CHEMICAL ENGINEERING TRANSACTIONS

VOL. 74, 2019

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at www.cetjournal.it

Guest Editors: Sauro Pierucci, Jiří Jaromír Klemeš, Laura Piazza

ISBN 978-88-95608-71-6; **ISSN** 2283-9216

DOI: 10.3303/CET1974120

Smart Implementation of Bender Equation of State

Filippo Bisotti[a], Alessandro di Pretoro[a,b], Anna Dell'Angelo[a], Daniele Previtali[a], Andre Furtado Amaral[a], Ecem Muge Andoglu[c], Flavio Manenti[a,*]

[a] Dipartimento CMIC "Giulio Natta", Politecnico di Milano, Piazza Leonardo da Vinci, 32, 20133, Milan, Italy
[b] Laboratoire de Génie Chimique, Université de Toulouse, CNRS/INP/UPS, Toulouse, France
[c] Chemical Engineering Department, Bilecik Seyh Edebali University, Gülümbe, 11230, Bilecik, Turkey
flavio.manenti@polimi.it

In this paper matrix and vector products are exploited to reformulate Bender Equation of State. Finally, the new formulation is used to generate results which has been compared with experimental data sets available in literature and the analogous findings coming from different thermodynamic packages commonly used in Aspen Hysys for Air Separation Unit.

1. Introduction

In the last years, the need for more powerful and detailed thermodynamic tools to be used in process simulators has exponentially increased. A more precise prediction allows to save energy, to have a better control and to optimize of each unity (Lasala et al., 2018). For cryogenic separations it is very difficult to have robust and reliable thermodynamic packages; generally, mixtures are at low temperatures (so very far from ideal behaviour) or close to critical point for one or more compounds. In such operative conditions, for example, Cubic Equations of State (CEoS) exhibit some convergence and oscillation problems that are solved by using fitting-interaction parameters (Lasala et al., 2018). This numerical solution however is suitable only for specific mixtures. In 60's and 70's of the last century, Bender developed an Equation of State tailored on Air Separation Unit, however, his methodology in the development of the Equation of State can be easily translated to other compounds as already done by several researchers (Bühner et al., 1981; Platzer et al., 1993; Cibulka et al., 2001; Ghazouani et al., 2005). In any case, Bender Equation of State was originally developed to predict thermodynamic behaviour and properties in cryogenic conditions for nitrogen, argon and oxygen both pure or in mixture. However, in the original doctorate thesis by Bender, units of measure and univocal definitions of mixing rules for parameters and additional coefficients are missing. In this work, a smart and complete implementation of Bender Equation of State is proposed exploiting vector and matrix products to make the code more compact and to optimize the calculations.

2. Bender Equation of State for mixtures

Bender Equation of State is an evolution of the Benedict – Webber – Rubin EoS. As stated by Bender, among the many empirical equations of state published, only two have been largely applied for predicting phase equilibria in multicomponent systems. It is well known that BWR Equation is not suitable for use in the liquid region of both pure fluid and mixtures. Whereas, RKS and PR equation, despite their capacity to easily fit experimental PVT data at low density gas region or those of the liquid region, have unique sets of coefficients that, even if these are temperature dependent, are not able to provide good accuracy and reliability on the whole range of temperature and pressure. Bender EoS tries to achieve a good representation of the gas region as well as of the condensed phase including the two-phase region with one single function that has an expansive but still rational form (Bender, 1973). Bender EoS contains twenty fitting parameters (for each pure compound $a_{i,k}$) and six virial terms.

As shown in equation (1), Bender Equation of State relates pressure and temperature with the density of the system (therefore the reciprocal of the molar volume) and with prominent nonlinearity related to density:

Paper Received: 20 June 2018; Revised: 16 September 2018; Accepted: 17 December 2018

Please cite this article as: Bisotti F., Di Pretoro A., Dell'Angelo A., Previtali D., Furtado Amaral A., Andoglu E.M., Manenti F., 2019, Smart Implementation of Bender Equation of State, Chemical Engineering Transactions, 74, 715-720 DOI:10.3303/CET1974120

$$p = d_m T \left[R + \left(a_1 - \frac{a_2}{T} - B\right) d_m + C d_m^2 + D d_m^3 + E d_m^4 + F d_m^5 + \ (G + H d_m^2) d_m^2 \cdot \exp(-\mathrm{a}_{20} d_m^2)\right] \tag{1}$$

Parameters present in equation (1) are directly provided with both linear and nonlinear mixing rules. The mixing parameters are calculated starting from the twenty fitting parameters of pure compound and the phase composition. Indeed

- for mixing a_2, B and a_{20} geometrical mixing rule is applied

$$Y = \left(\sum_{k=1}^{3} \psi_k Y_k^{1/2}\right)^2 \tag{2}$$

- for a_1, D, E, F, G and H linear mixing rules

$$Y = \sum_{k=1}^{3} \psi_k Y_k \tag{3}$$

- for C cubic mixing rules are necessary

$$Y = \left(\sum_{k=1}^{3} \psi_k Y_k^{1/3}\right)^3 \tag{4}$$

The only exception to standard mixing rules is given by G mixing parameter. Bender found out that linear mixing rule alone was not correct due to binary mixture deviations. The additional term in the mixing rule, therefore, accounts for these deviations and it is the result of nonlinear regression on experimental data sets:

$$G = \sum_{k=1}^{3} \psi_k G_k + \sum_{i=1}^{3} \sum_{j=i+1}^{3} \left[\alpha_{ij} \left(\frac{100}{T}\right)^{m_{ij}} + \beta_{ij}\right] \psi_i \psi_j \tag{5}$$

Bender also estimated and provided α_{ij}, β_{ij} and m_{ij} values, that here are proposed in matrix form:

$$\alpha_{ij} = \begin{bmatrix} 0 & -0.0072 & 0.0057 \\ -0.0072 & 0 & 0.0095 \\ 0.0057 & 0.0095 & 0 \end{bmatrix} \quad \beta_{ij} = \begin{bmatrix} 0 & 0.007 & 0 \\ 0.007 & 0 & 0.004 \\ 0 & 0.004 & 0 \end{bmatrix} \quad m_{ij} = \begin{bmatrix} 0 & 6 & 8 \\ 6 & 0 & 4 \\ 8 & 4 & 0 \end{bmatrix} \tag{6}$$

The Y_k elements appearing in expressions (2-5) are functions of the twenty fitting parameters $a_{i,k}$ (obviously, a_1 is function of the k $a_{1,k}$ and the same is for a_2 and a_{20} with the right correspondences):

$$B_k = \frac{a_{3,k}}{T^2} + \frac{a_{4,k}}{T^3} + \frac{a_{5,k}}{T^4} \tag{7}$$

$$C_k = a_{6,k} + \frac{a_{7,k}}{T} + \frac{a_{8,k}}{T^2} \tag{8}$$

$$D_k = a_{9,k} + \frac{a_{10,k}}{T} \tag{9}$$

$$E_k = a_{11,k} + \frac{a_{12,k}}{T} \tag{10}$$

$$F_k = \frac{a_{13,k}}{T} \tag{11}$$

$$G_k = \frac{a_{14,k}}{T^3} + \frac{a_{15,k}}{T^4} + \frac{a_{16,k}}{T^5} \tag{12}$$

$$H_k = \frac{a_{17,k}}{T^3} + \frac{a_{18,k}}{T^4} + \frac{a_{19,k}}{T^5} \tag{13}$$

Moreover, starting from equation (1) and applying the definition of fugacity in mixture, it is possible to obtain an analytical expression. The result shows a dependence on temperature, pressure and phase compositions:

$$f_k^* = RT d_m \psi_k \cdot \exp\left(\frac{\vartheta}{R}\right) \tag{14}$$

$$\vartheta = \left(a_1^F + \frac{2a_2^F}{T} - 2B_F\right) d_m + \frac{3}{2} C_F d_m^2 + D_F d_m^3 + E_F d_m^4 + F_F d_m^5 + \left[\beta_1 - \beta_2 - (\beta_3 + \beta_4)\left(\frac{a_{20,k}}{a_{20}}\right)^{\frac{1}{2}}\right] d_m^2 \tag{15}$$

As for the pressure, the coefficients appearing in the fugacity equation (14) are function of both the a_i parameters and mixing ones (2-4). Their expressions are provided below:

$$a_1^F = \sum_{k=1}^{3} \psi_k a_{1,k} + a_{1,k} \tag{16}$$

$$a_2^F = \left(\sum_{k=1}^{3} \psi_k a_{1,k}^{1/2}\right) \cdot a_{1,k}^{1/2} \tag{17}$$

$$B_F = \left(\sum_{k=1}^{3} \psi_k B_k^{1/2}\right) \cdot B_k^{1/2} \tag{18}$$

$$C_F = \left(\sum_{k=1}^{3} \psi_k C_k^{1/3}\right)^2 \cdot C_k^{1/3} \tag{19}$$

$$D_F = \sum_{k=1}^{3} \psi_k D_k + \frac{D_k}{3} \tag{20}$$

$$E_F = \sum_{k=1}^{3} \psi_k E_k + \frac{E_k}{4} \tag{21}$$

$$F_F = \sum_{k=1}^{3} \psi_k F_k + \frac{F_k}{5} \tag{22}$$

$$H_F = 4\left(\sum_{k=1}^{3} \psi_k H_k\right) + H_k \tag{23}$$

While parameter G_F has slightly more complex expression that depends on the considered species:

$$G_F^{k=1} = 2G + G_k + \left\{\left[-0.0072\left(\frac{100}{T}\right)^6 + 0.007\right]\psi_2(1-\psi_1) + 0.0057\left(\frac{100}{T}\right)^8 \psi_3(1-\psi_1)\right\} \tag{24}$$

$$G_F^{k=2} = 2G + G_k + \left\{\left[-0.0072\left(\frac{100}{T}\right)^6 + 0.007\right]\psi_1(1-\psi_2) + \left[0.0095\left(\frac{100}{T}\right)^4 + 0.004\right]\psi_3(1-\psi_2)\right\} \tag{25}$$

$$G_F^{k=3} = 2G + G_k + \left\{0.0057\left(\frac{100}{T}\right)^8 \psi_1(1-\psi_3) + \left[0.0095\left(\frac{100}{T}\right)^4 + 0.004\right]\psi_2(1-\psi_3)\right\} \tag{26}$$

Finally

$$\beta_1 = \frac{G_F + H_F/a_{20}}{2a_{20}d_m^2} \tag{27}$$

$$\beta_2 = \exp(-a_{20}d_m^2)\left[\frac{G_F}{2a_{20}d_m^2} + \frac{H_F}{2a_{20}}\left(1 + \frac{1}{a_{20}d_m^2}\right)\right] \tag{28}$$

$$\beta_3 = \frac{G}{a_{20}d_m^2}\left[1 - \exp(-a_{20}d_m^2) \cdot (a_{20}d_m^2 + 1)\right] \tag{29}$$

$$\beta_4 = \frac{H}{(a_{20}d_m)^2}\left\{2 - \exp(-a_{20}d_m^2) \cdot \left[(a_{20}d_m^2 + 1)^2 + 1\right]\right\} \tag{30}$$

3. Matrix and vector product to estimate Bender Equation of State coefficients

The equations of the previous section show a very high complexity degree. In order to speed up the calculations, it is worth to exploit matrixes and vectors products especially for vapour-liquid equilibria. Indeed, looking at expressions (7-13) it is evident that Y_k coefficients are elements of vectors whose length is NC; moreover, they are composition independent.

Therefore, defining a composition matrix whose dimensions are $NP \times NC$ (NP number of phase and NC number of compounds) as follows:

$$\bar{\bar{\psi}} = \begin{bmatrix} \overline{\psi_{liq}} \\ \overline{\psi_{vap}} \end{bmatrix} = \begin{bmatrix} \bar{x} \\ \bar{y} \end{bmatrix} = \begin{bmatrix} x_1 & x_2 & x_3 \\ y_1 & y_2 & y_3 \end{bmatrix} \tag{31}$$

Is straightforward to compute all the parameters defined in expressions (2-4) through matrix products.

These operations will provide as results vectors of length NP whose first elements are related to the liquid phase, while the second ones to the vapour:

$$\underset{[NP \times 1]}{\bar{Y}} = \underset{[NP \times NC]}{\bar{\bar{\psi}}} \cdot \underset{[NC \times 1]}{\bar{Y_k}} \tag{32}$$

$$\bar{Y} = \left(\bar{\bar{\psi}} \cdot \overline{Y_k^m}\right)^n = \left(\begin{bmatrix} x_1 & x_2 & x_3 \\ y_1 & y_2 & y_3 \end{bmatrix} \cdot \begin{bmatrix} Y_1^m \\ Y_2^m \\ Y_3^m \end{bmatrix}\right)^n = \begin{bmatrix} \left(\sum_{k=1}^{3} x_k Y_k^m\right)^n \\ \left(\sum_{k=1}^{3} y_k Y_k^m\right)^n \end{bmatrix} = \begin{bmatrix} Y_{liq} \\ Y_{vap} \end{bmatrix} \tag{33}$$

Obviously, for linear mixing rule (3) $m = 1$ and $n = 1$, while according to nonlinear combination rules (2) and (4) the power exponents are $m = 0.5$, $n = 1$ and $m = 1/3$, $n = 3$ respectively.

The evaluation is fairly more complex for the fugacity coefficients (16-30). In this case, instead of vectors, the results are matrixes with dimensions $NP \times NC$. Neglecting powers, which have to be applied as explained before element-by-element, the results are:

$$\underset{[NP \times NC]}{\overline{\overline{Y_F}}} = \left(\underset{[NP \times NC]}{\bar{\bar{\psi}}} \cdot \underset{[NC \times 1]}{\overline{Y_k}}\right) \cdot \underset{[1 \times NC]}{\overline{Y_k^T}} \tag{34}$$

$$\overline{\overline{Y_F}} = \bar{Y} \cdot \overline{Y_k^T} = \begin{bmatrix} Y_{liq} \\ Y_{vap} \end{bmatrix} \cdot \begin{bmatrix} Y_1 & Y_2 & Y_3 \end{bmatrix} = \begin{bmatrix} Y_{liq}Y_1 & Y_{liq}Y_2 & Y_{liq}Y_3 \\ Y_{vap}Y_1 & Y_{vap}Y_2 & Y_{vap}Y_3 \end{bmatrix} \tag{35}$$

analogously,

$$\underset{[NP \times NC]}{\overline{\overline{Y_F}}} = \left(\underset{[NP \times NC]}{\bar{\bar{\psi}}} \cdot \underset{[NC \times 1]}{\overline{Y_k}}\right) + \underset{[1 \times NC]}{\overline{Y_k^T}} \tag{36}$$

$$\overline{\overline{Y_F}} = \bar{Y} + \overline{Y_k^T} = \begin{bmatrix} Y_{liq} \\ Y_{vap} \end{bmatrix} + \begin{bmatrix} Y_1 & Y_2 & Y_3 \end{bmatrix} = \begin{bmatrix} Y_{liq} + Y_1 & Y_{liq} + Y_2 & Y_{liq} + Y_3 \\ Y_{vap} + Y_1 & Y_{vap} + Y_2 & Y_{vap} + Y_3 \end{bmatrix} \tag{37}$$

Calculation are furtherly speeded up by decomposing the third additive terms in expressions (24-26). These can be collected inside a vector by previously setting:

$$\alpha = -0.0072\left(\frac{100}{T}\right)^6 + 0.007; \quad \beta = 0.0057\left(\frac{100}{T}\right)^8; \quad \gamma = 0.0095\left(\frac{100}{T}\right)^4 + 0.004 \tag{38}$$

$$\overline{G_k^p} = \begin{bmatrix} (\alpha\psi_2 + \beta\psi_3)(1 - \psi_1) \\ (\alpha\psi_1 + \gamma\psi_3)(1 - \psi_2) \\ (\beta\psi_1 + \gamma\psi_2)(1 - \psi_3) \end{bmatrix} \tag{39}$$

$$\overline{G_k^p} = \begin{bmatrix} 1 - \psi_1 & 0 & 0 \\ 0 & 1 - \psi_2 & 0 \\ 0 & 0 & 1 - \psi_3 \end{bmatrix} \cdot \begin{bmatrix} (\alpha\psi_2 + \beta\psi_3) \\ (\alpha\psi_1 + \gamma\psi_3) \\ (\beta\psi_1 + \gamma\psi_2) \end{bmatrix} \tag{40}$$

$$\overline{G_k^p} = \begin{bmatrix} 1 - \psi_1 & 0 & 0 \\ 0 & 1 - \psi_2 & 0 \\ 0 & 0 & 1 - \psi_3 \end{bmatrix} \cdot \left\{ \begin{bmatrix} 0 & \alpha & \beta \\ \alpha & 0 & \gamma \\ \beta & \gamma & 0 \end{bmatrix} \cdot \begin{bmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \end{bmatrix} \right\} = \overline{\overline{\psi_D}} \cdot \left\{\bar{\bar{M}} \cdot \bar{\psi}\right\} \tag{41}$$

Matrix products have to be performed for each phase present in the system. Finally, a matrix is obtained:

$$\overline{\overline{G_k^f}} = \begin{bmatrix} \left(\overline{G_k^p(\bar{\psi} = \bar{x})}\right)^T \\ \left(\overline{G_k^p(\bar{\psi} = \bar{y})}\right)^T \end{bmatrix} \tag{42}$$

$$\underset{[NP \times NC]}{\overline{\overline{G_F}}} = \underset{[NP \times 1]}{2\bar{G}} + \underset{[1 \times NC]}{\overline{G_k^T}} + \underset{[NP \times NC]}{\overline{\overline{G_k^f}}} \tag{43}$$

4. Comparison with largely-used Equation of State in ASU

At this point it is useful and interesting to test and compare Bender Equation of State (B) performance with respect to two among the most commonly used thermodynamic packages in Air Separation Unit: Peng-Robinson (PR) and Benedict-Webber-Rubin (BWR). For simplicity, the bubble and dew problems in pressure are performed on fixed dry air composition. This means that the composition vector $\bar{z}$ is equal to $z_{N_2} = 0.7812$, $z_{O_2} = 0.2096$ and $z_{Ar} = 0.0092$. In the case of bubble problem, the assigned composition corresponds to that of the liquid, while in the dew one to that of the vapour phase. Experimental data set is directly taken from NIST Database published in several specialized papers (Jacobsen at al., 2000). Bender Equation of State has been implemented in a MatLab® code and in a Visual Studio C++ 2013 source in which BzzMath Library© was embodied, while, concerning BWR and PR Equation of State, the thermodynamic packages available in Aspen Hysys V10 ware used. The results are compared in Figure 1 and Figure 2.

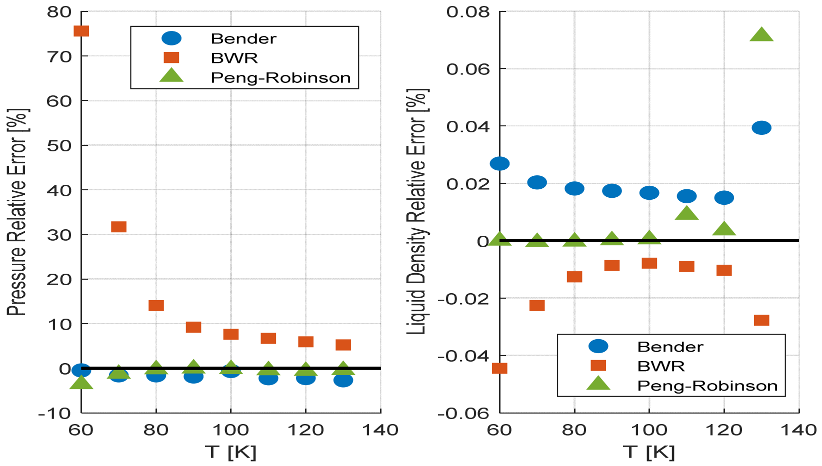

Figure 1: comparison of bubble pressure (left) and liquid phase density (right) relative errors of dry air at different temperatures

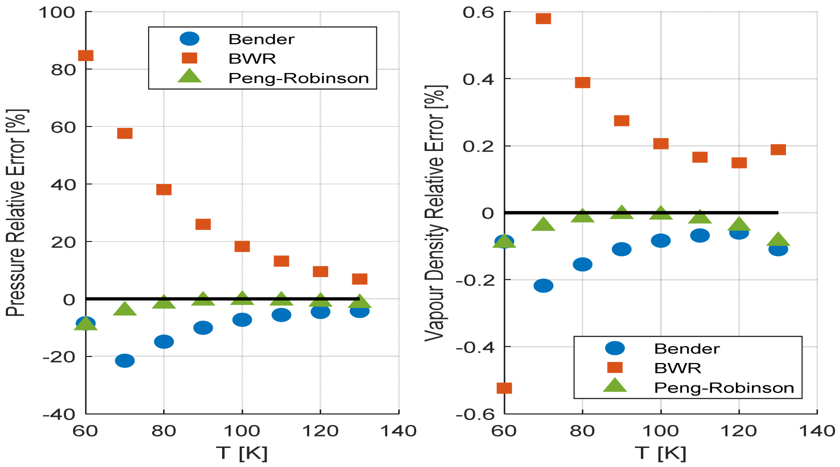

Figure 2: comparison of dew pressure (left) and vapour phase density (right) relative errors of dry air at different temperatures

5. Conclusions

Despite its complexity, Bender Equation of State shows a very good accuracy and reliability both in the bubble and dew problem in the region of interest for Air Separation Unit. With respect to PR Equation of State, Bender model exhibit more stability near the critical point due to special nonlinear fitting and regression performed in this region by Bender in order to a very robust response of his Equation of State. Whereas, both thermodynamics models show lower accuracy and precision near the triple point. Considering that, generally, Air Separation Unit works far from both, extremely low temperature and the critical point of the mixtures, due to control and technical reasons, the temperature range is limited to moderate temperature. Therefore, future developments may concern on how to increase Bender Equation of State prediction capacity in this range of interest in order to improve its performance and reliability comparing to another thermodynamic tools already available in simulation software.

Notation and Unit of Measure

Symbol	Meaning	Unit of measure / notes
p	System Pressure	$[kPa]$ using original $a_{i,k}$ (Bender, 1973)
d_m	Molar density	$[mol/L]$ using original $a_{i,k}$ (Bender, 1973)
R	Ideal gas constant	$R = 8.314472\ [kPa \cdot L/(mol \cdot K)]$
T	Temperature	$[K]$ absolute temperature
k	Compound Index	Nitrogen (1), argon (2) and oxygen (3) following (Bender, 1973)
$a_{i,k}$	Bender coefficients	$i = 1{,}2{,}3 \ldots .20$ are provided in Bender thesis (Bender, 1973)
ψ_k	Generic molar fraction	
$\bar{\psi}$	Generic composition vector	$\bar{x}, \bar{y}$ are respectively vapour liquid composition vectors
NP	Number of phases	
NC	Number of compounds	
$\bar{\bar{\psi}}$	Composition matrix $[NP \times NC]$	First row for liquid phase and second one for vapour phase
Y_k	Pure virial coefficients	Reference expressions are (7-13)
$\bar{Y_k}$	Vector of pure virial coefficients	Vector collecting the generic Y_k elements previously defined
$\bar{Y}$	Mixing coefficient in equation (1)	a_1, a_2, a_{20}, B, C, D, E, F, G, H. Mixing rules are classified and given in equations (2-5); they are vectors of length $[NP \times 1]$
$a_{ij}, \beta_{ij}, m_{ij}$		Matrix element for estimation of mixing parameter G in (5)
f_k^*	Fugacity coefficient in mixture	$[kPa]$ fugacity in mixture defined in equation (15)
Y_F	Generic coefficients for fugacity	Y_F is a matrix element in multiphase system
$\overline{\overline{Y_F}}$	Matrix of fugacity parameters	Reference equations (16-28), matrix dimensions $[NP \times NC]$
α, β, γ		Elements of matrixes defined in (38)

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