Brazilian Journal
of Chemical
Engineering

ISSN 0104-6632
Printed in Brazil
www.scielo.br/bjce

CC BY

Vol. 35, No. 03, pp. 1129-1140, July - September, 2018
dx.doi.org/10.1590/0104-6632.20180353s20170216

FRACTIONATION PROCESS OF ESSENTIAL OILS BY BATCH DISTILLATION

Rafael N. Almeida[1], Rafael de P. Soares[1] and Eduardo Cassel[2,]*

[1] PPGEQ – DEQUI, Universidade Federal do Rio Grande do Sul, Rua Engenheiro
Luiz Englert, s/nº - Prédio 12204, 90040-040. Porto Alegre, RS, Brasil.
[2] Faculdade de Engenharia, Pontifícia Universidade Católica do Rio Grande do Sul,
Avenida Ipiranga 6681, Pr.30, 90619-900, Porto Alegre, Brasil.

(Submitted: April 24, 2017; Revised: August 4, 2017; Accepted: August 7, 2017)

Abstract - The greatest obstacle in simulating processes involving essential oils is the small number of thermophysical properties and experimental data available in the literature. In this work, thermodynamic models are investigated in order to predict such properties, which are requisites for the modelling and simulation of the *Eucalyptus* essential oil batch distillation processes. A group contribution method was used to predict the vapor pressure (CSGC-PVR) when experimental data were unavailable. Regarding the activity coefficients, a fully predictive model based on quantum calculations (COSMO-SAC) is used. Moreover, this work also uses those predicted properties in a dynamic model, capable of describing the fractionation process by batch distillation. The simulations were performed in the equation-oriented simulator EMSO to demonstrate the feasibility of the proposed method. The proposed method suggests a simulated recovery of a 98.89% eucalyptol fraction from *E. globulus* and a 98.53% citronellal fraction from *E. citriodora*.

Keywords: *Eucalyptus* essential oil, thermodynamic modeling, simulation, COSMO-SAC, dynamic model.

INTRODUCTION

Essential oils are a mixture of terpenes and other volatile compounds, many of them with important industrial applications, in medicine, pharmacology, cosmetics and food industry (Bonaccorsi *et al*. 2009). However, if any specific compound has a practical application, it is desirable to properly separate the mixture, adding value to the final product. *Eucalyptus citriodora* oil contains about 85% of the monoterpenoids citronellol and citronellal, whereas *Eucalyptus globulus* oil contains 70-90% of eucalyptol (1,8-cineole), another major monoterpenoid (Juergens *et al*., 1998). Both citronellol and citronellal are used as starting materials for the production of fragrances (Bauer *et al*., 2008). The first is also used in insect repellents (Guenther, 2013) and the second is effective against bacterial and fungal infections (Pattnaik *et al*., 1996; Ramezani *et al*., 2002). Eucalyptol is widely used in medicinal, perfumery and flavor preparations (Babu and Singh, 2009; Baxendale, 2015) and notably it has been reported to present various tumor inhibitory properties (Juergens *et al*., 1998).

Most terpenes are thermally unstable, decomposing or oxidizing at high temperatures or in the presence of light or oxygen (Simoes, 2001). Batch vacuum distillation works at lower temperatures and offers flexibility to operate with different mixtures in the same industrial plant and also the possibility of operating with small volumes (Jimenez *et al*., 2002; Mujtaba, 2004). The quality of the distillate can be controlled through manipulation of the reflux ratio, which affects the dynamics of the process (Adari and Jana, 2008; Garcia *et al*., 2014; Reid *et al*., 1987).

**Corresponding author.* E-mail address: cassel@pucrs.br

The literature is limited about fractionation of essential oil components using batch vacuum distillation. Farah *et al.* (2006) report the use of fractional distillation to separate components of *Myrtus communis* L. without the use of vacuum. Castillo-Herrera *et al.* (2007) reported the use of fractional distillation during the hydrodistillation process to obtain *Lippia graveolens* H.B.K essential oil and to increase the phenolic content. Regarding the modeling and simulation of essential oil fractionation processes, it has received little attention from the scientific community because of its complexity and highly specific application. Since an essential oil is a mixture of thermolabile compounds and has little known physical properties, studies on the subject are scarce. Other registered studies treat the distillation process as a step to obtain fractions in order to perform chemical and biological analysis, describing the laboratory scale apparatus, but not considering it as the main objective (Babu and Singh, 2009; Babu and Kaul, 2007; Castillo-Herrera *et al.*, 2007; Farah *et al.*, 2006). Two of them even use the reflux ratio strategy and are focused on the batch distillation process, but none of them describe the phenomena involved in the process and all the aspects of the phase equilibrium (Beneti *et al.*, 2011; Silvestre *et al.*, 2016).

The essential oil industry is mostly built on a heuristic basis, due to its long tradition and relation to the perfumery industry. The development of tools that could assist the design and project of essential oil fractionation columns is indispensable when one tries to predict the behavior of such complex mixtures. The estimation of physical properties is the crucial step when it comes to the simulation of essential oil rectification processes, due to the reduced experimental data available. Thus, this work seeks to define thermodynamic correlations that describe the properties required for the calculation of phase equilibrium, vapor pressure and activity coefficient.

Most of the empirical equations for the vapor pressure are based on integrated forms of the Clausius-Clapeyron relation, varying according to the dependence of the enthalpy of vaporization on temperature, the Antoine equation (Antoine, 1888) being the most widespread of all. However, the parameters for such equations must be estimated by correlation of experimental data and care should be taken when extrapolating these equations. In this way, there are numerous equations based on the theory of corresponding states and group contribution method in order to estimate the vapor pressure (Ambrose and Walton, 1989; Asher *et al.*, 2002; Pankow and Asher, 2008; Riedel, 1954; Tu, 1994; Wagner, 1973).

The most significant method for the prediction of activity coefficients is the UNIFAC method and its variations (Fredenslund, 2012). Despite the wide application of this method, it requires a large number of experimental data for the determination of the interaction parameters between each pair of groups. For the application in the present work, parameters for some of the groups and subgroups of the molecules of interest were not found in the literature, preventing the direct use of these models. The COSMO-SAC (Gerber and Soares, 2010) method arises as an alternative for obtaining the activity coefficient.

On the other hand, the batch distillation process is widely studied and numerous models have been developed, but all these were employed for the separation of well-known mixtures such as petroleum fractions (Galindez and Fredenslund, 1988; Greaves *et al.*, 2003; Logsdon and Biegler, 1993; Mujtaba and Macchietto, 1997; Wendt *et al.*, 2000). Therefore, this work also aims to define a dynamic model, validating the proposed method by combining the mass balance model and the thermodynamic correlations in order to describe the separation of essential oil constituents by batch vacuum distillation.

METHODOLOGY

Essential oils

For the proposed method, the essential oils extracted from two different plant species were selected: *Eucalyptus citriodora* Hook and *Eucalyptus globulus* Labill. These essential oils were chosen due to their large production and economical potential of the fractions (Batish *et al.*, 2008). The characterizations performed by Maciel *et al.*, (2010) are used as the standard compositions for the two essential oils in this work. *Eucalyptus citriodora* essential oil has citronellal as the major component, and eucalyptol is the main constituent of *Eucalyptus globulus* essential oil.

Phase equilibrium

At low pressures, one can perform the calculation of phase equilibrium using the modified Raoult's law (Eq. 1) without loss of accuracy, since the vapor phase behaves as an ideal gas and the effects of non-ideality in the liquid phase are accounted for by the activity coefficient (Reid *et al.*, 1987):

$$y_i P = x_i \gamma_i P_i^{sat} \quad (1)$$

where P is the system pressure; y_i and x_i are the molar fractions in the vapor and liquid phases, respectively. Eq. 1 depends on two main thermodynamic properties, the vapor pressure of pure substances $\left(P_i^{sat}\right)$ and the activity coefficient of component i in a mixture (γ_i).

Vapor pressure

The vapor pressure $\left(P_i^{sat}\right)$ of pure substances is one of the crucial properties of chemical engineering process design. Although the literature contains a large experimental database for most of the usual compounds, the data availability for essential oil constituents is still small, due to its characteristics, long chains and specific functional groups. This justifies the need of predictive methods to relate the vapor pressure as a function of temperature for these compounds (Pankow and Asher, 2008).

Li *et al.* (1994) proposed a method to estimate the physical properties of pure components by combining the theory of corresponding states with the group contribution method. The feature of this method, referred to as CSGC (Corresponding-States with Group Contribution), is the use of the internal critical properties concept, determined by the group contribution method (Eqs. 2 and 3).

$$T_c^* = T_b / \left[A_T + B_T \sum_i^M n_i \Delta T_i + C_T \left(\sum_i^M n_i \Delta T_i \right)^2 + D_T \left(\sum_i^M n_i \Delta T_i \right)^3 \right] \quad (2)$$

$$P_c^* = \frac{101{,}325 \ln(T_b)}{\left[A_P + B_P \sum_i^M n_i \Delta P_i + C_P \left(\sum_i^M n_i \Delta P_i \right)^2 + D_P \left(\sum_i^M n_i \Delta P_i \right)^3 \right]} \quad (3)$$

The parameters ΔT_i and ΔP_i are estimated by the author and are presented for each functional group in the original work, as well as the constants A_T, B_T, C_T e D_T e A_P, B_P, C_P and D_P . Once these internal critical properties are obtained, they are applied in the corresponding states method (Eq. 4) to calculate the reduced vapor pressure. Therefore, this method combines the simplicity and precision of the first method and the extensive estimation capacity of the second method.

$$\ln P_r^{sat*} = A - \frac{B}{T_r^*} + C \ln T_r^* + D T_r^{*6} \quad (4)$$

The CSGC method is capable to estimate numerous physical properties, but since in this paper we only deal with vapor pressure, it will be designated as CSGC-PRV, as presented by the author. This method has only two input variables; the functional groups of the molecule and its normal boiling temperature (T_b).

Activity coefficient

In this study the COSMO-SAC method (Lin and Sandler, 2002) was employed to calculate activity coefficients. This method is based on the COSMO theory (Conductor-like Screening Model) (Klamt, 1995). This model, based on computational quantum mechanics, allows the prediction of activity coefficients without any experimental data. COSMO-RS was the first model of this type proposed by Klamt (1995) and, since then, various versions have been published aiming at both a greater range of possible applications and higher accuracy of the method. The calculations required for using this kind of models have been implemented in numerous quantum chemistry software packages. In this work the MOPAC (Molecular Orbital Package) (Stewart, 1990) package was used.

Lin and Sandler (2002) proposed a variation of the COSMO-RS, called COSMO-SAC (COSMO Segment Activity Coefficient). The COSMO-SAC technique, as well as the COSMO-RS method, use only the molecular structure and its surface charge density determined by COSMO computations to predict the activity coefficient of substances in mixtures. In the COSMO-SAC model, the activity coefficient can be defined as the result of two contributions (Eq. 5):

$$\ln \gamma i = \frac{\beta (\Delta G_S^{*res} - \Delta G_i^{*res})}{RT} + \ln \gamma_i^{SG} \quad (5)$$

The first contribution is the difference between the free energies of restoring the charges around the solute molecule in solution S and restoring the charges in a pure liquid i, scaled by an empirical factor β. The second contribution is the Staverman-Guggenheim (SG) combinatorial term. The residual part accounts mainly for the effects that arise from energetic interactions between groups, as the combinatorial part accounts for size and shape differences in the molecules (Garber and Soares, 2013). In the present work, this variant of the COSMO-SAC method implemented in the JCOSMO package is used and consists of a Java code developed by Gerber and Soares (2010).

Dynamic model - batch distillation

Simulating the rectification process of a complex mixture can require a considerable computational effort. Thereby, the introduction of a few simplifications leads to a reduction in the number of equations and variables, without significant loss of accuracy (Mujtaba, 2004). The model implemented in this work consisted of the differential molar balances and equilibrium relationships. It takes as fundamental considerations a constant liquid holdup on each tray and in the condenser; negligible vapor holdup and total condensation. These hypotheses generate constant internal flowrates and eliminate the need to use hydrodynamic correlations between trays. The vaporization rate is determined as a function of the enthalpy of vaporization and the reboiler composition. The temperature profile is calculated as a result of the thermodynamic equilibrium. Other important assumptions are also made, such as the established phase equilibria and perfect tray, reboiler and condenser mixing, adiabatic operation and no sub cooling in the condenser (Domenech and Enjalbert, 1981).

The mass balance for a column with N trays (stages), in reference to a generic compound i in the condenser, can be written as:

$$\frac{dx_{i,N+1}}{dt} = \frac{V}{H_{N+1}}\left(\mathrm{y}_{i,N} - x_{i,N+1}\right) \tag{6}$$

where V is the vapor molar flow rate; H_{N+1} is the condenser holdup; and y_i and x_i are the vapor and liquid compositions, respectively. The mass balance for the trays from $p=1,2,..,N$ is given by:

$$\frac{dx_{i,p}}{dt} = \frac{V}{H_p}\left[\mathrm{y}_{i,p-1} - \mathrm{y}_{i,p} + \frac{R}{R+1}\left(x_{i,p+1} - x_{i,p}\right)\right] \tag{7}$$

where H_p is the liquid holdup in the tray p and R is the reflux ratio. The reboiler and the global mass balances are described in Eq. 8 and Eq. 9, respectively:

$$\frac{dx_{i,0}}{dt} = \frac{V}{S}\left[x_{i,0} - \mathrm{y}_{i,0} + \frac{R}{R+1}\left(x_{i,1} - x_{i,0}\right)\right. \tag{8}$$

$$\frac{dS}{dt} = -\frac{V}{R+1} \tag{9}$$

The vapor molar flow rate V is constant (Eq. 10) because there is no holdup in both vapor and liquid phases and is determined according to the heat power $\dot{Q}$ supplied to the system:

$$V = \frac{\dot{Q}}{\sum_{i=1}^{n} x_{i,0}\,\Delta h_i^{vap}} \tag{10}$$

The model also incorporates for the vapor and liquid phases the thermodynamic equilibrium relationship (Eq. 1) and the restriction on the composition sums (Eq. 11 and Eq. 12) as follows:

$$\sum_{i=1}^{n} x_{i,T} = 1 \tag{11}$$

$$\sum_{i=1}^{n} \mathrm{y}_{i,T} = 1 \tag{12}$$

The dynamic nature of the batch distillation process implies the withdrawal of distillate cuts, each one determined by a pre-established endpoint (temperature, composition, etc.). At the beginning of the process, the top product is essentially constituted by the most volatile substances. They should be collected in a vessel until their depletion in the mixture. Subsequently, heavier substances will become part of the top product and must be collected in a different vessel, featuring different cuts in the distillate.

A possible way to mathematically describe the collection of different cuts in different vessels is via integrators (Eq. 13), as follows:

$$\frac{dD_i^{Ta}}{dx} = D \cdot x_{i,N+1} \cdot k_{Ta} \tag{13}$$

where D is the distillate rate, D_i^{Ta} is the accumulation of component i in the tank Ta and K_{Ta} is the tank trigger key. This key is always zero, except for the case where the vessel Ta is collecting the desired fraction. The total accumulation (Eq. 14) and composition (Eq. 15) are calculated based on the accumulation by component:

$$D_T^{Ta} = \sum_{i=1}^{n} D_i^{Ta} \tag{14}$$

$$x_i^{Ta} = D_i^{Ta} \Big/ \sum_{i=1}^{n} D_i^{Ta} \tag{15}$$

where $\mathrm{x}_\mathrm{i}^{Ta}$ is the composition of component i in the tank Ta and D_T^{Ta} is the total molar accumulation in the tank. With these indicators, the recovery and the different cut composition can be computed in the simulator.

A specific cutoff criterion for each processed mixture should be adopted in order to obtain a product with high purity. In general, the instant composition analysis of the distillate is not possible, but can be inferred from the top temperature of the column, since the two properties are closely related. Thus, the top temperature plateaus are used for making a decision about when the distillate accumulation tanks must be switched.

The enthalpy of vaporization of each substance is obtained directly through the Clausius-Clapeyron relationship valid for moderate pressures and vapor behavior as an ideal gas, since the vapor pressure is known in the desired temperature range. The calculation (Eq. 16) is performed in an external routine and the values entered in the model.

$$\frac{dP_i^{sat}}{dT} = \frac{P_i^{sat}\Delta h^{vap}}{RT^2} \quad (16)$$

Simulations

Once the mixture to be separated is defined and the substances involved are known, the molecules were created in the software Avogadro (Hanwell *et al.*, 2012), where the molecular structure is first optimized in order to reach the lowest energy state via the Universal Force Field (UFF) with a steepest descent algorithm. The file with the atomic coordinates is then processed by the quantum chemical package MOPAC (Stewart, 1990), screening the surface charge density which generates a COSMO distribution profile (σ-profile).

The process model was implemented in the generic process simulator EMSO (Soares and Secchi, 2003). EMSO is an equation-oriented process simulator, suitable for dynamic simulations. The thermodynamic properties required for the dynamic model were calculated by the methods described above and loaded into the industrial processes simulator iiSE thermodynamic package, where the creation and edition of substances and properties take place quite efficiently. A communication plugin is established between the two programs, so that the properties are updated dynamically. Thus, the σ-profile and the coefficients for the estimation of the vapor pressure are inserted to iiSE, which in turn returns the equilibrium data to the EMSO simulator.

The batch distillation model developed in this work, due to its transient nature, requires the liquid molar fractions in each tray as initial conditions. Since most batch distillation processes start first by putting the column in total reflux until a steady state is achieved (Mujtaba, 2004), in this work, the model initial conditions are set by submitting the column to a system of total reflux, establishing the equilibrium throughout the column. Once the steady state of a total reflux system is reached, the compositions are stored and used as a starting point to the separation batch.

The essential oil rectification process simulation main objective is to determine the total number of fractions, the recovery of each cut and its composition. For this, a constant reflux ratio, R = 8, was assumed for all experiments, which was defined in accordance with the Mujtaba (2004) recommendation. Different strategies can be adopted in this regard, but extensive research is required for an optimum reflux ratio. The column has 18 trays and a total column holdup of 5%, with constant pressure of 10 kPa.

RESULTS AND DISCUSSION

Vapor Pressure

The first step of this study was the validation of the predictive method CSGC-PRV used to calculate the vapor pressure of pure compounds. With the exception of compounds with more economic importance, vapor pressure experimental data for most of the compounds required for this work were not found in the literature.

The vapor pressure of four substances found in the eucalyptus essential oils (α-pinene, β-pinene, citronellol, isopulegol) was compared with the values obtained by the predictive method (CSGC-PRV). All the experimental data were obtained from the NIST Standard Reference Database Number 69, except for isopulegol (Kobe *et al.*, 1941). Figure 1 shows curves for experimental data and CSGC-PRV model data.

The differences between the experimental data and the values predicted from the CSGC-PRV model reach the maximum of 5.39%, and the maximum absolute error of 3.53 kPa. The results are good, taking into account the complexity of the molecules and the fact that the model uses only the normal boiling temperature and their functional groups. Li *et al*. (1994) also indicate the use of this model for compounds with long carbon chains as well as for polar compounds, in accordance with the molecules used in this work. As a demonstration of the accuracy of the method, the authors performed a comparison between other predictive methods, and the CSGC-PRV showed deviations smaller than the Riedel (1954), Vetere (1991) and Gomez-Nieto and Thodos (1977) methods.

Activity coefficient

As for the activity coefficient calculations, to the best of our knowledge there are no experimental data available for all the components present in eucalyptus essential oils, implying the use of predictive models. However, since all molecules involved have similar chemical nature, activity coefficients near to an ideal behavior ($\gamma \approx 1$) are expected. Table 1 lists the activity coefficients predicted by the COSMO-SAC method for the initial composition of two eucalyptus essential oils.

Most of the eucalyptus essential oil constituents are terpenoids, with different chain sizes, conferring significant differences in their vapor pressures, but still preserving a high chemical affinity. The JCOSMO program allows the visualization of the charge density surface of the molecule, predicted by the COSMO

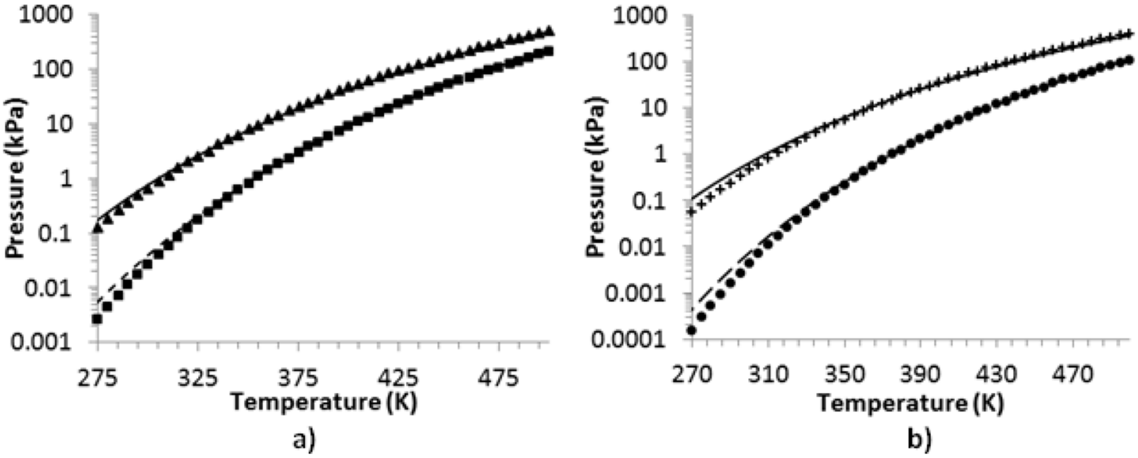

Figure 1. Vapor pressure vs. temperature. Continuous lines: CSGC-PRV model; symbols: experimental data. (NIST Database; Kobe et al., 1941). (a) Isopulegol (■) and α-pinene (△). (b) β-pinene (+) and citronellol (●).

Table 1. Experimental composition and predicted activity coefficients by COSMOS-SAC method for *E. citriodora* and *E. Globulus* experimental oils.

	E. citriodora		***E. globulus***	
Constituents	**Mole fraction**[1]	**Activity Coeficient**[2]	**Mole fraction**[1]	**Activity Coeficient**[2]
eucalyptol	0.0194	1.1336	0.8463	1.0004
α-pinene	0.0064	1.3775	0.0419	1.0341
o-cymene	-	-	0.0296	0.9960
citronellol	0.1446	0.9961	-	-
citronellal	0.7126	1.0057	-	-
isopulegol	0.0764	1.0354	-	-
limonene	0.0041	1.2850	0.0823	1.0199
β-pinene	0.0102	1.3549	-	-
myrcene	0.0022	1.2861	-	-
(E)-caryophyllene	0.0171	1.5860	-	-
(Z)-β-ocimene	0.0037	1.2195	-	-
γ-terpinene	0.0033	1.2337	-	-

[1] Maciel et al., 2010;
[2] predicted at 373 K.

method. The major compounds of eucalyptus essential oils (α-pinene, eucalyptol, isopulegol, and citronellal) were selected to illustrate (Figure 2) the charge density surfaces, highlighting the areas where there are significant surface charge gradients, generating possible non-idealities in mixture behavior.

Dynamic model - batch distillation

The main objective was to insert all the thermodynamic information in the dynamic model, describing an essential oil batch distillation process. Therefore, the model is initially set without any accumulation tank and a complete batch is simulated in order to determine the temperature levels and the behavior of the top composition. The top temperature of the column is the criterion adopted for the change of the accumulation tank. Figure 3 shows the well-defined temperature levels produced by the simulation, which have been used as a principle for essential oil fractionation.

It should be noted that the temperature profile is achieved only through the established equilibrium in each tray. The main cuts are those with a well-defined and constant temperature plateau, as a representation of the relationship between equilibrium temperature and composition. The temperature transitions characterize the off-cuts. Once each level is defined in correspondence with each cut, the simulation is performed again with the tank switching on.

E. globulus oil has an initial composition restricted to four components (Table 2), as determined by Maciel *et al.*, (2010), and it was chosen to show the efficiency of the separation when the original mixture has a main component desired in higher purity. Table 2 shows the results of simulation of *E. globulus* essential oil, where two main-cuts (MC) and two recycle cuts were obtained (OC). The recovery of MC11 and MC12 cuts was 2.84% and 30.46% of the initial amount of essential oil, respectively. The other two off-cuts have variable composition, but from the industrial point of view, they can be treated in a recycle batch. The recovered oil fractions are rich in α-pinene (98.82%) and eucalyptol (98.89%), respectively.

Figure 4 shows the evolution of the distillate composition along the batch time for *E. globulus* essential oil, and one can note the correlation between the composition profiles and the temperature levels in Figure 3. After 25 min a temperature threshold is established, determined by the equilibrium between limonene and eucalyptol. In the specific case of this

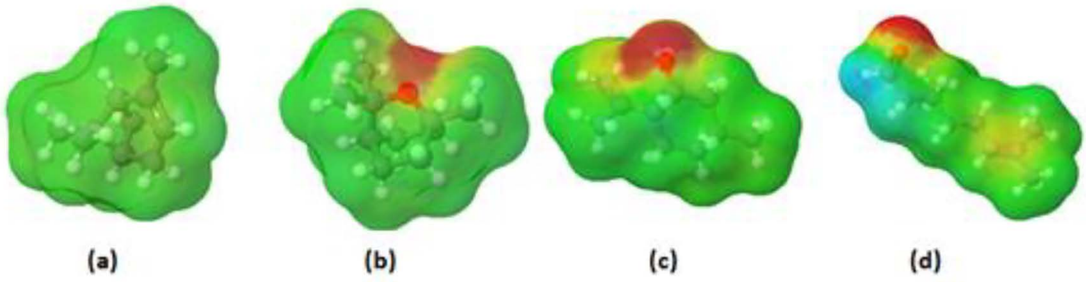

Figure 2. Three-dimensional images of charge density surfaces generated by JCOSMO. (a) α-pinene; (b) eucalyptol; (c) isopulegol; (d) citronellal.

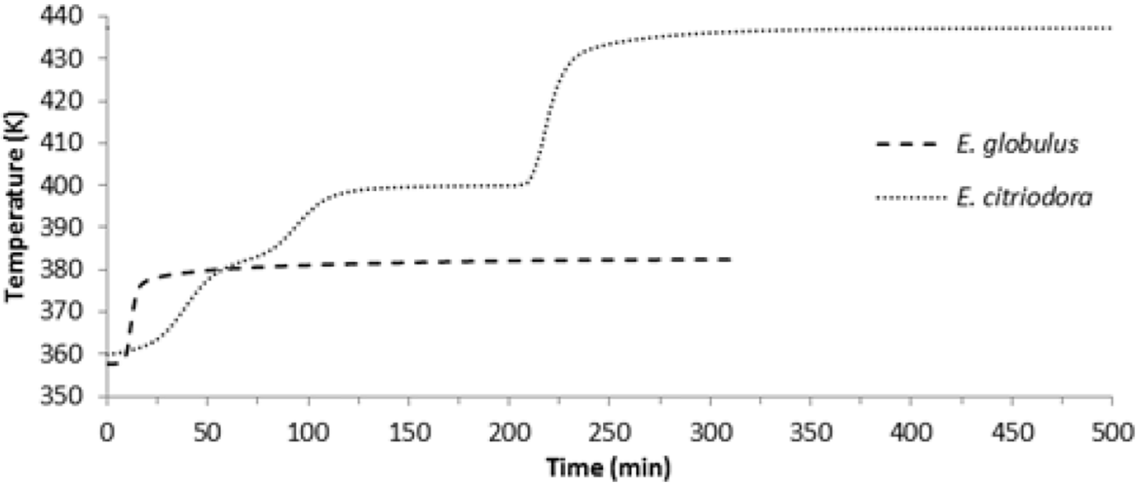

Figure 3. Temperature vs. time - column top profile for the E. globulus and E. citriadora essential oils. Simulated conditions: 18 trays, column holdup of 5%, 10 kPa, reflux ratio = 8.

Table 2. Crude oil compositions of *E. globulus* and major cuts obtained from the simulation of the fractionation process.

Constituents	Initial	MC11	OC11	OC12	MC12
eucalyptol	0.8463	0.0019	0.4028	0.8280	0.9889
α-pinene	0.0419	0.9882	0.2237	0.0063	-
o-cymene	0.0296	0.0025	0.1002	0.0437	0.0028
limonene	0.0823	0.0075	0.2733	0.1220	0.00827
Recovery	-	2.84%	5.48%	55.56%	30.46%

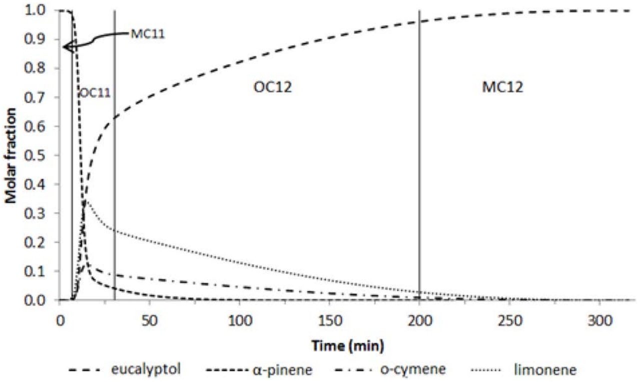

Figure 4. Composition vs. time – distillation product of the E. globulus essential oil. Simulated conditions: 18 trays, column holdup of 5%, 10 kPa, reflux ratio = 8.

essential oil, these two compounds compete equally, which prevents a higher purity for MC12. The four cuts are represented by vertical bars, of which the first one corresponds to MC11. The two intermediate fractions have high potential for recycling.

E. citriodora essential oil, a much more complex mixture with 11 components (Table 3), also determined by Maciel *et al*., (2010), produced two main-cuts and four off-cuts. This simulation is intended to show that even a complex mixture can produce cost-effective fractions. The first main-cut obtained represents 4.26% recovery of the initial essential oil with 99.22% isopulegol purity, which could be directly put on the market. Isopulegol is used in the manufacture of fragrances with blossom compositions; it is also important as an intermediate in the manufacture of menthols (Chuah *et al*., 2001). Silva *et al*. (2007) have also reported depressant and anxiolytic-like effects of isopulegol.

The other main-cut, with 90.03% citronellal purity and 18.55% recovery, must be redirected to a new batch if a higher concentration is desired. This is a useful strategy and frequently used in order to obtain a high purity compound, such as citronellal used as a precursor in several organic syntheses (Chemat and Esveld, 2001; Lenardao *et al*., 2007). The off-cuts OC21 and OC22 can be reused in a single recycle batch to produce eucalyptol and isopulegol. The two remaining off-cuts, OC23 and OC24, could be added to the original oil on a next batch, since they have a very similar composition to the crude oil. Table 3 shows the complete composition of all fractions.

Figure 5 shows quite clearly the link between the equilibrium temperatures at the column top in Figure 3 and the distillate composition profile. Two plateaus correspond exactly to the greater purity cuts. MC22 does not reach higher values of purity due to a strong competition between the citronellal and citronellol, which have almost identical structure, differing only by their oxygenated segments.

As mentioned before, a recycle batch is a recurrent strategy to obtain substances in such purity they could be put on the market. Thus, MC22, which has 90.03% citronellal purity, is submitted to a new distillation process in the same column configuration: 18 trays, 5% column holdup and internal reflux ratio equals to 8. The distillate profile of this new batch is shown in Figure 6, which produces a 98.53% citronellal fraction, recovering 53.09% of this recycle batch feed.

The results show that the vapor pressure is the determining factor in the equilibrium relationships of the mixtures. Due to the similar chemical nature of the compounds, the non-idealities in the liquid phase (activity coefficient) are a less significant property for the given essential oils. On the other hand, volatility differences can be visualized by a parallel with the product composition at the top of the column in Figures 4 and 5; those with higher volatility (in this case, lower vapor pressure) are the first components to appear in the composition profile.

In the case of *E. globulus* oil, α-pinene ($C_{10}H_{16}$) presents no oxygenated group, different from eucalyptol ($C_{10}H_{18}O$), despite having similar carbon structures. In the case of *E. citriodora* essential oil,

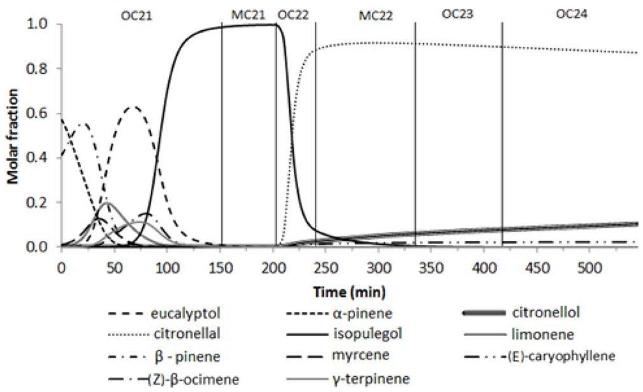

Figure 5. Composition vs. time – distillation product of E. citriodora essential oil. Simulated conditions: 18 trays, column holdup of 5%, 10 kPa, reflux ratio = 8.

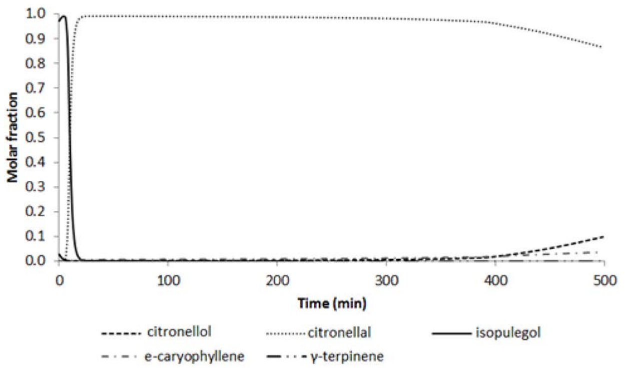

Figure 6. Composition vs. time – distillation product of the MC22 recycle batch. Simulated conditions: 18 trays, column holdup of 5%, 10 kPa, reflux ratio = 8.

Table 3. Crude oil compositions of *E. citriodora* and major cuts obtained from the simulation of the fractionation process.

Constituents	Initial	OC21	MC21	OC22	MC22	OC23	OC24
eucalyptol	0.0193	0.2438	0.0044	0.0003	-	-	-
α-pinene	0.0063	0.0955	-	-	-	-	-
citronellol	0.1442	-	0.0001	0.0130	0.0677	0.1310	0.2094
citronellal	0.7126	-	0.0015	0.5419	0.9003	0.8444	0.7725
isopulegol	0.0763	0.3286	0.9921	0.4362	0.0114	-	-
limonene	0.0040	0.0575	0.0001	-	-	-	-
β-pinene	0.0102	0.1539	-	-	-	-	-
myrcene	0.0022	0.0326	-	-	-	-	-
(E)-caryophyllene	0.0171	-	-	0.0082	0.0205	0.0244	0.0179
(Z)-β-ocimene	0.0037	0.0463	0.0005	-	-	-	-
γ-terpinene	0.0033	0.0415	0.0010	0.0001	-	-	-
Recovery	-	9.05%	4.26%	1.35%	18.55%	16.27%	40.79%

citronellal ($C_{10}H_{18}O$) and isopulegol ($C_{10}H_{18}O$) are isomers, the first being an aldehyde and the second an alcohol, a determining factor in the molecular interactions which significantly changes their vapor pressure. Thus, the oxygenated groups determine the volatility differences observed in the system.

The goal of this work was to create a computational tool using a dynamic model to simulate essential oil fractionation. Once this tool is established, there are several strategies to improve both purity and the amount of distillate. The adopted approach enables one to extend the fractioning calculations to other essential oils, using different operational strategies and column configurations. The simulations presented for the fractional distillation process of essential oils extend the knowledge, already so well established for petroleum fractions, to a not yet explored field. The vast majority of the scientific literature on essential oils is based on their different forms of extraction and biological activities of the compounds obtained. Studies aimed at the processing of these essential oils are still rare, and the lack of thermodynamic properties for their representation is still the biggest restriction. The branch of natural products is one of the fastest growing due to the concern for toxicity in preservatives and synthetic additives in food, cosmetics and hygiene industries, making the development of processing technologies for natural products inherent to this process.

CONCLUSIONS

The predictive method to estimate the vapor pressure of eucalyptus essential oil components was used and proved to be reliable when compared to a few experimental data previously published. The σ-profiles were generated for the substances with MOPAC and the COSMO-SAC package produced consistent values of activity coefficients for the given mixtures. These predictive thermodynamic models were successfully applied to a batch column dynamic model, generating consistent and promising results with respect to the commercial potential of these products. The *E. globulus* simulation allows predicting a high purity eucalyptol recovery (98.89%) and a small α-pinene recovery, but still with 98.82%. For *E. citriodora* two main-cuts were obtained, isopulegol (99.21%) and citronellal (90.03%). The citronellal cut exposes the situation where the essential oil composition can vary and different strategies are presented for a higher composition to be obtained.

ACKNOWLEDGMENTS

The authors are grateful to the Brazilian agency CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico) for the financial support.

NOMENCLATURE

Δh^{vap}	enthalpy of vaporization (kJ/mol)
D	distillate rate (mol/s)
D_i^{Ta}	Molar holdup of component *i* in the tank *Ta* (-)
D_T^{Ta}	total molar holdup in the *Ta* (-)
H_{N+1}	condenser molar holdup (-)
H_p	molar holdup on stage *p=1,2..N* (-)
k_{Ta}	tank *Ta* activation switch (-)
M	molar mass (g/mol)
N	number of theoretical stages (-)
n_i	number of moles of component *i* (-)
P	total system pressure (kPa)
P_c	critical pressure (kPa)
P_c^*	CSGC-PRV internal critical pressure (kPa)
P_i^{sat}	component *i* vapor pressure (kPa)
P_r	reduced pressure (kPa)
P_r^*	CSGC-PRV internal reduced pressure (-)
P_{vpr}	reduced vapor pressure (-)
Q	power supplied to the reboiler (W)
R	reflux ratio (-)
S	reboiler molar holdup (-)
T	temperature (K)
T_b	normal boiling temperature (K)
T_c	critical temperature (K)
T_c^*	CSGC-PRV internal critical temperature (K)
T_r	reduced temperature (-)
T_r	*CSGC-PRV internal reduced temperature (-)
V	vapor rate (mol/s)
x_i	component *i* mole fraction in the liquid phase (-)
$x_{i,p}$	liquid phase mole fraction on stage *p=1,2..N* (-)
x_i^{Ta}	component *i* mole fraction in tank *Ta* (-)
y_i	component *i* mole fraction in the vapor phase (-)
$y_{i,p}$	vapor phase mole fraction on stage *p=1,2..N* (-)

REFERENCES

Adari, P. V. and Jana, A. K., Comparative Control Study of a High-Purity Ternary Batch Distillation. Chem. Prod. Process Model., 3(1), 1934-2659 (2008).

Ambrose, D. and Walton, J., Vapour Pressures up to Their Critical Temperatures of Normal Alkanes and 1-Alkanols. Pure Appl. Chem., 61(8), 1395-1403 (1989).

Antoine, M. C., Tensions Des Vapeurs; Nouvelle Relation Entre Les Tensions et Les Températures. Comptes Rendus des Séances l'Académie des Sci., 107, 681-684 (1888).

Asher, W. E., Pankow, J. F., Erdakos, G. B., Seinfeld, J. H., Estimating the Vapor Pressures of Multi-Functional Oxygen-Containing Organic Compounds Using Group Contribution Methods. Atmos. Environ., 36(9), 1483-1498 (2002).

Babu, G. D. K. and Singh, B., Simulation of Eucalyptus Cinerea Oil Distillation: A Study on Optimization of 1, 8-Cineole Production. Biochem. Eng. J., 44(2-3), 226-231(2009).

Babu, K. G. D. and Kaul, V. K., Variations in Quantitative and Qualitative Characteristics of Wild Marigold (*Tagetes minuta* L.) Oils Distilled under Vacuum and at NTP. Ind. Crops Prod., 26(3), 241-251 (2007).

Batish, D. R., Singh, H. P., Kohli, R. K., Kaur, S., Eucalyptus Essential Oil as a Natural Pesticide. For. Ecol. Manage., 256(12), 2166-2174 (2008).

Bauer, K., Garbe, D., Surburg, H., Common Fragrance and Flavor Materials: Preparation, Properties and Uses, John Wiley & Sons (2008).

Baxendale, I. R., A Short Multistep Flow Synthesis of a Potential Spirocyclic Fragrance Component. Chem. Eng. Technol., 38(10), 1713-1716 (2015).

Beneti, S. C., Rosset, E., Corazza, M. L., Frizzo, C. D., Di Luccio, M., Oliveira, J. V., Fractionation of Citronella (*Cymbopogon winterianus*) Essential Oil and Concentrated Orange Oil Phase by Batch Vacuum Distillation. J. Food Eng., 102(4), 348-354 (2011).

Bonaccorsi, I., Dugo, P., Trozzi, A., Cotroneo, A., Dugo, G., Characterization of Mandarin (*Citrus deliciosa* Ten.) Essential Oil. Determination of Volatiles, Non-Volatiles, Physico-Chemical Indices and Enantiomeric Ratios. Nat. Prod. Commun., 4(11), 1595-1600 (2009).

Castillo-Herrera, G. A., García-Fajardo, J. A., Estarrón-Espinosa, M., Extraction Method That Enriches Phenolic Content in Oregano (*Lippia graveolens* HBK) Essential Oil. J. Food Process Eng., 30(6), 661-669 (2007).

Chemat, F. and Esveld, E., Microwave Super-Heated Boiling of Organic Liquids: Origin, Effect and Application. Chem. Eng. Technol., 24(7), 735-744 (2001).

Chuah, G. .,Liu, S. .,Jaenicke, S., Harrison, L., Cyclisation of Citronellal to Isopulegol Catalysed by Hydrous Zirconia and Other Solid Acids. J. Catal., 200(2), 352-359 (2001).

Domenech, S. and Enjalbert, M., Program for Simulating Batch Rectification as a Unit Operation. Comput. Chem. Eng., 5(3), 181-184 (1981).

Farah, A., Afifi, A., Fechtal, M., Chhen, A., Satrani, B., Talbi, M., Chaouch, A., Fractional Distillation Effect on the Chemical Composition of Moroccan Myrtle (*Myrtus communis* L.) Essential Oils. Flavour Fragr. J., 21(2), 351-354 (2006).

Fredenslund, A., Vapor-Liquid Equilibria Using UNIFAC: A Group-Contribution Method, Elsevier, (2012).

Galindez, H. and Fredenslund, A. A., Simulation of Multicomponent Batch Distillation Processes. Comput. Chem. Eng., 12, 281-281 (1988).

Garcia, A. N., Loria, J. C. Z., Marin, A. R., Quiroz, A. V. C., Simple multicomponent batch distillation procedure with a variable reflux policy. Braz. J. Chem. Eng., 31(2), 531-542 (2014).

Gerber, R. P. and Soares, R. de P. , Prediction of Infinite-Dilution Activity Coefficients Using UNIFAC and COSMO-SAC Variants. Ind. Eng. Chem. Res., 49(16), 7488-7496 (2010).

Gerber, R. P. and Soares, R. P., Assessing the reliability of predictive activity coefficient models for molecules consisting of several functional groups. Braz. J. Chem. Eng., 30(1), 1-11 (2013).

Gomez-Nieto, M. and Thodos, G., Generalized Treatment for the Vapor Pressure Behavior of Polar and Hydrogen-bonding Compounds. Can. J. Chem. Eng., 55(4), 445-449 (1977).

Greaves, M. A., Mujtaba, I. M., Barolo, M., Trotta, A., Hussain, M. A., Neural-Network Approach to Dynamic Optimization of Batch Distillation: Application to a Middle-Vessel Column. Chem. Eng. Res. Des., 81(3), 393-401 (2003).

Guenther, E., The Essential Oils-Vol 1: History-Origin in Plants-Production-Analysis, Read Books Ltd, (2013).

Hanwell, M. D., Curtis, D. E., Lonie, D. C., Vandermeersch, T., Zurek, E., Hutchison, G. R. Avogadro: An Advanced Semantic Chemical Editor, Visualization, and Analysis Platform. J. Cheminformatics, 4(1), 1-17 (2012).

Jiménez, L., Basualdo, M.S., Gómez, J.C., Toselli, L., &Rosa, M., Nonlinear dynamic modeling of multicomponent batch distillation: a case study. Braz. J. Chem. Eng.,19(3), 307-317 (2002).

Juergens, U. R., Stöber, M., Schmidt-Schilling, L., Kleuver, T., Vetter, H., Antiinflammatory Effects of Euclyptol (1.8-Cineole) in Bronchial Asthma: Inhibition of Arachidonic Acid Metabolism in Human Blood Monocytes Ex Vivo. Eur. J. Med. Res., 3, 407-412 (1998).

Juergens, U. R., Stöber, M., Vetter, H., Inhibition of Cytokine Production and Arachidonic Acid Metabolism by Eucalyptol (1.8-Cineole) in Human Blood Monocytes in Vitro. Eur. J. Med. Res., 3, 508-510 (1998).

Klamt, A., Conductor-like Screening Model for Real Solvents: A New Approach to the Quantitative Calculation of Solvation Phenomena. J. Phys. Chem., 99(7), 2224-2235 (1995).

Kobe, K. A., Okabe, T. S., Ramstad, M. T., Huemmer, P. M. P-Cymene Studies., VI. Vapor Pressure of p-Cymene, Some of Its Derivatives and Related Compounds. J. Am. Chem. Soc., 63(12), 3251-3252 (1941).

Lenardão, E. J., Botteselle, G. V., de Azambuja, F., Perin, G., Jacob, R. G., Citronellal as Key Compound in Organic Synthesis. Tetrahedron, 63(29), 6671-6712 (2007).

Li, P., Ma, P.-S., Yi, S.-Z., Zhao, Z.-G., Cong, L.-Z., A New Corresponding-States Group-Contribution Method (CSGC) for Estimating Vapor Pressures of Pure Compounds. Fluid Phase Equilib., 101, 101-119 (1994).

Lin, S.-T. and Sandler, S. I., A Priori Phase Equilibrium Prediction from a Segment Contribution Solvation Model. Ind. Eng. Chem. Res., 41(5), 899-913 (2002).

Logsdon, J. S. and Biegler, L. T., Accurate Determination of Optimal Reflux Policies for the Maximum Distillate Problem in Batch Distillation. Ind. Eng. Chem. Res., 32(4), 692-700 (1993).

Maciel, M. V,Morais, S. M., Bevilaqua, C. M. L., Silva, R. A., Barros, R. S., Sousa, R. N., Sousa, L. C., Brito, E. S., Souza-Neto, M. A., Chemical Composition of *Eucalyptus Spp.* Essential Oils and Their Insecticidal Effects on *Lutzomyia Longipalpis*. Vet. Parasitol., 167(1), 1-7 (2010).

Mujtaba, I. M. Batch Distillation, Imperial College Press, (2004).

Mujtaba, I. M. and Macchietto, S., Efficient Optimization of Batch Distillation with Chemical Reaction Using Polynomial Curve Fitting Techniques. Ind. Eng. Chem. Res., 36(6), 2287-2295 (1997).

Pankow, J. F. and Asher, W. E., SIMPOL.1: A Simple Group Contribution Method for Predicting Vapor Pressures and Enthalpies of Vaporization of Multifunctional Organic Compounds. Atmos. Chem. Phys., 8(1), 2773-2796 (2008).

Pattnaik, S., Subramanyam, V. R., Bapaji, M., Kole, C. R., Antibacterial and Antifungal Activity of Aromatic Constituents of Essential Oils. Microbios, 89(358), 39-46 (1996).

Ramezani, H., Singh, H. P., Batish, D. R., Kohli, R. K., Antifungal Activity of the Volatile Oil of *Eucalyptus Citriodora*. Fitoterapia, 73(3), 261-262 (2002).

Reid, R. C., Prausnitz, J. M., Poling, B. E., The Properties of Gases and Liquids. McGraw Hill, New York (1987).

Riedel, L., Eine Neue Universelle Dampfdruckformel Untersuchungen Über Eine Erweiterung Des Theorems Der Übereinstimmenden Zustände. Teil I. Chemie Ing. Tech., 26(2), 8-893 (1954).

Silva, M. I. G., de Aquino Neto, M. R., Teixeira Neto, P. F., Moura, B. A., doAmaral, J. F., de Sousa, D. P., Vasconcelos, S. M. M., de Sousa, F. C. F., Central Nervous System Activity of Acute Administration of Isopulegol in Mice. Pharmacol. Biochem. Behav., 88(2), 141-147 (2007).

Silvestre, W. P., Agostini, F., Muniz, L. A. R., Pauletti, G. F., Fractionating of Green Mandarin (*Citrus deliciosa Tenore*) Essential Oil by Vacuum Fractional Distillation. J. Food Eng., 178, 90-94 (2016).

Simoes, C. M. O., Farmacognosia: Da Planta Ao Medicamento, UFRGS, Florianópolis: UFSC, (2001).

Soares, R. de P. andSecchi, A. R., EMSO: A New Environment for Modelling, Simulation and Optimisation. Comput. Aided Chem. Eng., 14, 947-952 (2003).

Stewart, J. J. P., MOPAC: A Semiempirical Molecular Orbital Program. J. Comput. Aided. Mol. Des., 4(1), 1-103 (1990).

Tu, C.-H., Group-Contribution Method for the Estimation of Vapor Pressures. Fluid Phase Equilib., 99, 105-120 (1994).

Vetere, A., The Riedel Equation. Ind. Eng. Chem. Res., 30(11), 2487-2492, (1991).

Wagner, W., New Vapour Pressure Measurements for Argon and Nitrogen and a New Method for Establishing Rational Vapour Pressure Equations. Cryogenics (Guildf)., 13(8), 470-482 (1973).

Wendt, M., Li, P., Wozny, G., Batch Distillation Optimization with a Multiple Time-Scale Sequential Approach for Strong Nonlinear Processes. Comput. Aided Chem. Eng., 8, 121-126 (2000).