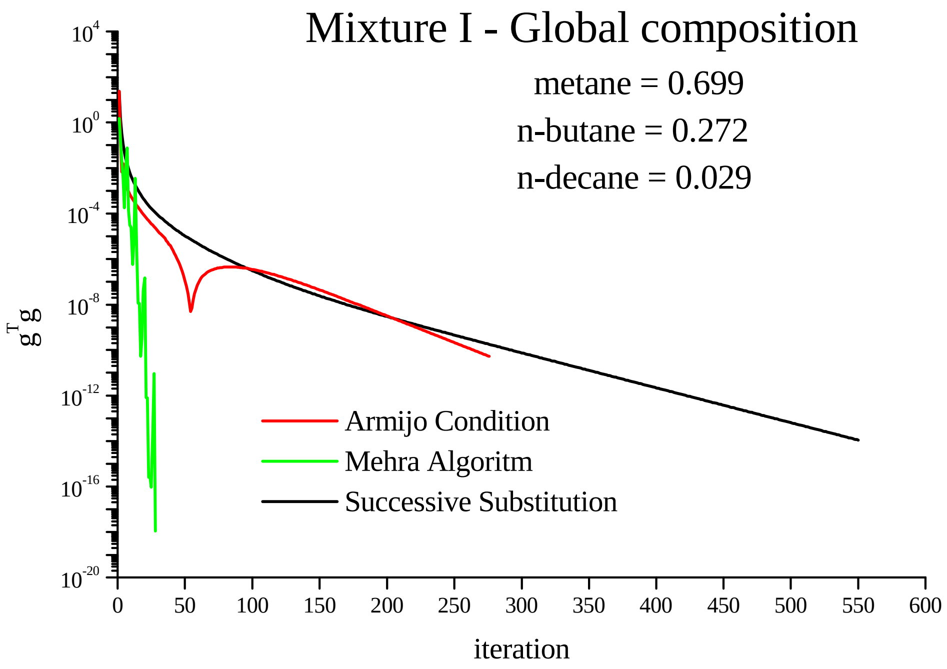


Figure 2 – Convergence rate versus iteration for the Mixture I



The number of iterations necessary to solve the Isothermal Flash Calculations and the resulting molar volume of the vapor phase for mixture II at several pressures are shown in Table 4. As can be noticed, the convergence of the Mehra *et alii* (1983) algorithm is faster then the convergence of the SSM and the SSM-Armijo. However, at pressures of 5520 and 5580 KPa, only the SSM-Mehra was able to correctly calculate the molar fraction of the vapor phase.

Table 3: Evaluation of the three methodologies for the mixture I

		SS		**Mehra**		**Armijo**	
$Z_{n-C_4H_{10}}$	$Z_{n-C_{10}H_{22}}$	iteration	v	iteration	v	iteration	v
0.240	0.061	45	0.48632	14	0.48632	27	0.48633
0.250	0.051	59	0.49500	15	0.49500	34	0.49502
0.260	0.041	91	0.50744	18	0.50744	50	0.50749
0.270	0.031	266	0.55002	21	0.55002	136	0.55029
0.271	0.030	352	0.56829	21	0.56829	178	0.56865
0.272	0.029	550	0.60647	28	0.60648	276	0.60702

Table 4: Evaluation of the three methodologies for the mixture II

	SS		**Mehra**		**Armijo**	
Pressure (kPa)	iteration	v	iteration	v	iteration	v
4310	15	0.83360	8	0.83360	7	0.83360
4480	17	0.78577	8	0.78577	11	0.78577
4830	22	0.66454	8	0.66454	16	0.66453
5170	33	0.48567	10	0.48567	23	0.48567
5340	47	0.33216	11	0.33216	33	0.33216
5410	60	0.23327	11	0.23327	43	0.23328
5448	73	0.16024	15	0.16024	51	0.16024
5500	114	0.01431	16	0.01431	78	0.01430
5520	299	1.00000	5	0.00000	225	1.00000
5580	90	0.00000	4	0.00000	59	1.00000

5. Conclusion

It is clear that the inclusion of the relaxation parameter suggested by Mehra *et alii* (1983) changes the behavior of the Successive Substitution method. With this relaxation parameter, it was necessary lesser iterations to solve all problems showed herein. Furthermore, for temperatures or/and pressures near of the critical point, the Mehra *et alii* (1983) algorithm is very successful in calculating the molar fraction of the vapor phase correctly and is faster than the other two methods.

7. Acknowledgements

The first and the second author acknowledge the financial support provided by CAPES – Coordenação de Aperfeiçoamento de Pessoal de Nível Superior and by FAPERJ – Fundação Carlos Chagas Filho de Amparo à Pesquisa do Estado do Rio de Janeiro

BIBLIOGRAPHICAL REFERENCES

Armijo, L., 1966, Minimization of Functions Having Lipschitz Continous First-Partial Derivatives, Pacific J. Mathematics, vol. 16, 1-3.

Callen, H. B., 1985, “Thermodynamics and an Introduction to Thermostatistics”, 2nd ed., John Wiley, New York.

Henderson, N. , 1993, “Minimizing the Gibbs Free Energy in a Box. A New Approach to the Problem of Vapor-Liquid Equilibrium” Ph.D. Thesis, Universidade Estadual de Campinas (UNICAMP), São Paulo, Brazil. (in Portuguese)

Henderson, N., Oliveira, J. R. Jr., Amaral Souto, H. P. e Pitanga Marques, R., 2001, *Modeling and Analysis of Isothermal Flash Problem and Its Calculation with the Simulated Annealing Algorithm*, Ind. Eng. Chem. Res., 6028-6038.

Henley, E. J. and Seader J. D., 1993, “Equilibrium-Stage Separation Operations in Chemical Engineering”, Wiley, New York.

Lima, M. J. N., 2003, Aceleração do Método de Substituição Sucessiva para o Problema do Flash Isotérmico. M. Sc. Dissertation, IPRJj/UERJ. *(in portuguese)*

Mehra, R.K., Heidemann, R. A. and Aziz, K 1982, *Soc. Pet. Eng. J, vol 22*, p. 61-68.

Mehra, R.K., Heidemann, R. A. and Aziz, K., 1983, *An Accelerated Sucessive Substituion Algorithm*, The Canadian Journal of Chemical Engineering, vol: 61, 590-596.

Peng, D. Y. and Robinson, D. B., 1976, “A New Two-Constant Equation of State”, Ind. Eng. Chem. Fundam. Vol. 15, pp. 59-64.

Rachford, H. H., Jr, e Rice, J. D., 1952, Procedure for Use of Eletronic Digital Computers in Calculation of Flash Vaporization Hidrocarbon Equilibrium, J, Pet, Technol,, 4-9.

Wilson, G., 1969, *A Modified Redlich-Kwong Equation of State, Application to General Physical Data Calculations*, Paper presented at the 65th National AICHE Meeting, Cleveland.