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ABSTRACT

Modelling and experimental validation of solvent recovery from an aroma mixture by batch distillation process is presented, with particular emphasis of the effect of the prediction of the physicochemical properties and the phase equilibrium data on the content of the aroma compounds in the distillate cuts. The illustrative case study refers to an industrial batch distillation to recover dimethyl carbonate (DMC) from an extract generated by a solvent extraction process involving variable natural raw materials for tailored perfume and fragrance applications. Due to the high number of aroma compounds in natural extracts, a synthetic mixture containing six target aroma compounds (α-pinene, eucalyptol, linalool, cis-3-hexenol, fenchone and benzyl acetate) was mixed with DMC for the modelling and experimental studies of the batch distillation process. The methodology is tested through the simulation of the process with BatchColumn® software. As physicochemical properties of the aroma compounds and the vapour – liquid equilibrium (VLE) of all involved mixtures are required for simulation study, group contribution methods are used to predict missing properties such as vapour pressure, vaporisation enthalpy and liquid and vapour heat capacities. For VLE calculation, the modified UNIFAC group contribution method is considered and new binary interaction parameters for the main groups COO and CH2O are regressed from experimental data. Simulation results are in good agreement with experiments carried out in a fully automated batch distillation column at 15 kPa and help optimise the industrial process operation. The proposed methodology can be applied for the design of other solvent recovery process in fragrance industry.

Keywords: aroma compounds, solvent recovery, batch distillation, process simulation, group contribution methods

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1.   Introduction

Extracts of aroma compounds from natural resources are widely used in the perfume and fragrance industry, pharmaceutical sector, food and human nutrition field. They are complex mixtures of volatile compounds mainly constituted of monoterpenes, sesquiterpenes and their oxygenated derivatives as well as aliphatic aldehydes, alcohols and esters. The oxygenated fraction is highly odoriferous and mainly responsible for the odor properties (Basile et al., 1998). Organoleptic properties of the natural extracts for aromas and perfumes are directly related to the quality of the natural raw materials from which they are extracted as well as the fabrication method. The preparation of perfumes, fragrances and aromas from natural resources is often not easy to achieve nor to reproduce and may be very expensive. Both, the hydrodistillation and the solvent extraction, are the most used processes. The second process is preferred because denaturation of target aroma compounds can be better avoided by using low operation temperature. However, the use of solvent extraction process, dimethyl carbonate in our case, involves a further separation step for recovering and recycling this green solvent as a new alternative for n-hexane substitution (Rodriguez Donis et al., 2018). Batch distillation under deep vacuum is the typical operation for solvent recovery since setting a low pressure correlates with low boiling temperatures and help to avoid thermal degradation and to preserve the organoleptic properties of the aroma paste retained into the reboiler at the end of the process and usually known as "concrete". Due to the high composition variability of the natural extracts and the required concentration of the aroma molecules in the concrete, the scale-up from laboratory developments to full-scale applications is frequently not completed or is completed without optimising the operating conditions, resulting in a huge economic cost.

Computer simulation and optimisation studies have proven successful in many areas of pharmaceutical and chemical processing. Such techniques have been also extended for the design and the optimisation of distillation of wines and musts for alcohol beverage production mainly using continuous distillation column. The complexity of these beverage processes is a good illustration of the challenges that have to be addressed by fragrance industry for optimising their processes. Several studies have demonstrated that commercial simulation programs relate with a reasonable accuracy the operating variables of the distillation process and the key organoleptic properties of the alcoholic beverage products. ASPEN Plus, ChemCAD and ProSim Plus are the most used commercial process simulators for wine and must distillation because they perform rigorous mass and energy balance calculations (Decloux et al., 2005; Batista and Meirelles, 2011; Valderrama et al., 2012). Their strength

lies in their accurate computation of the phase equilibria of the mixtures under a wide-ranging of operating conditions thanks to their extensive databases of physicochemical properties and thermodynamic models.

Decloux et al. (2005) validated the modelling with ProSim Plus software of a continuous industrial plant to produce neutral spirits including seven interconnected distillation columns where they considered seven representative congeners (acetaldehyde, ethyl acetate, acetal, methanol, 2-butanol, 1-propanol and allyl alcohol). In addition to water and ethanol, all binary liquid – vapour equilibria (VLE) including the congeners, were assessed by using UNIFAC model. An optimisation study allowed the understanding of the congener's distribution along the distillation column with the operating conditions in order to maximise the ethanol recovery yield and the quality of the neutral spirit. Batista and Meirelles (2011) simulated the continuous cachaça production with ASPEN Plus software by considering 10 congeners (methanol, isopropanol, isobutanol, 1-propanol, isoamyl alcohol, ethyl acetate, acetaldehyde, acetone, acetic acid, CO_2) into the feeding of the mixture ethanol – water. NRTL thermodynamic model was selected for computing the VLE where the interaction parameters of the 66 related binary mixtures were adjusted from experimental data or from UNIFAC predicted values. Simulation results were in good agreement with the industrial plant results producing 300 m^3 per day of anhydrous ethanol. Valderrama et al. (2012) used ChemCad process simulator to design a continuous distillation column for the brandy production and including five congeners (acetaldehyde, ethyl acetate, methanol, n-propanol and isobutanol) from fermented juice. Simulation results provided the best operating conditions for achieving the quality specification of brandy. The simulation studies of two beer compositions in the main feed of a small plant (180 m^3/day) allowed to determine the suitable operating conditions for the optimal location of the main feed and the lateral product streams along the column.

In the case of batch distillation, Osorio et al. (2005) developed their own process model in order to define the optimal operating recipe of Pisco brandy distillation. Simulation and experimental studies were performed by considering a synthetic mixture of the main eight congeners (ethyl hexanoate, ethyl octanoate, methanol, cis-3-hexenol, isoamyl alcohol, octanoid acid, linalool, acetaldehyde) commonly found in real muscat wines. The binary interaction parameters for computing the non-ideal VLE were fitted from existing experimental data. Scanavini et al. (2010) performed a comparable study for improving the cachaça quality as a distillate product in a laboratory alembic. The minor components such as methanol, n-propanol, isobutanol, isoamyl alcohol, acetic acid, ethyl acetate and acetaldehyde

in addition to water and ethanol, were added to real multidistilled commercial cachaça based on the concentration limit established by the Brazilian legislation. The modelling of the VLE was done by using activity coefficient models and equations of state to consider the non-ideal behavior in the liquid and in the vapour phase, respectively. Experimental data of all binary VLE were well described in the literature simplifying the task of VLE calculation. The simulation studies helped to define the appropriate sequence of the distillate cuts according to spirits quality specifications. Carvallo et al. (2011) developed a pseudo-stationary simulator for minimising the content of methanol in fruit wines production by batch distillation. A synthetic ternary mixture methanol – ethanol – water were considered and the simulated methanol concentration in the distillate varied in the same range as measured values during the spirits distillation of Bartleet pears. Sacher et al. (2013) developed a rigorous dynamic model for simulating the batch distillation process in a Cognac copper alembic of 2 L. The raw material was pear wine distillate of 17.9 % v/v of ethanol obtained from a prior first distillation. The simulation of the process enables the definition of the operation guidance to maximise the spirit's quality by controlling the concentration of 15 congeners such as acetaldehyde, methyl acetate, acetal, ethyl acetate, methanol, 2-butanol, 1-propanol, 2-methyl-1-propanol, 1-butanol, ethyl hexanoate, 2-methyl-1-butanol, 3-methyl-1-butanol, furfural, ethyl decanoate and phenethyl alcohol. The VLE was predicted by UNIFAC method under the assumption of ideal vapour phase.

The studies aforementioned on spirits production by batch distillation process have been mainly performed by in-house software and rare papers have been devoted to simulation studies using commercial software. In Valderrama et al. (2012), the module CC-Batch of ChemCAD was used for simulation studies of a bi-distillation process for whisky production. Similarly, Decloux et al. (2014) demonstrated the suitability of using the BatchColumn® software (Prosim S.A) for simulating the batch distillation process of an orange bitter distillate product. The raw material was the alcoholic extract of bitter orange peels macerated during three weeks. In addition to water and ethanol, four other aroma molecules defining the quality of the bitter were selected such as two monoterpene hydrocarbons, α-pinene and d-limonene, and two oxygenated hydrocarbons linalool and linalool oxide. NRTL model was used for VLE modelling with binary interaction coefficients computed from experimental data. Simulation and experimental results demonstrated that the two monoterpenes were withdrawn in the first distillate cut and the oxygenated monoterpenes in the tails cut.

Concerning the production of natural extracts for aromas and perfumes, no studies as those cited above for the wine and spirit industry exist. In the fragrance industry, the concrete

extraction step is not an issue, being either empirically mastered or based on antique undisclosed recipes that one should not change. On the other hand, some improvement can be made in the solvent recovery step where one should minimise the loss of the key aroma compounds during distillation. Similar to spirits production, process simulations can help to understand the relationship between the operating parameter values and the distribution of the aroma compounds along the distillation column and in the distillation cuts. Therefore, optimal operation can be investigated in order to increase both solvent recovery yield and purity by minimising the content of aroma compounds. However, unlike to the alcohol beverage production where most of congeners can be found in the database of the commercial simulators, the most significant aroma molecules found in the perfume and fragance industry are missing or their properties are partially described in experimental databases. Consequently, VLE predictions are incomplete, mass and energy balances are not calculated and the process cannot be simulated by commercial process software. This paper aims to simulate dimethyl carbonate solvent recovery from an aroma mixture by a batch distillation software and to validate it with experimental measurements. We address several challenges. The first challenge concerns the modelling of the multicomponent real mixture. For that we build a synthetic mixture including six aroma molecules defined by the industrial partner as target molecules in the concrete for fragrances end uses. Second, group contribution methods were applied to compute the required physicochemical properties of aroma compounds because the scarcity of experimental data in the commercial process simulators. Similarly, modified UNIFAC first order group contribution method is applied for computing the VLE of the 21 involved binary mixtures exhibiting a non-ideal behavior (Gmehling et al., 1993). However, its application for aroma compounds is not straightforward because decomposition of the complex aroma molecular structure into UNIFAC chemical groups requires a trial and error procedure in order to find the chemical groups that better fit with experimental data including the same aroma compounds or other compounds having the same UNIFAC chemical groups. The last challenge refers to the validation of the batch distillation process simulations at 15 kPa through the application of BatchColumn® software (Prosim S.A). Experimental measurements are carried out to validate the models used for predicting the physicochemical properties of aroma compounds and the thermodynamic method.

The paper is organised as follow. First, the methodology is presented and the computer-aided methods are described along with experimental data needed to develop them. Next, each step of the methodology is discussed through the separation of dimethyl carbonate from a mixture of aroma compounds by batch distillation under reduced pressure. Finally, Simulation

results are presented and compared with experimental runs that are carried in a fully automated laboratory batch distillation column.

2. Methodology for solvent recovery from a mixture with aroma compounds

Fig. 1 shows the main steps of the methodology for the design and analysis of the solvent recovery process from aroma compounds mixture in the perfume and cosmetic industry.
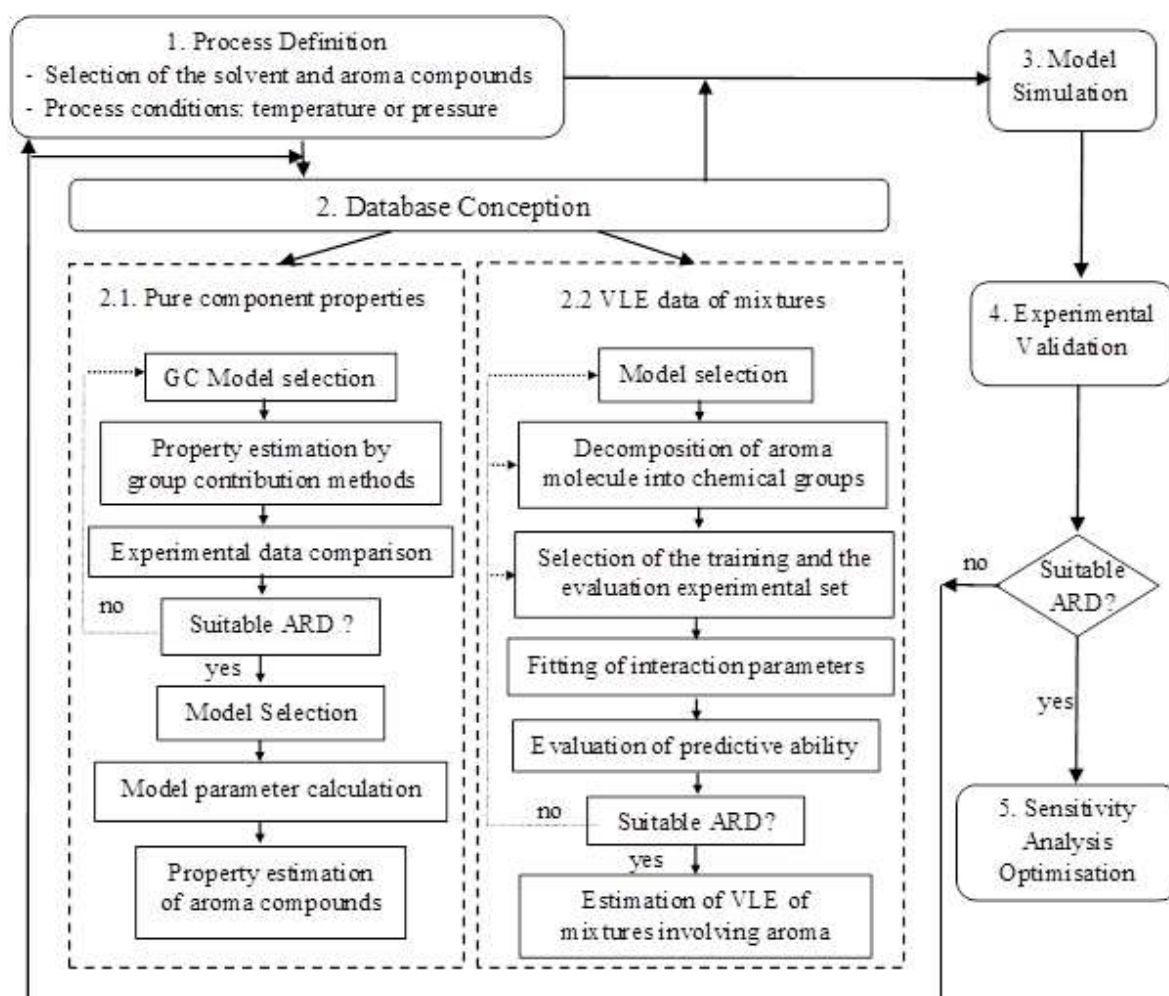
Fig. 1. Block diagram of the based model methodology for the design and anlysis of solvent recovery process from a mixture of aroma compounds

Step 1 - Process Definition:

It comprises the selection of the operating conditions as well as the list of typical aroma compounds. The working region of the separation process is defined by the total pressure or temperature condition.

Step 2 - Database Conception

Step 2.1 - Pure component properties:

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A model describing the variation of properties with temperature has to be set in order to carry out the simulation studies in a commercial process simulator. For distillation processes, vaporisation enthalpy, heat capacity and vapour pressure properties are needed. First, a predictive method based on group contribution (GC) is chosen for missing property values. Both group selection and their contribution values must be carefully selected. Suitability of the GC method can be assessed by comparison of the predicted values with available experimental data. In the next step, the temperature dependence of the property is regressed upon a mathematical formulation that be chosen among those available in DIPPR database.

Step 2.2 - Vapour - liquid equilibrium of mixtures

Reliable computation of phase equilibrium data is crucial for simulation studies on distillation processes. It is a complex task because aroma compounds are mainly multi-cyclic molecules often including shared oxygen atoms. The resulting complex intermolecular interactions in the liquid phase (such as van der Waals interactions and hydrogen bonds) imply the use of an excess Gibbs free energy model (activity coefficient model), such as predictive group contribution methods. The UNIFAC method was first proposed by Fredenslund et al. (1975) and came directly from the formalism of the UNIQUAC method (Abrams and Prausnitz, 1975). The non-ideality of the component in the liquid state is characterised by the activity coefficient which includes two terms (eq. 1): "combinatory term" resulting from differences in sizes and shape between components and the "residual term" taking into account the interaction between two any chemical groups m and n conforming the chemical structure of each component in the mixture.

$$\ln \gamma_i = ln\gamma_i^C + ln\gamma_i^R \tag{1}$$

the combinatorial term is expressed as:

$$\ln \gamma_i^C = ln\frac{W_i}{x_i} + 1 - \frac{W_i}{x_i} - Z\frac{q_i}{2}(1 - \frac{\emptyset_i}{\theta_i} + ln\frac{\emptyset_i}{\theta_i}) \tag{2}$$

$$W_i = \frac{r_i^{3/4}}{\sum_j x_j r_j^{3/4}} \tag{3}$$

$$\emptyset_i = \frac{r_i}{\sum_j x_j r_j} \tag{4}$$

$$\theta_i = \frac{q_i}{\sum_j x_j q_j} \tag{5}$$

Where $z = 10$ and, r_i and q_i are computed taking into account the contribution of the functional chemical subgroup volume parameter R_k and the functional subgroup surface parameter Q_k together with the occurrence frequency $(v_K^{(i)})$ of the functional chemical subgroup k in the molecular structure.

$$r_i = \sum v_k^{(i)} R_k$$

(6)

$$q_i = \sum v_k^{(i)} Q_k \tag{7}$$

the residual term is defined as:

$$\ln\gamma_i^R = -\sum_{k=1}^{N} v_k^{(i)} \left(\ln\Gamma_k - \ln\Gamma_k^i \right) \tag{8}$$

$$\ln\Gamma_k = Q_k * \left[1 - \ln \sum_m \Theta_m \Psi_{m.k} - \sum_m \frac{\Theta_m \Psi_{k.m}}{\sum_n \Theta_n \Psi_{k.n}} \right] \tag{9}$$

the fraction Θ_k for each functional group is determined as:

$$\Theta_m = \frac{Q_m * X_m}{\sum_n Q_n * X_n} \tag{10}$$

and the molar fraction X_k of each functional group in the molecule is computed as:

$$X_m = \frac{\sum_j v_m^{(i)} x_j}{\sum_j \sum_n v_n^{(i)} x_j} \tag{11}$$

The binary interaction parameters between the chemical functional groups k and j $\Psi_{k.j}$ follows:

$$\Psi_{n.m} = EXP\left(-\frac{a_{n.m} + b_{n.m} * T + c_{n.m} * T^2}{T} \right) \tag{12}$$

One advantage of the modified UNIFAC method (Gmehling et al. 1993) compared to the Original UNIFAC (Fredenslund et al. 1975) is the inclusion of temperature dependent interaction parameters between two main structural chemical groups m and n according to the equation (12). Hence, the computation of the constants $a_{m,n}; b_{m,n}; c_{m,n}$ in equation (12) have been carried out for the most typical structural chemical groups m and n as they are defined available in commercial process simulators, like BatchColumn®. But some are missing for the complex aroma molecules considered in the study mixture. Versatility of UNIFAC methods is that one can define new chemical functional groups and fit the missing constants from experimental data including components, which have the same chemical group interactions even if they don't belong exactingly to the same chemical family.

The quality of the predicted results depends on the decomposition of the aroma molecular structure into functional chemical groups and on the regression of interaction parameters between groups. In the gas phase, since distillation units for solvent recovery commonly operate under vacuum pressure conditions in order to avoid the thermal decomposition of aroma compounds, the vapour phase can be represented as an ideal gas. For a reliable computation of the interaction parameters between groups, the experimental data are classified in two groups: the training set and the validation set. If high average relative error (ARD) is obtained from the fitting of the interaction parameters between UNIFAC main groups, the molecular decomposition of the aroma compound can be revised as well as the accuracy of the experimental data considered in both, the training and validation sets. Other predictive methods can be tested if the average relative errors remain unacceptably high.

Step 3 – Process Simulation:

A proper process simulator is selected allowing the implementation of pure component and mixture databases and the further study of the design operating variables on the solvent recovery process. For the sake of simplicity, commonly assumptions related to the hydrodynamic, heat transfer loss and separation efficiency are retained and they have to be validated in the experimental prototype.

Step 4 – Experimental validation:

Experimental runs are carried out in an adequate equipment satisfying the main assumptions in the previous process simulation study. The average relative deviation (ARD) or the maximum absolute deviation (MAD) between the experimental data and the simulated results will check the suitability of the models implemented in the database for predicting the pure component properties and the phase equilibrium data of the mixtures in step 2.

Step 5 – Sensitivity analysis and optimisation

If good agreement exists between the simulation and the experimental results, further simulation studies can be carried out in order to identify the key operating parameters and the computation of their optimal values satisfying one or several objective functions.

3. Case study: dimethyl carbonate recovery by vacuum batch distillation

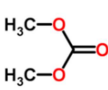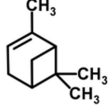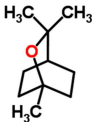Charabot S.A has patented the use of DMC as a novel green solvent for extracting aroma compounds from natural resources (Lavoine-Hanneguelle, 2014). The industrial implementation of using DMC for the extraction of aroma compounds has demonstrated that the solvent recovery under vacuum batch distillation process is the most critical step. Currently, the loss of aroma compounds in the distillate is affecting the organoleptic

properties of the final concrete fraction. It is attributed to a lack of knowledge about the interactions between the aroma compounds and DMC in the liquid and the vapour phases and about the distillation column it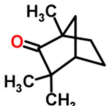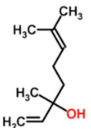self, which operation is not optimised. Simulation studies using commercial batch distillation process simulators could help the monitoring of the target aroma molecules in the distillate product during the recovery of DMC in a batch distillation column under various operating conditions. We apply the methodology described earlier.

3.1. Problem Definition: Operating total pressure and aroma compounds selection

Simulation studies of the distillation process require firstly the definition of the total pressure or the operating temperature as well as the list of aroma compounds into the mixture to be separated. Aromatic plant extracts are complex multicomponent mixtures mainly constituted by monoterpenes, sesquiterpenes and their oxygenated derivatives, together with aliphatic aldehydes, alcohols and esters. Real composition measurements by spectroscopic and chromatographic techniques of natural extracts showed that there are several hundred molecules. Such a number cannot be handled in chemical process simulators. The aroma compounds in the synthetic mixture were selected by the industrial partner based on the criterion that each molecule represents a chemical family, which had to be a vital component in most of formulations in the fragrance industry. These aroma assortments can be represented by α-pinene, eucalyptol and fenchone, cis-3-hexenol, linalool and benzyl acetate, respectively. Properties of the dimethyl carbonate, are also shown in Table 1. The advantages of using DMC as a solvent can be hinted from values on Table 1.

Table 1
Physicochemical properties of the solvent and aroma compounds in the synthetic mixture.

Properties	Compounds						
Name	DMC	α-Pinene	Cis-3-Hexenol	Eucalyptol	Fenchone	Linalool	Benzyl acetate
Chemical structure							
CAS	616-38-6	7785-70-8	928-96-1	470-82-6	4595-62-9	78-70-6	140-11-4
Boiling Point (K)	363.15	428.15	429.15	449.65	468.15	471.65	479.15
Boiling Point (K) at 15 kPa	313.15	366.35	372.95	383.85	399.55	408.35	421.65
Melting Point (K)	277.15	218.15	212.15[a]	271.65[a]	279.15[a]	253.15[a]	221.65
Flash Point (K)	289.15	306.15	317.15[b]	322.15[b]	325.15[b]	349.15[b]	368.15

ΔH_{vap} (298K) (kJ/mol)	33.3	44.6	53.8[a]	47.8[a]	61.2[a]	76.9[a]	45
CP_{liquid} (298K) (J/mol.K)	170.4	222.9	253.4[c]	261.1[c]	265.1[c]	342.6[c]	244.4
ρ (293K) (g/cm^3)	1.07	0.856	0.932[a]	0.921[a]	0.771[a]	0.865[a]	1.054
μ (298K) 10^{-3}(Pa.s)	0.58	1.49	2.96[c]	2.32[c]	4.2[c]	6.94[c]	2.12

[a]Marrero and Gani (2001), [b]Constantino and Gani (1995), [c]Joback and Reid (1987)

DMC has a favourable boiling temperature/flash point ratio, low values of properties linked to energy consumption such as the vaporisation enthalpy and the liquid heat capacity, as well as excellent transport properties because of the low density (ρ) and viscosity (μ). However, it should be noted that DMC has a melting point of 277.15 K which imposes a minimal working value for the condenser temperature in order to prevent the solidification of DMC. As stated by Charabot S.A, the DMC recovery is performed at 15 kPa of pressure according to the industrial available distillation column to avoid thermal degradation of aromas. This operating pressure provides a working temperature range of the distillation process between the boiling point of DMC 313.15 K and the least volatile component benzyl acetate 421.65K (see Table 1).

3.2. Database conception

3.2.1 Pure component properties database

Correlation models of the vapour pressure, the vaporisation enthalpy and the liquid and the vapour heat capacities are required for all components listed in Table 1, DMC and the aroma compounds α-pinene, eucalyptol, linalool, cis-3-hexenol, fenchone and benzyl acetate. Values for DMC, α-pinene and benzyl acetate are provided by the DIPPR database available in BatchColumn® software (Prosim, 2017a). However, eucalyptol, linalool, cis-3-hexenol and fenchone are missing compounds in the DIPPR database. Therefore, they are introduced in the database thanks to the Simulis®Thermodynamics property server interface (Prosim, 2017b) and property values are predicted by using group contribution methods implemented in the computational tool IBBS (Heintz et al., 2014).

Table 2 shows the mathematical models selected for the missing components in DIPPR database: eucalyptol, linalool, cis-3-hexenol and fenchone. The constants of the models are fitted from experimental data found in literature. In the case of lacking experimental values, the constants of the models are determined from predicted data using IBSS tool where many group contribution models are available. Indeed, IBSS tool suggests the more suitable group

contribution methods as the Joback and Reid method (1987) for predicting the vapour pressure and the heat capacity of vapors and liquids. Similarly, the Marrero and Gani method (2001) is a proper method for calculating the vaporisation enthalpy. Both methods are used and compared with experimental data.

Experimental data of vapour pressure for eucalyptol were published by Torcal et al. (2010) in the temperature range of 326.65 to 419.95 K. Štejfa et al. (2014a) also reported experimental data into the range of 253.15 to 308.15K along with data of liquid heat capacity. Constants for the vapour pressure equation in Table 2 were computed from both reported experimental data and they are displayed in Fig. 2a as well as the predicted values using the Joback and Reid method (1987). There is a very good agreement between experimental and predicted results (Fig. 2a). Two experimental values of vaporisation enthalpy of 53.2 kJ/mol and 45.4 kJ/mol at 298.15K were reported by Roon et al. (2002) and Hazra et al. (2002) while predicted values were 47.23 kJ/mol and 54.58 kJ/mol using Joback and Reid method (1987) and Marrero and Gani method (2001), respectively. Constants of the model for computing the vaporisation enthalpy in Table 2 were fitted using the predicted results from Marrero and Gani method (2001).
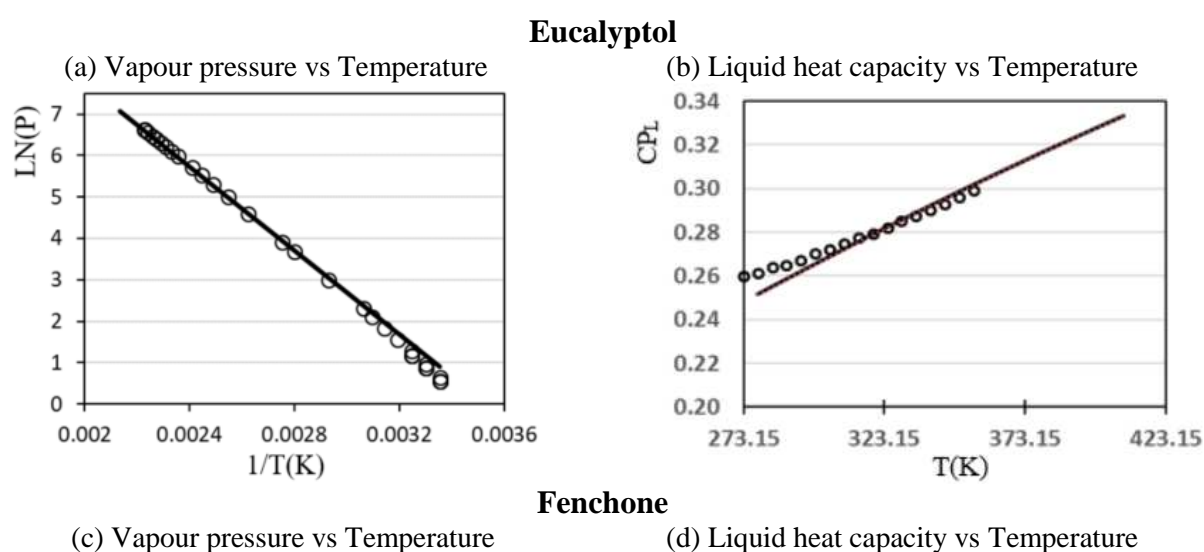
Table 2
Correlation models for missing aroma compounds in DIPPR database.

Compound	Vapour Pressure $\ln P = A + B/(T)$ P(mm Hg); T(K)	Vaporisation enthalpy $\Delta H_{vap} = A + BT + CT2$ ΔH_{vap} (kJ/mol); T(K)	Liquid Heat capacity $CP_{liquid} = A + BT + CT2$ CP_{liquid} (kJ/molK); T(K)	Vapour Heat capacity $CP_{vapour} = A + BT + CT2$ CP_{vapou}(kJ/molK); T(K)
Eucalyptol	A = 19.235 B = -5592.2 R^2 = 0.9985	A = 57.087 B = -0.018 C = -5E-05 R^2 = 0.9999	A = 0.234 B = -0.0003 C = 1E-06 R^2 = 0.9996	A = -0.1607 B = 0.0015 C = -1E-06 R^2 = 0.9999
Fenchone	A = 19.939 B = -6046.2 R^2 = 0.9976	A = 68.35 B = -0.0226 C = -4E-05 R^2 = 0.9999	A = 0.0207 B = 0.001 C = -5E-07 R^2 = 0.9999	A = -0.1378 B = 0.0014 C = -9E-07 R^2 = 0.9999
Linalool	A = 21.611 B = -6933.6 R^2 = 0.9977	A = 140.25 B = -0.3498 C = 3E-04 R^2 = 0.9999	A = 0.023 B = 0.0003 C = 2E-07 R^2 = 0.9999	A = -0.0307 B = 0.001 C = -6E-07 R^2 = 0.9999
Cis-3-Hexenol	A = 21.966 B = -6559.6 R^2 = 0.9991	A = 73.552 B = -0.036 C = -7E-05 R^2 = 0.9999	A = 0.0241 B = 0.0001 C = 5E-07 R^2 = 0.9999	A = -0.0057 B = 0.0006 C = -3E-07 R^2 = 0.9999

Fig. 2b shows the experimental values of the liquid heat capacity published by Štejfa et al. (2014a) and they are compared with predicted values of Joback and Reid method (1987). Constants of the model of the liquid heat capacity in Table 2 were computed from these experimental data. In the case of vapour heat capacity, we did not find any experimental data and the constants of the model in Table 2 were fitted from the predicted values using Joback and Reid method (1987). The same methodology was carried out to compute the constants of the models (see Table 2) for linalool, fenchone and cis-3-hexenol.

Batiu (2002) determined experimentally the vapour pressure of fenchone into the temperature range of 365.65K - 373.75K whereas Štejfa et al. (2014b) reported experimental values of the vapour pressure and the liquid heat capacity from 243.15 K to 308.15K. Parameters of the vapour pressure model in Table 2 were regressed by considering all experimental values displayed in Fig. 2c. A better agreement was obtained with the predicted values using Marrero and Gani method (2001) in IBSS tool. Experimental values of the liquid heat capacity reported by Štejfa et al. (2014b) are displayed in Fig. 2d and they were used for determining the model parameters reported in Table 2. Experimental values of the vaporisation enthalpy and the vapour heat capacity at several temperatures were not found in literature. Hence, both properties were estimated using the Joback and Reid method (1987) in IBSS tool and the results were used for computing the constants of their respective model in Table 2. In the case of vaporisation enthalpy, Atik et al. (1987) and Kusano (1985) reported experimental values of 51.40 kJ/mol and 51.26 kJ/mol at 298.15K, respectively. Joback and Reid method (1987) predicted the most appropriate value of 57.61 kJ/mol.

Eucalyptol

(a) Vapour pressure vs Temperature

(b) Liquid heat capacity vs Temperature

Fenchone

(c) Vapour pressure vs Temperature

(d) Liquid heat capacity vs Temperature

Linalool

(e) Vapour pressure vs Temperature   (f) Vaporisation enthalpy vs Temperature
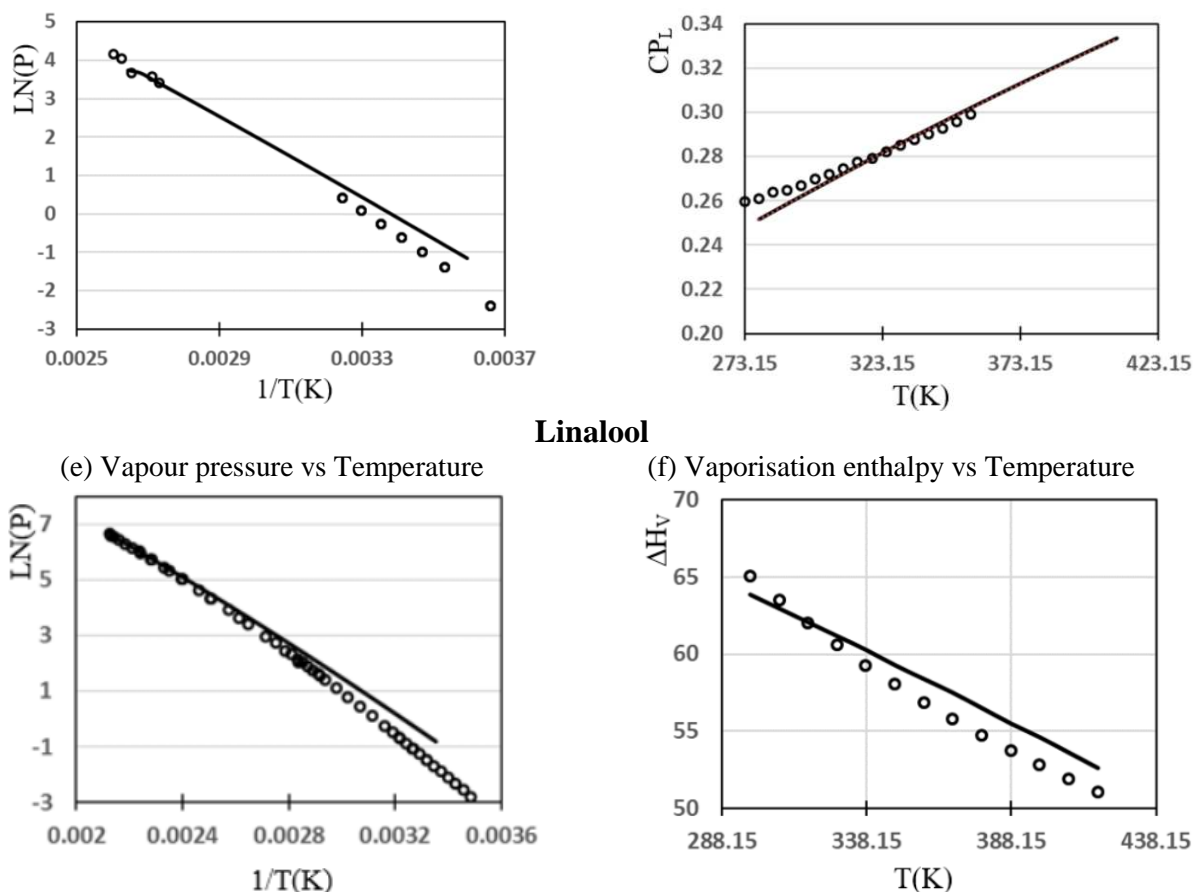
Fig. 2. Experimental physicochemical properties for several aroma molecules (circles) vs predicted values (solid lines)

Linalool is an acyclic terpenoid tertiary alcohol and some physicochemical properties were published by Batiu et al. (2012). Clará et al. (2009) and Zaitsau et al. (2015) performed experimental measurements of the boiling temperatures at different pressures as well as the vaporisation enthalpy. Fig. 2e shows the good agreement between all experimental data and the predicted values from Joback and Reid method (1987) by IBSS tool. Clará et al. (2009) determined the vaporisation enthalpy with temperature by combining the Clausius-Clapeyron equation and the experimental data of vapour pressures. Fig. 2f shows the experimental vaporisation enthalpy from Clará et al. (2009) and these values were used for computing the constants of the model reported in Table 2. Predicted values from Joback and Reid method (1987) by IBSS tool are also displayed in Fig. 2f showing a good agreement with the reported values of Clará et al. (2009). Experimental values were not found for the liquid and the vapour heat capacities of linalool. Hence, the constants of each respective model in Table 2 were computed from predicted values using Joback and Reid method (1987) using IBSS tool.

Scarce experimental data were found for cis-3-hexenol which is a naturally occurring leaf alcohol with a delicate green odour. Therefore, all constants of the model in Table 2 were determined from predicted values. Cis-3-hexenol doesn't have a complex chemical structure.

Hence, reliable predicted values are expected because the molecule can be represented by simple chemical groups CH2, CH3, C=C and OH whose contribution parameters are well established based on the vast experimental data of molecules including these chemical groups. Normal boiling temperature of 429.7 K is reported by Weast and Grasselli (1989) while Joback and Reid model (1987) provided 433.02 K, which agrees well with the experimental value.

3.2.2 Vapour – liquid equilibrium database

3.2.2.1 Thermodynamic modelling of the VLE of the synthetic mixture of six aroma compounds and DMC

Thermodynamically speaking, natural plant extracts behave as non-ideal mixture due to the formation of hydrogen bonds, the dipole/dipole interactions between polar chemical functional groups such as hydroxyl group, ketones group, ester group, cyclic oxygen atom, and π interactions of benzyl group. Furthermore, DMC has three oxygen atoms connected to a carbon atom mainly behaving as a proton acceptor. Nearness of the dew and the boiling temperature curves in VLE of binary mixtures as well as the azeotrope formation will promote the escape of the aroma molecules in the distillate. Because of the lack of experimental data, the estimation of binary and multicomponent VLE is performed using the group contribution modified UNIFAC model. Table 3 displays the chemical structure of each aroma molecule and DMC as well as the chemical group assignments for each component indicating the main group and their respective subgroups according to the classification of modified UNIFAC method (Gmehling et al. 1993).

Table 3. Group assignment for the modified UNIFAC method (Gmehling et al., 1993)

Group modified UNIFAC		Compounds						
Main group	Subgroup	Dimethyl carbonate	α-Pinene	Cis-3-Hexenol	Eucalyptol	Linanool	Fenchone	Benzyl acetate
CH3 (1)	CH3(1)	1	**3**	1	3	3	3	
	CH2(2)			3		2		
	C(4)					1		
C=C(2)	CH2=CH(5)					1		
	CH=CH(6)			1				
	CH=C(8)		**1**			1		
AcH(3)	ACH(9)							5
	ACCH2(12)							1
OH(5)	OHp(14)			1				
	OHt(82)					1		
CH2CO(9)	CH2CO(19)						1	
CCOO(11)	CH3COO(21)	0						1

CH2O(13)	CH3O(24)	1		
	CHO(26)			
COO(41)	COO(77)	1		
cyCH2(42)	cyCH2(78)	**2**	4	3
	cyCH(79)	**2**	1	1
	cyC(80)	**1**	1	1
cyCH2O(43)	THF(27) (CH2)O(CH2)			
	cyCH2O(83) (CH2)O(CH2)$^{1/2}$			
	Trioxane(84) (CH2)$^{1/2}$O(CH2)$^{1/2}$		1	

DMC is a well-known solvent and several papers have been devoted to experimental measurements of VLE with compounds from several chemical families such as saturated hydrocarbons, alcohols, esters, ketones, aromatics and carbonates. DMC is decomposed into chemical subgroups according to the existing decomposition in the modified UNIFAC method available in the thermodynamic calculator Simulis®Thermodynamics (Prosim, 2017b): one carbonate main group COO, one ether group CH3O and one CH3 group. In the case of α-pinene having a double carbon ring linked to two different carbon atoms, the main UNIFAC group cyCH2 allows considering the cyclic structure with the exception of the double bond C=C that is considered as a linear chain. Similar conditions exist for fenchone where a linear ketone group CH2CO was considered as proposed by Batiu (2002, 2005) due to the absent of a cyclic ketone group as a main group in the modified UNIFAC method (Gmehling et al. 1993). A more complex situation exists for eucalyptol that is a heterocycle sharing an oxygen atom because the subgroup cyCO doesn't exist in modified UNIFAC method (Gmehling et al. 1993). Hence, the most appropriate UNIFAC main group is CyCH2O which involves three different subgroups in order to characterise the cyclic oxygen atom in tetrahydrofuran (THF), 1,3 dioxane and trioxane as it is displayed in Table 4, cy(CH2-O-CH2), cy[(CH2)O(CH2)$^{1/2}$] and cy[(CH2)$^{1/2}$O(CH2)$^{1/2}$], respectively.

Table 4. Functional groups for molecules containing cyclic oxygen atom in modified UNIFAC method.

Molecule	Chemical Structure	Main Group	Subgroup	Decomposition	number
Tetrahydrofuran (THF)		42 43	78 27	cy-CH2 cy(CH2-O-CH2)	2 1
1.3 dioxane		42 43	78 83	cy-CH2 cy[(CH2)O(CH2)$^{1/2}$]	1 2

| Trioxane | | 43 | 84 | cy[(CH2)$^{1/2}$O(CH2)$^{1/2}$] | 3 |

Batiu (2005) proposed the eucalyptol UNIFAC decomposition by taking one contribution of trioxane subgroup cy[(CH2)$^{1/2}$O(CH2)$^{1/2}$]. However, the half of the contribution of each CH2 group linked to oxygen atom was only considered and one main group of cyCH2 was missing in the description of the total molecular structure of eucalyptol. Therefore, according to Table 3, we found three alternative ways for decomposing the whole molecular structure of eucalyptol by using separately each main chemical groups, trioxane(I) and tetrahydrofuran (II) from Table 4. Decomposition (III) consider the cyclic ether group like a linear CH2O chemical group in modified UNIFAC method as it is implemented in Simulis®Thermodynamics software (ProSim, 2017b):

(I)   1- cy[(CH2)$^{1/2}$O(CH2)$^{1/2}$] + 1-cyC + 1-cyCH + 4-CyCH2 + 3-CH3;

(II)   1-cy(CH2-O-CH2) + 1-cyCH + 4-CyCH2 + 3-CH3;

(III)   1-CH2O + 1-cyC + 1-cyCH + 4-CyCH2 + 3-CH3.

Table 5 displays the interaction parameters of the main chemical groups required for computing all binary VLE between the seven components composing the synthetic solution. Critical situation appears for the prediction of VLE involving DMC because the absence of the interaction parameters between the UNIFAC groups CH2O(13) and COO(41). As it can be observed in Table 3, both functional chemical groups are included in the molecular group decomposition of DMC when using modified UNIFAC method. Furthermore, the prediction of VLE between DMC and eucalyptol cannot be performed because the lack of the constants of the Eq. (12) between the carbonate group COO (41) and the cyclic ether group cyCH2O(43) in the modified UNIFAC database of the Simulis®Thermodynamics software (ProSim, 2017b). The missing parameters of Eq. 12 (N.A. in Table 5) can be computed from available experimental VLE data of binary mixtures including one component that contains carbonate group COO(41) in the chemical structure while the second component has a cyclic oxygen atom cyCH2O(43) or a linear ether group CH2O(13) according to Table 3.

Table 5. Modified UNIFAC parameters in Simulis®Thermodynamics software (1 ($a_{m,n}$) ; 2($a_{m,n}.b_{m,n}$) and 3($a_{m,n}; b_{m,n}; c_{m,n}$))

Groups	CH3	C=C	AcCH	AcCH2	OH	CH2CO	CCOO	CH2O	COO	CyCH2	CyCH2O
CH3(1)	0	2	2	2	3	2	3	2	2	3	3
C=C(2)	2	0	2	2	3	2	2	2	2	2	3

AcCH(3)	2	2	0	2	3	3	2	2	2	3	2
AcCH2(4)	2	2	2	0	3	3	3	2	2	2	2
OH(5)	3	3	3	3	0	3	3	3	2	3	3
CH2CO(9)	2	2	3	3	3	0	2	3	1	2	2
CCOO(11)	3	2	2	3	3	2	0	3	2	3	1
CH2O(13)	2	2	2	3	3	3	3	0	N.A.	2	2
COO(41)	2	2	2	2	2	1	3	N.A.	0	2	N.A.
CyCH2(42)	3	2	3	2	3	2	3	2	2	0	2
CyCH2O(43)	3	3	2	2	3	2	1	2	N.A.	2	0

Table 6 displays the experimental VLE data found in the specialty literature. Most of data were measured in the temperature range between 298.15 K and 413.15 K at low pressure. It should be noted that all experimental VLE data of binary mixtures with carbonates involve acyclic compounds only. Hence, we cannot determine the parameters between the groups COO(41) and CyCH2O(43) as described in Table 5. We can only take into account the chemical group decomposition (III) for eucalyptol which includes the functional groups CH2O(13) and COO(41) as for DMC .

Table 6. VLE experimental data for computing the interaction parameters COO – CH2O of Modified UNIFAC method. (N: number of experimental data points)

components		VLE Type	N	ΔP	ΔT	Δy
[1]dimethyl carbonate	2-ethoxyethanol	P= 66.66 kPa	58	-	0.3150	1.9463
		P= 93.32 kPa			0.2979	2.1256
[2]dimethyl carbonate	methyl ethyl carbonate	P= 101.3 kPa	49	-	0.0195	0.1110
[2]methyl ethyl carbonate	diethyl carbonate				0.0076	0.0677
[2]dimethyl carbonate	diethyl carbonate				0.0242	0.4246
[2]dimethyl carbonate	propylene carbonate				0.0696	0.0318
[3]dimethyl carbonate	methyl tert-butyl ether	T= 298.15 K	43	0.2942	-	0.5240
[3]diethyl carbonate	methyl tert-butyl ether			0.6600		1.9889
[4]dimethyl carbonate	dimethyl oxalate	T= 373.15 K	40	0.6729	-	0.1075
		T= 393.15 K		0.4057		0.1779
		T= 413.15 K		0.3492		0.1611

[1] Matsuda et al. (2011); [2]Luo et al. (2001), [3] Francesconi R. (1997), [4]Ma et al. (2004)

The three constants $a_{k.j}; b_{k.j}; c_{k.j}$ of the group interaction parameters of Modified UNIFAC method were determined from the experimental data reported in Table 6 by using Simulis®Thermodynamics software (ProSim, 2017b) and minimising the following objective function:
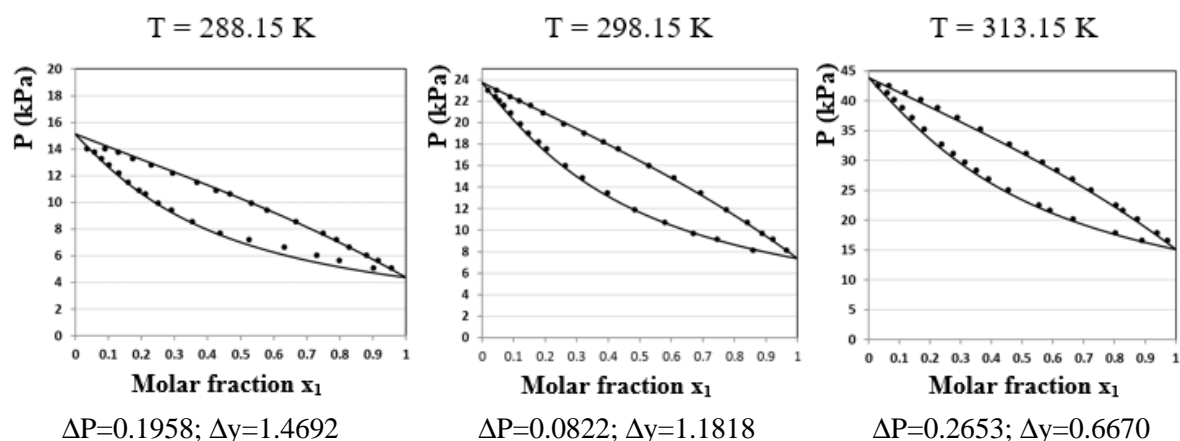
$$O.F = \sum_{i=1}^{N} ABS\left(\frac{P_i^{exp}-P_i^{cal}}{\left(\frac{P_i^{exp}+P_i^{cal}}{2}\right)}\right) + ABS\left(\frac{T_i^{exp}-T_i^{cal}}{\left(\frac{T_i^{exp}+T_i^{cal}}{2}\right)}\right) + ABS\left(\frac{x_{1.i}^{exp}-x_{1.i}^{cal}}{\left(\frac{x_{1.i}^{exp}+x_{1.i}^{cal}}{2}\right)}\right) + ABS\left(\frac{y_{1.i}^{exp}-y_{1.i}^{cal}}{\left(\frac{y_{1.i}^{exp}+y_{1.i}^{cal}}{2}\right)}\right)$$

(13)

Table 7 displays the interaction parameters between the main chemical group of linear ether CH2O(13) and the carbonate group COO(41) according to the chemical functional groups defined in the Modified UNIFAC method. The six constants $a_{m,n}; b_{m,n}; c_{m,n}$ in Table 7 provided the minimal value of the O.F at 28.2357. The relative errors ΔP, ΔT and Δy of the respective term in the Eq. (13) are reported in table 6 for the training set. It should be noted that the best fitting occurs for the binary mixtures only including carbonates compounds. The worst fitting corresponds to the binary mixture DMC - 2-ethoxyethanol that could be explained by the presence of the OH group promoting the formation of hydrogen bonds in addition to the dipole/dipole interactions due to the presence of the ether group.

Table 7. Parameters of Eq. (12) between the carbonate group (COO) and the linear ether group (CH2O) for Modified UNIFAC method.

Main Group	$a_{m,n}$ (K)	$b_{m,n}$	$c_{m,n}$(K^{-1})
(41)COO $\rightarrow$ (13)CH2O	-897.3714	-9.4579	0.03067
(13)CH2O $\rightarrow$ (41)COO	-518.1647	4.7562	-0.00653

The interaction parameters $a_{m,n}; b_{m,n}; c_{m,n}$ were then used for computing the binary VLE data between DMC and 1,2-epoxybutane which was selected for the validation set. Experimental VLE data were measured at three temperatures 288.15 K, 298.15 K and 313.15 K (Francesconi and Comelli, 1996). Modified UNIFAC decomposition of 1,2-epoxybutane was defined as 1CH3+1CH2+1CH+1CH2O. Fig. 3 displays the boiling and the dew temperature curves versus the molar fraction of DMC as well as the values of relative errors ΔP and Δy in the Eq. (13) showing the satisfactory agreement of the predicted results with the experimental points. Therefore, these parameters can be used for predicting the VLE of binary mixtures including DMC and especially for the mixture DMC – eucalyptol.

T = 288.15 K   T = 298.15 K   T = 313.15 K

$\Delta P=0.1958$; $\Delta y=1.4692$ $\Delta P=0.0822$; $\Delta y=1.1818$ $\Delta P=0.2653$; $\Delta y=0.6670$

Fig. 3. Binary VLE for $DMC(x_1)$ – 1,2-epoxybutane at different temperatures. Experimental values (dot). Calculated values (solid line).

The suitability of the Modified UNIFAC method for predicting binary VLE of the aroma molecules was also studied by comparing experimental data with predicted results. Table 8 displays the average relative deviation of the temperature (or pressure) and the vapour composition of the binary mixtures including α-pinene, fenchone, eucalyptol or linalool with linear alcohols, alkanes, alkenes and cyclic compounds. Some experimental VLE data of binary mixtures including only aroma compounds were also considered. The experimental set contains VLE data under a great variability of temperature and pressure conditions. Most of data were measured at reduced total pressure and low temperature. Overall, very good agreement occurs between the experimental data and the predicted results from Modified UNIFAC model. These results indicate the suitability of applying the Modified UNIFAC model for predicting binary VLE of mixtures including aroma compounds.

Table 8. Comparison between experimental VLE data and predicted values by Modified UNIFAC model.

Mixture	N	P(kPa)	T(K)	ΔT	ΔP	Δy	data source
α-pinene – 1-butanol	12	26.66	-	0.0447	-	0.9932	1
α-pinene – 1-butanol	12	40	-	0.0418	-	0.8382	1
α-pinene – 1-butanol	12	53.33	-	0.0383	-	0.7363	1
α-pinene – 1-pentanol	11	26.66	-	0.0402	-	0.7022	1
α-pinene – 1-pentanol	11	40	-	0.0211	-	0.4571	1
α-pinene – 1-pentanol	11	53.33	-	0.0230	-	0.2973	1
α-pinene – 1-hexanol	11	26.66	-	0.0185	-	0.2142	1
α-pinene – 1-hexanol	11	40	-	0.0194	-	0.1604	1
α-pinene – 1-hexanol	11	53.33	-	0.0166	-	0.1220	1

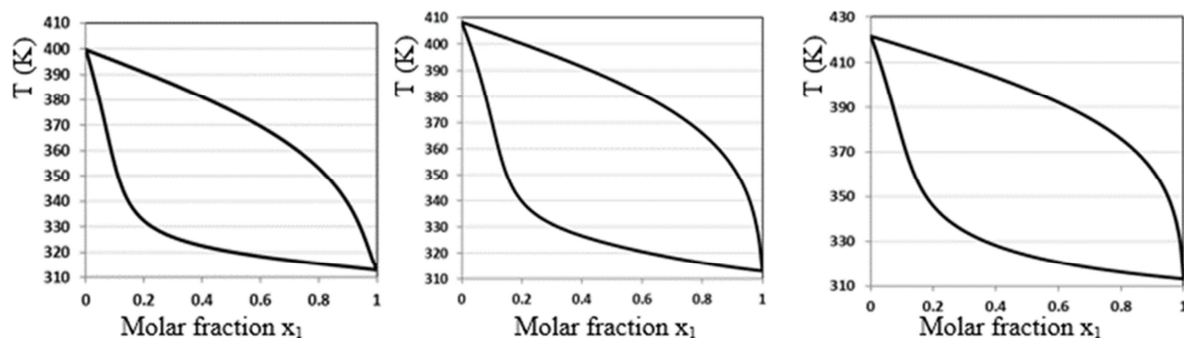|	N	P	T	ΔP	ΔT	Δy	ref
α-pinene - (+)-limonene	31	101.3	-	0.0156	-	0.2483	2
α-pinene - eucalyptol	31	101.3	-	0.0713	-	1.179	2
α-pinene - cyclohexane	14	-	338.15	-	0.8112	0.3099	3
α-pinene - heptane	18	-	358.15	-	0.5523	0.8359	3
α-pinene - octene	13	-	368.15	-	0.4894	0.5644	3
α-pinene - cyclohexene	17	-	343.15	-	0.2019	0.1476	3
eucalyptol – (+)-limonene	31	101.3	-	0.0742	-	1.1104	2
fenchone - decane	13	6.67	-	0.0068	-	0.1243	4
Linalool – n-propanol	11	20	-	0.0148	-	0.8703	5
Linalool – 1-butanol	11	60	-	0.0117	-	0.2775	5
Linalool – n-propanol	11	20	-	0.0273	-	1.0327	5
Linalool – 1-butanol	11	60	-	0.0171	-	0.7363	5

[1]Congmin et al. (2003); [2]Reich et al. (1992), [3]Farelo et al. (1991), [4]Batiu (2002), [5]Dongshun et al. (2002)

$$\left(\Delta P = \sum_{i=1}^{N} ABS\left(\frac{P_i^{exp}-P_i^{cal}}{\left(\frac{P_i^{exp}+P_i^{cal}}{2}\right)}\right), \quad \Delta T = ABS\left(\frac{T_i^{exp}-T_i^{cal}}{\left(\frac{T_i^{exp}+T_i^{cal}}{2}\right)}\right), \quad \Delta y = ABS\left(\frac{y_{1.i}^{exp}-y_{1.i}^{cal}}{\left(\frac{y_{1.i}^{exp}-y_{1.i}^{cal}}{2}\right)}\right)\right.$$

3.2.2.2 Determination of binary and ternary VLE for the synthetic mixture at reduced pressure

The working pressure of the batch distillation process of 15 kPa was defined by the industrial partner taking into account the vapour pressure model of DMC available in DPPR database (see Table 2) and fixing the condensation temperature of the distillate product at 313.15K (the DMC boiling temperature at 15 kPa). Fig. 4 displays the binary VLE between DMC and each aroma molecule considered in the synthetic mixture at 15 kPa by using the Modified UNIFAC method.

(a) DMC – α-Pinene   (b) DMC– cis-3-hexenol   (c) DMC – Eucalyptol

(d) DMC – Fenchone   (e) DMC – Linalool   (f) DMC–Benzyl acetate
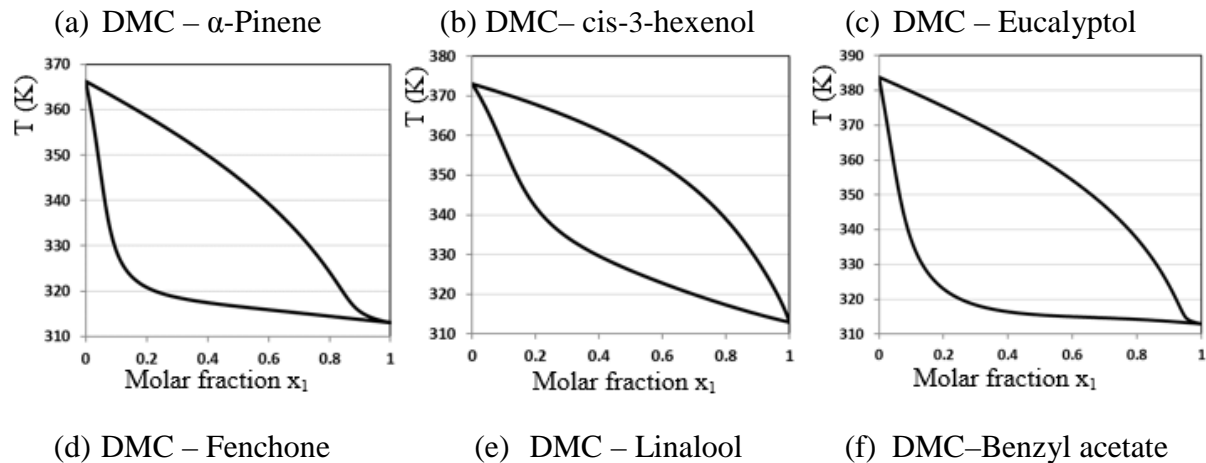
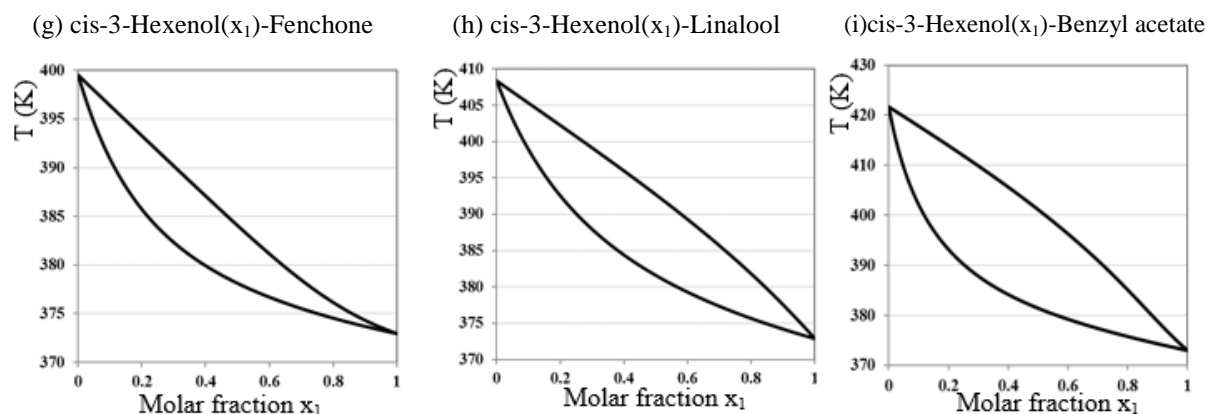**Fig. 4.** Binary VLE between DMC (x_1) and each aroma compound in the synthetic mixture computed by Modified UNIFAC method at 15 kPa (molar fraction)

Due to the closeness between the boiling and dew temperature curves at high composition of DMC in Fig. 4a and 4c, potential loss of α-pinene and eucalyptol could happen during the DMC recovery by batch distillation process. The loss of these aroma molecules in the distillate will decrease the olfactive quality of the concrete recovered into the reboiler at the end of the batch distillation process. These VLE results indicate that DMC recovery will require a high number of equilibrium trays and reflux ratio in order to avoid the loss of α-pinene and eucalytol. For completing all information about the thermodynamic scenario of the multicomponent synthetic mixture, the binary VLE were also determined for each pair of aroma compounds in order to detect the eventual formation of azeotropic mixtures.

(a) α-Pinene(x_1) – cis-3-Hexenol   (b) α-Pinene(x_1) – Eucalyptol   (c) α-Pinene(x_1) – Fenchone

(d) α-Pinene(x_1) – Linalool   (e) α-Pinene(x_1) – Benzyl Acetate   (f) cis-3-Hexenol(x_1)-Eucalyptol

(g) cis-3-Hexenol(x_1)-Fenchone (h) cis-3-Hexenol(x_1)-Linalool (i)cis-3-Hexenol(x_1)-Benzyl acetate
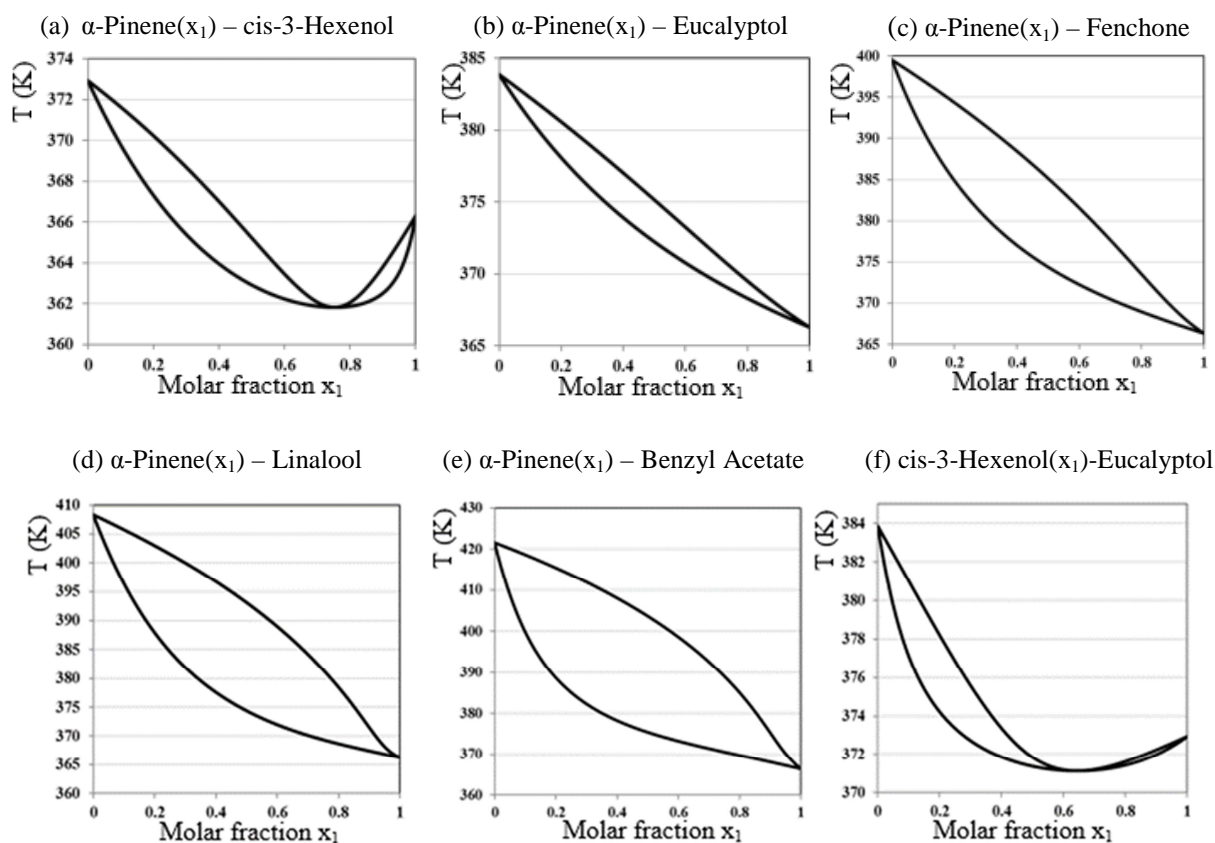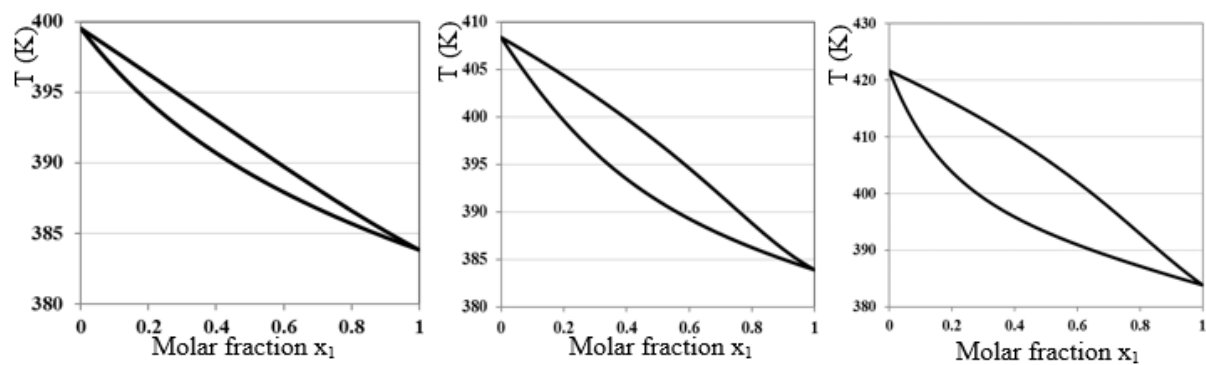

Fig. 5. Prediction of VLE between each pair of aroma compounds in the synthetic mixture computed by Modified UNIFAC method at 15 kPa (molar fraction).

Fig. 5 displays the binary VLE at P = 15kPa between all possible binary combinations. It can be observed in Fig. 5 that α-pinene(x_1) forms a binary azeotropic mixture with cis-3-hexenol having a molar fraction of x_1 = 0.756 and a boiling temperature of BP = 361.8K. Another binary azeotrope is formed under this working pressure between cis-3-hexenol(x_1) and eucalyptol with x_1 = 0.654 and BT = 371.1K. The loss of α-pinene with DMC could also promote the loss of cis-3-hexenol and eucalyptol in the distillate because both binary azeotropic mixtures are minimum boiling temperature type (see Figs 5a and 5f). Indeed, the boiling temperature of the azeotropic mixtures is close to those of α-Pinene (366.35K) at 15 kPa. Furthermore, the existence of a ternary azeotrope between α-pinene, cis-3-hexenol and eucalyptol was checked because it is usually promoted by the existence of two binary azeotropic mixtures with close boiling temperatures. A minimum boiling ternary azeotrope would increase even more the loss of these molecules in the distillate together with DMC. Ternary residue curve map was computed by Simulis®Thermodynamics at P = 15 kPa. Fig. 6 displays the computed residue curve map of the ternary mixture by using Modified UNIFAC and predicting that there is not formation of a ternary azeotropic mixture.

(j) Eucalyptol(x_1) - Fenchone   (k) Eucalyptol(x_1) - Linalool   (l) Eucalyptol(x_1)-Benzyl Acetate
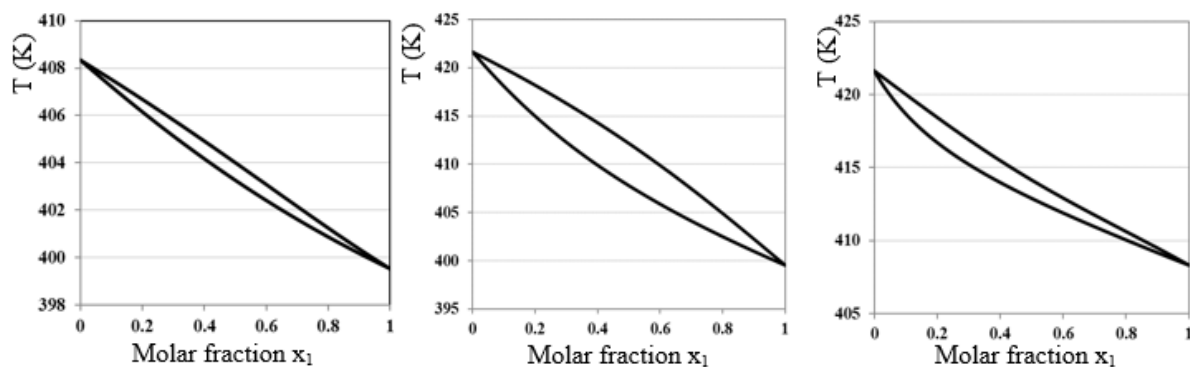
23

| (m) Fenchone(x_1) - Linalool | (n) Fenchone(x_1) - Benzyl Acetate | (o) Linalool(x_1) - Benzyl Acetate |

Fig. 5. (continued). Prediction of VLE between each pair of aroma compounds in the synthetic mixture computed by Modified UNIFAC method at 15 kPa (molar fraction).

We can now proceed with the use of the process simulator that will help to minimise the loss of aroma compounds in the distillate product by finding the suitable operating conditions for DMC recovery. We present in the next section the simulation results as well as the experimental validation of the process in a laboratory batch distillation column.
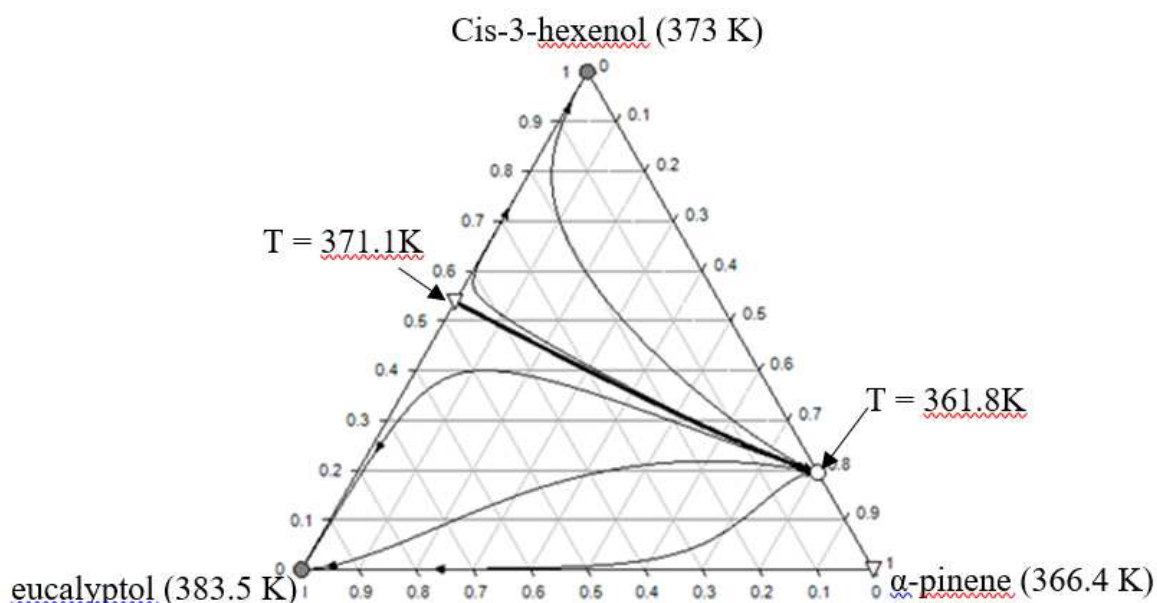
Fig. 6. Residue curve map for the ternary mixture of α-Pinene - cis-3-hexenol – eucalyptol predicted by Modified UNIFAC model at 15 kPa (mass fraction).

3.3. Process simulation and experimental validation

3.3.1. Chemicals, methods and experimental setup

3.3.1.1. Standards and solvents

Chemicals for preparing the synthetic mixture used in the batch distillation experiments have the following features: Dimethyl carbonate (99 wt%) was purchased from Fluka, α-pinene (98% of purity), eucalyptol (99% of purity) and (+)-fenchone (>98% of purity) were provided by Aldrich, cis-3-hexenol (>98% of purity), linalool (97% of purity) and benzyl acetate (99% of purity) were purchased from Sigma-Aldrich. All components were used without any additional purification.

3.3.1.2. Analytical methods

GC analysis was carried out using an Agilent 7890 equipped with a flame ionization detector and fitted with a 20m x 0.1mm x 0.1µm VF-1MS column programmed at 3°C/min from 70°C to 250°C held for 60 minutes. Helium was the carrier gas with a flow rate of 0.5 mL/min. Split ratio: 500. Relative amounts of individual components are based on peak areas obtained without FID response factor correction. GC–MS analysis was carried out using an Agilent 6890 GC coupled with an Agilent 5975 MSD operated in EI mode at 70 eV, fitted with a 60 m x 0.25 mm x 0.25 µm VF-1ms column programmed at 2°C/min from 70°C to 250°C held for 90 minutes. Helium was the carrier gas with a flow rate of 1 mL/min. Split ratio: 50. Identifications were achieved by comparison of the mass spectra and retention indices (RIs) with those of both in-house and commercial MS libraries. Three replicates were

25

performed for each sample. The average of these three values and the standard deviation were determined for each identified component.

3.3.1.3. Experimental setup at laboratory scale.

Experiments of the separation of DMC from the synthetic mixture at 15 kPa were carried out in a fully automated FISCHER technology® LABODEST® HRS 500C. The experimental distillation setup is displayed in Fig. 7.

Fig. 7. Experimental batch distillation column. Model LABODEST® HRS 500C of Fischer Technology.

The FISCHER® LABODEST® HRS 500 C is a compact and versatile distillation unit where the column is packed with a special packing providing up to 90 theoretical plates as separation efficiency. The liquid hold-up inside the column and the pressure drop can be neglected. A vacuum pump system connected at the column top allows the separation of mixtures until 0.1 mbar. The reboiler flask with a maximal capacity of 500 mL is submerged into an oil bath while the packed column is heated by an external electric mantle. The condenser and the subcooler are connected to a cryostat. The modular system has a control panel allowing the monitoring of the pressure and the temperature at several locations of the column. Pt100 sensors are placed into the reboiler, in the main condenser and in five positions along the height of the column. The reflux ratio is controlled by the open/close time of a

solenoid valve located between the column top and the vertical main condenser. Distillate product is collected in 10 ml flasks under vacuum pressure conditions.

3.3.2 Experiments and simulation studies

The synthetic mixture of seven components was prepared by mass control providing a DMC mass fraction of 0.6652 and 0.0558 for each aroma molecule. Three batch distillation runs were carried out at pressure of 15 kPa with an initial mass charge of 0.211 kg into the reboiler. The temperature of the cryostat condenser was set at 276.15 K to prevent solidification of DMC (see Table 1). The initial temperature of the heating oil surrounding the reboiler was 323.15 K that is 10 K higher than the boiling temperature of DMC under the working pressure. A difference of 2 K was set between the temperatures of the oil bath and of the liquid into the reboiler during the distillate withdrawal. This set of temperature difference allows the increasing of the heating fluid temperature along with the increasing of the liquid temperature into the reboiler because the enrichment in high boiler compounds with higher vaporisation enthalpy and specific heat coefficients. The distillate flow rate remains most the time stable with this type of power supply control. The external heat mantle around the packed column was set at 2 K lower than the temperature of the internal vapour in order to avoid the flooding condition into the column. After the reboiler was charged with the initial mixture and the working pressure was set at the condenser, the distillation column was run with no reflux until the first condensate drops were visually detected into the condenser. Next, the solenoid valve was closed and the column run under total reflux during one hour. Steady state operation was corroborated by the constant temperature of the liquid into the reboiler and of the vapour at the column top. The withdrawal of DMC started under a reflux ratio of 0.5, which provided a good compromise between the total operating time and the purity of DMC according to the preliminary simulation tests. The temperature at the top of the column and into the reboiler were recorded along with the filling time of each distillate flask. Batch distillation process was stopped when a significant increasing of the temperature was detected at the top of the column between two consecutive distillation cuts. Samples of the distillate flask were taken for further mass quantification of DMC and each aroma molecule. Experimental variation of the distillation composition and the temperatures of the liquid into the reboiler and of the vapour at the top of the column with the operating time were compared with the simulation results given by BatchColumn® software (Prosim, 2017a).

Technical features of the experimental batch distillation column and the operating conditions were taken into account for simulation studies in order to corroborate the predicted

VLE using Modified UNIFAC at 15 kPa (Figs 4-6) with the computed interaction parameters of the chemical groups COO and CH2O (see Table 7). The simulation studies of DMC recovery were carried out at reduced pressure of 15kPa, taking into account the total amount and the experimental composition of the initial charge. We considered adiabatic operation of the distillation column and negligible liquid hold-up and pressure drop.

While there exist several shortcut methods for the design of continuous distillation processes to assess operating parameter values (reflux ratio, tray number, feed tray location), only a few have been extended to dynamic batch distillation processes (Mujtaba, 2004, Diwekar, 2012). Adaptations of Fenske equation work well for nearly ideal mixtures with constant volatility, however, they are not suited in our case where the non-ideal thermodynamic behavior in the mixture DMC – aroma compounds gives rise to pinch and azeotropes. Instead, analysis of residue curve maps (RCM) is necessary (Gerbaud et al., 2006) to get an estimate of tray numbers under total reflux operation, combined with computation of composition profiles under finite reflux value to refine tray numbers and assess feasibility regions. In our case multicomponent mixture makes the RCM analysis difficult because of the absence of graphical representations. As an alternative to computing composition profiles maps, simulation was used spanning several tray number configurations from 90 (maximum separation capacity of the experimental column). A distillation column having between 50 and 55 equilibrium trays provides a high separation of DMC as well as a minimum absolute error between the computed and experimental values of the temperature of the liquid into the reboiler after one hour of operation under total reflux. The computed reflux ratio of 0.5 maintains the high separation performance of the column as the DMC content decreases into the reboiler during the batch distillation process. The vapour flow rate was adjusted from the experimental measurements of the averaged distillate flow rate and the reflux ratio. The start-up condition of the batch distillation column was considered as the steady state liquid profile inside the column at total reflux. The stop criterion for simulation runs was the experimental final temperature of the vapour at the top of the column.

Fig. 8 displays the variation of experimental and simulation values of the temperature of the vapour at the top condenser of the column (Fig. 8a) and the liquid into the reboiler (Fig. 8b). Very good agreement exists between both results particularly for the vapour temperature at the column top that keeps at 313.15 K corresponding to the boiling temperature of pure DMC at 15 kPa (see Fig. 8a). High purity DMC was withdrawn as distillate product during almost the whole operation time with a reflux ratio of 0.5. Indeed, DMC was the most volatile component of the multicomponent mixture corroborating the prediction of modified UNIFAC

model (see Fig. 4-6) about the non-existence of a lower boiling temperature binary or ternary azeotrope in the multicomponent synthetic mixture. Fig. 8b displays a similar trend of the temperature variation of the liquid mixture into the reboiler for both, experimental and simulation results. The most significant deviations between the experimental and simulation values of the temperature inside the reboiler is observed during the last part of the distillation process when DMC is almost exhausted from the distillation column and the liquid mixture contained into the reboiler was very viscous and sticky. A sudden increase of the vapour temperature at the top of the column from 313.15 K to 362.15 K was computed by simulation providing a final operating time of 440 minutes. This simulation result agrees very well with the experimental operating time of 436 minutes.

(a) Temperature of the top vapour vs time   (b) Temperature into the reboiler vs time
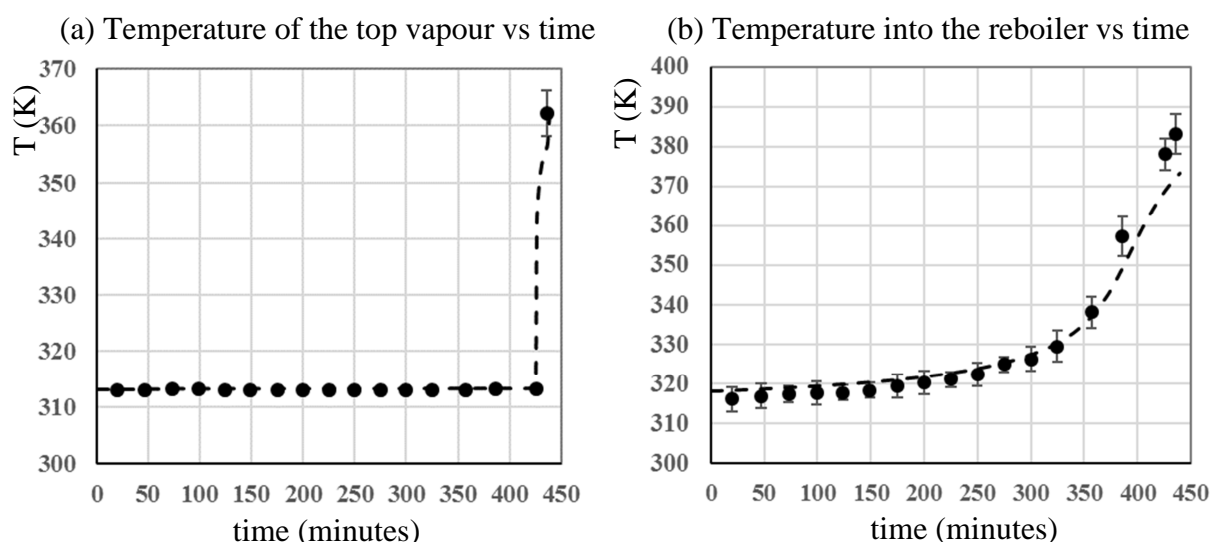
Fig. 8. Variation of the temperature at the top vapour of the column and of the liquid into the reboiler vs the operating time. Experimental values (dots). Simulation results (discontinuous line)

Table 9 displays the average values of the mass composition for DMC and for the detected aroma compounds in the experimental distillate cuts and their respective computed values by simulation. The maximum absolute error of the quantification of DMC, α-pinene and cis-3-hexenol of the three replicates was obtained for the last distillate cut and are reported in Table 9. A decrease of the DMC content in the last distillate cut occurred abruptly because 98.3% of its total mass in the initial charge had been withdrawn in all previous distillate cuts providing an average mass purity of the distillate product of 0.9872. Consequently, a significant amount of α-pinene and cis-3-hexenol were found in the last cut of distillate due to the quick temperature increase of 50 K of the vapour at the top of the column. In the last distillate cut, the experimental mass fraction of DMC is lower than the computed value by simulation and consequently, the α-pinene content is higher. Similar to simulation, α-pinene

was detected experimentally since the first distillate cut, corroborating that the loss of this aroma compound takes places because of the closeness of the boiling and dew temperatures curves at high DMC composition as it was predicted by Modified UNIFAC method (see Fig.4a). These experimental and simulation results demonstrate that loss of α-pinene will be barely avoided in the distillate product of the industrial solvent recovery process. Cis-3-hexenol was detected experimentally in the last distillate cut while eucalyptol was only identified by simulation. The presence of cis-3-hexenol in the experimental last distillation cut can be explained by the predicted formation of a minimum boiling binary azeotropic mixture with α-pinene by Modified UNIFAC method (see Fig. 5a). The final experimental temperature at the top of the column (362.15 K) is very close to the predicted temperature of 361.8K of the azeotrope α-pinene – cis-3-hexenol at is is shown in Fig. 6.

Table 9
Mass composition of the distillate cuts.

Time (minutes)	Experiments				Simulation results			
	x_{DMC}[a]	$x_{\alpha\text{-pinene}}$[b]	$x_{cis\text{-}3\text{-hexenol}}$[c]	$x_{eucalyptol}$	x_{DMC}	$x_{\alpha\text{-pinene}}$	$x_{cis\text{-}3\text{-hexenol}}$	$x_{eucalyptol}$
20	0.9956	0.0044	0	0	1	0	0	0
47	0.9977	0.0023	0	0	0.9984	0.0015	0	0
99	0.9981	0.0019	0	0	0.9922	0.0077	0	0
149	0.9970	0.0029	0	0	0.9896	0.0102	0	0
175	0.9966	0.0034	0	0	0.9890	0.0108	0	0
225	0.9964	0.0036	0	0	0.9885	0.0112	0	0
325	0.9951	0.0049	0	0	0.9876	0.0121	0	0
386	0.9944	0.0056	0	0	0.9866	0.0132	0	0
426	0.9939	0.0061	0	0	0.9854	0.0144	0.0020	0
436	0.2760[a]	0.6040[b]	0.1200[c]	0	0.3911	0.4825	0.1132	0.0130

Maximum Absolute Error: [a]0.0011; [b]0.023; [c]0.008

Fig. 9 shows the instantaneous variation of the mass composition of DMC and α-pinene in the distillate versus the operating time computed by simulation. It should be noted that the total operating time computed by simulation is four minutes longer. Hence, simulation results provides a more significant variation of the mass fraction of α-pinene during the withdrawal of the last distillate cut. The experimental mass fraction of α-pinene reached a maximum at 0.61 that is close to the composition of the binary azeotrope with cis-3-hexenol (see Fig 5a) which was predicted by Modified UNIFAC model. In general, there is a satisfactory agreement between the experimental and simulated values of the mass fraction of the solvent

and aroma compounds in the distillate cuts with the exception of eucalyptol, which was only detected in the last cut of distillate by simulation but with a low mass content of 1.3%.

The average total final mass recovered into the reboiler was 0.06597 kg from experiments that matched very well with the simulation value of 0.0645 kg. Component mass quantification of the experimental concrete was not carried out due to the high viscosity of the mixture retained into the reboiler with a burned appearance. In general, good agreement was obtained between simulation and experimental results, demonstrating the capability of the Modified UNIFAC method along with the new group interaction parameters (see Table 7) for modelling the complex thermodynamic behavior of the VLE between the aroma molecules with DMC. Experimental features of the separation of the complex multicomponent mixture by batch distillation process can be explained via the coupling of the group contribution method Modified UNIFAC with a rigorous process simulator by including a suitable molecular decomposition for each molecule as well as a proper computation of the missing parameters from current experimental data.
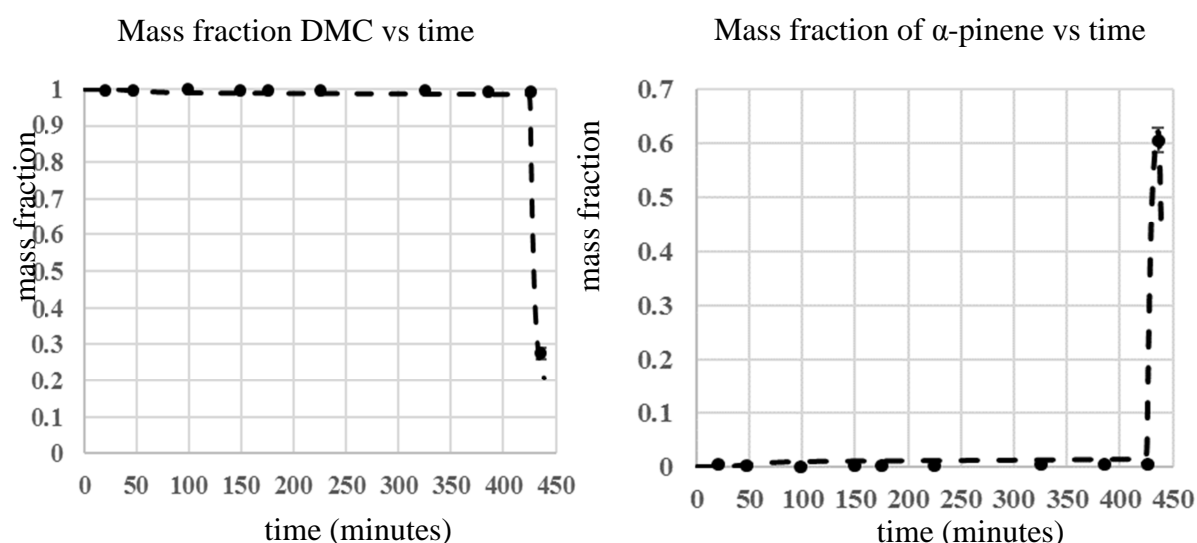
Fig. 9. Variation of the mass fraction of target molecules in the distillate product vs the operating time. Experimental values (dots). Simulation results (discontinuous line)

4. Conclusions

Within the context of aroma industry, we have presented the modelling and experimental validation of dimethyl carbonate solvent recovery from a synthetic six-compound aroma mixture by batch distillation under reduced pressure. The methodology deals with two main difficulties on process simulation study: the calculation of physicochemical properties of aroma compounds and the computation of the VLE of all involved mixtures with two or more

compounds exhibiting complex chemical interactions. The application of group contribution methods allowed the prediction of all required physicochemical properties of the missing aroma molecules in the database of the commercial process simulators. Besides, modified UNIFAC method has demonstrated the good capability of predicting the binary and the ternary VLE of these complex mixtures by using a suitable molecular decomposition of each aroma compound as well as a proper computation of the missing parameters from available experimental data. Simulation study of DMC recovery by using BatchColumn® software allows the prediction of the dynamic distribution of the aroma compounds inside the column and their contents in the distillate cuts. Experimental results in a laboratory batch distillation column were in good agreement with the simulation results. The loss of α-pinene in the distillate is promoted by the nearness of the boiling and dew temperature curves at high composition of DMC in the VLE of this binary mixture. Similarly, the prediction of a low boiling azeotrope between α-pinene and cis-3-hexenol can explain the loss of cis-3-hexenol in the last distillate cut. These results prove that the loss of α-pinene will be barely avoided in the distillate product of the industrial solvent recovery process. A co-solvent forming a low boiling binary azeotrope with DMC could be added into the reboiler at the end of the distillation process to fully recover this solvent while keeping the better organoleptic properties of the concrete. The methodology will be extended for a reliable calculation of the operating conditions in larger scales in order to maximise the recovery of the DMC and its recycling towards the preliminary extraction process. The proposed thermodynamic approach can be applied to the solvent recovery from natural extracts including other aroma compounds.

References

Abrams, D.S., Prausnitz, J.M., 1975. Statistical thermodynamics of liquid mixtures: a new expression for the excess Gibbs energy of partly or complete miscible systems. AIChE J. 21, 116-128.

Atik, Z., Saito, Y., Kusano K., 1987. Thermodynamic properties of liquid enantiomers I. Enthalpies of vaporization of fenchones, α-methylbenzylamines, and limonenes at 298.15 K. J. Chem. Thermodyn. 19, 99–102.

Basile, A., Jimenez-Carmona, M.M., Clifford, A.A., 1998. Extraction of rosemary by superheated water. J. Agric. Food Chem. 46, 5205-5209.

Batista, F.R.M., Meirelles, A.J.A., 2011. Computer simulation applied to studying continuous spirit distillation and product quality control. Food Control. 22, 1592–1603.

Batiu, I., 2002. Vapor–liquid equilibria in the binary systems n-decane + (−)-menthone and n-decane + (+)-fenchone at temperatures between 344.45 and 390.75 K. Fluid Phase Equilib. 198, 111–121.

Batiu, I., 2005. Vapor–liquid equilibria in the binary system (−)-beta-pinene + (+)-fenchone. Analysis in terms of group contributions models of some binary systems containing terpenoids. Fluid Phase Equilib. 227, 113–124.

Batiu, I., Radoias, G., Bosilcov, A. 2012. Vapor - liquid equilibria in the binary system (3R)-(-)-linalool + (3S)-(-)-beta-citronellol. Studia UBB Chemia, LVII, 2, 29 – 45.

Carvalo, J., Labbe, M., Perez-Correa, J.R, Zaror, C., Wisniak, J. 2011. Modelling methanol recovery in wine distillation stills with packing columns. Food Control. 22, 1322–1332.

Clara, R.A, Gomez Marigliano, A.C., Solimo, H.N, 2009. Density, viscosity, and refractive index in the range (283.15 to 353.15) K and vapor pressure of α-pinene, d-limonene, (±)-linalool, and citral over the pressure range 1.0 kPa atmospheric pressure. J. Chem. Eng. 54, 1087–1090.

Congmin, W., Haoran, L., Jun, T. Shijun, H., 2003. Vapor–liquid equilibria for binary α-pinene + alkanols system. Fluid Phase Equilib. 209, 147–154.

Constantinou, L., Gani R., O'Connell J.P., 1995. Estimation of the acentric factor and the liquid molar volume at 298 K using a new group contribution method. Fluid Phase Equilib. 103, 11-22.

Decloux, M., Coustel, J., 2005. Simulation of a neutral spirit production plant using beer distillation. Int. Sugar J. 107 (1223), 628–643.

Decloux, M., Deterre, S., Kadir, S., Giampaoli, P., Albet, J., Joulia, X., Baudouin, O., 2014. Two industrial examples of coupling experiments and simulations for increasing quality and yield of distilled beverages. Food Bioprod. Process. 92, 343–354.

Diwekar, U. M., 2012. Batch Distillation: Simulation, Optimal Design and Control; 2dª Edition,
U.S.A.: Editorial CRC Press.

Dongshun. D., Haoran. L., Shijun, H., 2002. Isobaric (vapour + liquid) equilibria of (linalool + 1propanol) and (linalool + 1butanol). J. Chem. Thermodynamics. 34, 1431–1437.

Farelo, F., Santos, F., Serrano, L., 1991. Isobaric vapor liquid equilibrium in binary mixtures of α-pinene. limonene and 1.8-cineole. Can J Chem Eng. 69, 794-799.

Francesconi, R. and Comelli, F., 1996. Vapor-Liquid Equilibria, Excess Molar Enthalpies, and Excess Molar Volumes of Dimethyl Carbonate + 1,2-Epoxybutane at 288.15, 298.15, or 313.15 K. J. Chem. Eng. Data. 41. 736-740.

Francesconi, R., 1997. Vapor-liquid equilibria. excess molar enthalpies et excess molar volumes of dialkyl carbonates + methyl tert-butyl ether at 298.15 K. J. Chem. Eng. Data. 42. 697-701.

Fredenslund, A., Jones, R.L., Prausnitz, J.M., 1975. Group contribution estimation of activity coefficients in non-ideal liquid mixtures. AIChE J. 21, 1086-1099.

Gerbaud, V., Joulia, X., Rodriguez-Donis, I., Baudouin, O., Rosemain, O. Vacher, A., Castelain, P. 2006. Practical residue curve map analysis applied to solvent recovery in non-ideal binary mixtures by batch distillation processes. Chem. Eng. Proc, 45(8), 672-683.

Gmehling, J., Jiding, L., Schiller, M., 1993. A modified UNIFAC model. 2. Present parameter matrix and results for different thermodynamic properties, Ind. Eng. Chem. Res., 32, 178-193.

Hazra, A., Dollimore, D., Alexander, K., 2002. Thermal analysis of the evaporation of compounds used in aromatherapy using thermogravimetry. Thermochim. Acta. 392-393, 221– 229.

Heintz, J., Belaud, J.P., Pandya, N., Teles dos Santos, M., Gerbaud, V., 2014. Computer aided product design tool for sustainable chemical product development. Comput. Chem. Eng., 71, 362–376.

Joback, R., Reid, R.C., 1987. Estimation of pure-component properties from group-contributions. Chem. Eng. Comm. 57, 233-243.

Kusano, K., 1985. Microconduction calorimeters to measure enthalpies of vaporization. Thermochim. Acta. 88, 109–120.

Lavoine-Hanneguelle S., Patent US20140094527 A1 (2014)

Luo, H.P., Zhou, J.H., Xiao, W.D., Zhu, K.H., 2001. Isobaric vapor-liquid equilibria of binary mixtures containing dimethyl carbonate under atmospheric pressure. J. Chem. Eng. Data. 46. 842-845.

Ma, X.B., Liu, X.G., Li, Z.H., Xu, G.H., 2004. Vapor–liquid equilibria for the ternary system methanol + dimethyl carbonate + dimethyl oxalate and constituent binary systems at different temperatures. Fluid Phase Equilib. 221, 51–56.

Marrero, J., Gani, R., 2001. Group-contribution based estimation of pure component properties. Fluid Phase Equilib. 183–184, 183–208.

Matsuda, H., Takahara, H., Fujino, S., Constantinescu, D., Kurihara, K., Tochigi, K., Ochi, K., Gmehling, J., 2011. Selection of entrainers for the separation of the binary azeotropic system methanol – dimethylcarbonate by extractive distillation". Fluid Phase Equilib. 310, 166-181.

Mujtaba I.M., 2004. Batch Distillation Design and Operation. Series on Chemical Engineering - Vol. 3. Imperial College Press.

Osorio, D., Perez-Correa, R., Biegler, L., Agosin, E., 2005. Wine distillates: practical recipe formulation for stills. J. Agric. Food Chem. 53, 6326–6633.

Prosim S.A, 2017a. Batch®Column Manual. http://www.prosim.net/en/software-batchcolumn-9.php

Prosim S.A, 2017b. Simulis®Thermodynamics Manual. http://www.prosim.net/en/software-simulis-thermodynamics-mixture-properties-and-fluid-phase-equilibria calculations-3.php

Reich, R., Sanhueza. V., 1992. Vapor-liquid equilibria for α-pinene and β-pinene and for these pinenes with heptane, cyclohexane, l-octene and cyclohexene. Fluid Phase Equilib. 77, 313-325.

Rodriguez-Donis I., Thiebaud-Roux S., Lavoine S., Gerbaud V., 2018. Computer-aided product design of alternative solvents based on phase equilibrium synergism in mixtures. Comptes Rendus Chimie, 21, 606 – 621.

Roon A. Van, Parsons, J.R., Govers, H.A.J., 2002. Gas chromatographic determination of vapour pressure and related thermodynamic properties of monoterpenes and biogenically related compounds. J. Chromatogr. A, 955,105–115.

Sacher, J., García-Llobodanin, L., Lopez, F., Segura H., Pérez-Correa, J.R., 2013. Dynamic modelling and simulation of an alembic pear wine distillation. Food Bioprod. Process. 91, 447–456.

Scanavini, H.F.A., Ceriani, R., Cassini, C.E.R., Souza, E.L.R., Filho, F.M., Meirelles, A.J.A., 2010. Cachaça production in a lab-scale alembic: modelling and computational simulation. J. Food Eng. 33, 226–252.

Štejfa, V., Fulem, M., Ruzicka, K., Cervinka C., 2014a. Thermodynamic study of selected monoterpenes III. J. Chem. Thermodyn. 79, 280-289.

Štejfa, V., Fulem, M., Ruzicka, K., Cervinka C., 2014b. Thermodynamic study of selected monoterpenes II. J. Chem. Thermodyn. 79, 272–279.

Torcal, M., Garcıa-Abarrio, S., Pardo, J. I, Mainar A.M., Urieta J.S., 2010. P. G. T Measurements and Isobaric Vapor-Liquid-Equilibria of the 1.3.3-Trimethyl-2-oxabicycle[2.2.2]octane + Propan-1-ol Mixture: Cubic and Statistical Associating Fluid Theory-Based Equation of State Analysis. J. Chem. Eng. Data 55, 5932–5940.

Valderrama, J.O., Toselli, L.A., Faundez, C.A., 2012. Advances on modelling and simulation of alcoholic distillation. Part 2: process simulation. Food Bioprod. Process. 90, 8832–8840.

Weast, R.C, Grasselli, J.G., 1989. Handbook of Data on Organic Compounds, 2nd Editon, and ed(s). Weast, R.C and Grasselli, J.G., CRC Press, Inc., Boca Raton, FL.

Zaitsau, D.H., Verevkin, S.P, Sazonova, A.Y., 2015. Vapor pressures and vaporization enthalpies of 5-nonanone, linalool and 6-methyl-5-hepten-2-one. Data evaluation. Fluid Phase Equilib. 386, 140–148.