

Impact of the Liquid-Vapour Equilibrium Modelling on the Simulation Performance of an Absorption Chiller

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Abstract: The simulation of an absorption chiller requires thermodynamic models to represent the liquid-vapour equilibrium and the different properties of the mixture. Three models are tried to find the one which leads to a realistic description according to the experimental data that we dispose of. The first study is based on the NRTL model to describe the liquid phase and the Virial equation of state to represent the vapour one. The second model is the Sovave-Redlich-Kwong equation of state and the last is the PC-SAFT equation of state. We realize that an acceptable deviation on the compositions and the temperatures calculated by the proposed methods has significant effects on the simulation of the column parameters, i.e. the number of theoretical stages necessary to accomplish the separation and the position of the feed stage as well as on the quantity of heat provided to the reboiler, which affects the value of the COP of the machine.

Key words: Absorption, liquid-vapour equilibrium, NRTL-virial approach, SRK EOS, PC-SAFT EOS, distillation column, COP

INTRODUCTION

Fallen into oblivion to the profit of vapour compression machines, the absorption machines know currently a rebirth. When it works with refrigerant mixtures of comparable volatilities, this process requires a separation of the components in the generator. This is the study for water/ammonia mixture as well as for mixtures of light alkanes when they have close volatilities. This separation takes place in a distillation column made of a succession of equilibrium stages.

In a first step we have simulated the absorption machine operating with ten alkane mixtures^[1]. Then we have passed to the second step, which consists on the simulation and the dimensioning of each component of the machine beginning from the distillation column. When modelling this apparatus we remarked that the chosen thermodynamic model for the description of the liquid-vapour equilibrium may affect the general parameters of the column.

The objective of this study is to study the influence of the method used for modelling the liquid-vapour equilibrium on the performances of the machine. In this study we will focus on the distillation column.

DESCRIPTION OF THE ABSORPTION CHILLER AND THE DISTILLATION COLUMN

The proposed configuration, presented on Fig. 1, is a single effect refrigeration chiller working with alkane

mixtures^[1]. The refrigerant vapour leaving the generator is liquefied in the condenser, by releasing a quantity of heat Q_c before being cooled in a pre-cooler. The subcooled liquid is expanded and then it is forwarded to the evaporator where it will evaporate by absorbing a quantity of heat Q_e from the medium to be cooled. The overheated vapour is put in contact with the poor solution leaving the generator in the absorber. The rich solution obtained is pumped towards the generator passing through a solution heat exchanger.

The alkane mixtures require a multistage separation in the generator, ensured by a distillation column^{[1], [2]}.

Figure 2 illustrates a simple distillation column separating the refrigerant-absorbent mixture. This column is composed of n theoretical equilibrium stages. The feed mixture is introduced in the stage na .

To ensure a complete description of the distillation process, we must identify the variables to be fixed during its operation^[3]. These fixed variables are:

- Concentrations or molar fractions of the two products, at the head and the bottom of the column, according to the desired separation quality.
- The working pressure.
- The feed state: its flow rate, its composition and its temperature must also be provided.
- The condenser temperature.
- The last variable to be imposed is the flow rate at an unspecified point, in our study we chose the reflux ratio.

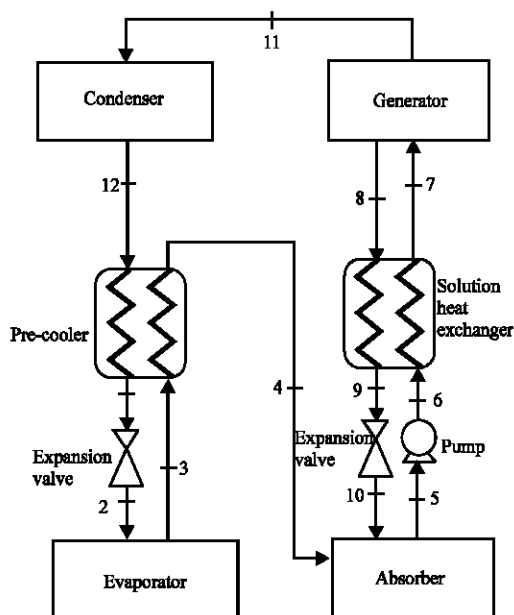


Fig. 1: A simple effect absorption chiller

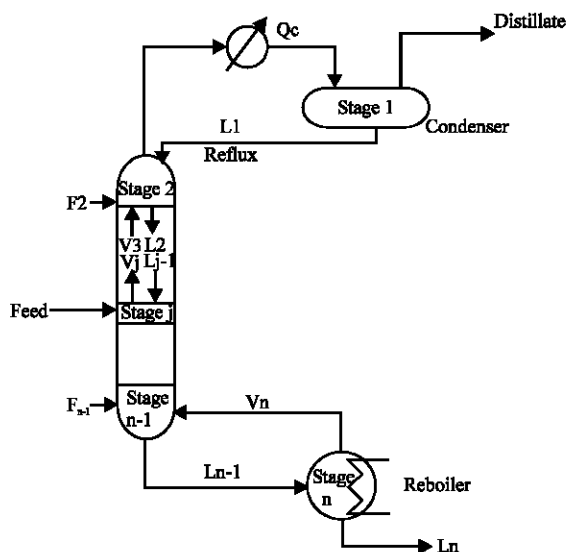


Fig. 2: Distillation column

The compositions and the molar flow rates of the liquid and the vapour entering and leaving each stage, the temperature, the quantity of heat released at the condenser Q_c and that provided to the reboiler Q_r are to be calculated by simultaneous resolution of the equilibrium equations, the mass and the energy balances on each stage.

The simulation of the column consists on the calculation of the number of the whole theoretical stages, the feed stage as well as the compositions, the flow rates and the temperatures on each stage. The discharged heat

from the condenser and the provided heat to the reboiler are also determined.

MODELLING THE LIQUID-VAPOUR EQUILIBRIUM

The liquid-vapour equilibrium of a binary mixture is completely described by six variables of state: the temperature T , the pressure P , the molar fractions of the components of the mixture in the liquid phase (x_1 for the most volatile compound and x_2 for the other) and the corresponding molar fractions in the vapour phase y_1 and y_2 . These variables are correlated by two equilibrium conditions and two mass balances, so the system has two degrees of freedom. Consequently two of the six variables must be given.

The equilibrium criteria are expressed by the equality of fugacities of each species present in the two phases. Fugacities are estimated using the suggested approaches. If the approach of calculation is based on an equation of state, two other variables must be added, the molar volume of the liquid phase V_L and that of the vapour phase V_V . This raises the number of variables to eight and the number of equations to six.

NRTL-Virial approach: According to this approach, the two phases are described differently; the liquid one is represented by the NRTL model (Non Random Two Liquid) while the vapour phase is described by the Virial equation of state truncated after the second term^[4].

For a binary mixture, the excess free energy is given as follow:

$$\frac{g^E}{RT} = x_1 x_2 \left(\frac{\frac{C_{21}}{RT} \exp\left(-\alpha_{21} \frac{C_{21}}{RT}\right)}{x_1 + x_2 \exp\left(-\alpha_{21} \frac{C_{21}}{RT}\right)} + \frac{\frac{C_{12}}{RT} \exp\left(-\alpha_{12} \frac{C_{12}}{RT}\right)}{x_2 + x_1 \exp\left(-\alpha_{12} \frac{C_{12}}{RT}\right)} \right) \quad (1)$$

Every binary system is described through three parameters calculated by fitting experimental data, C_{12} , C_{21} and $\alpha_{12} = \alpha_{21}$. This model is improved by adding the effect of the temperature on these parameters,

$$\begin{aligned} C_{ij} &= C_{ij}^0 + C_{ij}^T (T - 273.15) \\ \alpha_{ij} &= \alpha_{ij}^0 + \alpha_{ij}^T (T - 273.15) \end{aligned} \quad (2)$$

This model with six parameters used to describe the excess free energy will be used later to calculate the activity coefficients, which make a correction during the calculation of fugacity in the liquid phase given by Eq. 3.

$$f_i^L = \gamma_i(T, x_i) x_i P_i^s \exp\left(\frac{P_i^s B_{ii} + (P - P_i^s) v_i^{*L}}{RT}\right) \quad (3)$$

$$RT \ln \gamma_i = g^E + \sum_{j=1}^2 x_j \left(\frac{\partial g^E}{\partial x_i} - \frac{\partial g^E}{\partial x_j} \right) \quad (4)$$

Eq. 4 illustrates the expression of the activity coefficient using the excess free energy.

The fugacity of the vapour phase is given by

$$RT \ln \frac{f_i^V}{P y_i} = \int_0^P \left(\bar{v}_i - \frac{RT}{P} \right) dP \quad (5)$$

This integral is calculated using the suggested equation of state

$$Pv = RT + B^M P \quad (6)$$

B^M , the second coefficient of the Virial equation of the mixture, is calculated from the coefficients of the pure substances. The coefficient of fugacity ϕ_i is given by

$$\ln \phi_i = \left(2 \sum_{j=1}^2 y_j B_{ij} - B^M \right) \frac{P}{RT} \quad (7)$$

The coefficients B_{ij} are estimated using the empirical correlations of Connell et Prausnitz^[5].

The equilibrium state is defined by the following system of Equation:

$$\begin{cases} P y_1 \phi_1 = f_1^L \\ P y_2 \phi_2 = f_2^L \end{cases} \quad (8)$$

$$y_1 + y_2 = 1 \quad (9)$$

$$x_1 + x_2 = 1 \quad (10)$$

$$x_1 + x_2 = 1 \quad (11)$$

The Soave-Redlich-Kwong equation of state: This approach is based on the same equation of state to calculate the compositions of the two phases. The chosen equation is the Soave-Redlich-Kwong equation of state which describes rather well the liquid and the vapour phase in the study of non-polar mixtures^[6].

The relation between the temperature, the volume and the pressure is as follows

$$P = \frac{RT}{V - b} - \frac{a(T)}{V(V - b)} \quad (12)$$

a and b are the parameters of the equation of state. The mixture rules presented in Eq. 13 are used to estimate the parameters of the equation applied to mixtures.

$$a_m = \sum_i \sum_j x_i x_j a_{ij}, \quad b_m = \sum_i x_i b_i \quad (13)$$

where $a_{ii} = a_i$, $k_{ii} = k_{jj} = 0$ and

$$a_{ij} = (1 - k_{ij}) \sqrt{a_i a_j} \quad i \neq j$$

The additional parameter k_{ij} is introduced to account for the binary interaction of the two components i and j of the mixture.

The two equilibrium criteria become

$$\phi_i^L x_i = \phi_i^V y_i, \quad i = 1, 2 \quad (14)$$

The system of equations representing the equilibrium state has two more equations compared to the last approach, i.e. those of the equations of state of the two phases.

The expressions of ϕ_i^V and ϕ_i^L are estimated using the equation of state according to the following equations^[6]

$$\ln \phi_i^V = \frac{b_m^V}{b_i} (z_V - 1) - \ln(z_V - B) - \frac{A}{B} \left[2 \frac{\sqrt{a_m^V}}{\sqrt{a_i}} - \frac{b_m^V}{b_i} \right] \ln \left(1 + \frac{B}{z_V} \right) \quad (15)$$

$$\ln \phi_i^L = \frac{b_m^L}{b_i} (z_L - 1) - \ln(z_L - B) - \frac{A}{B} \left[2 \frac{\sqrt{a_m^L}}{\sqrt{a_i}} - \frac{b_m^L}{b_i} \right] \ln \left(1 + \frac{B}{z_L} \right) \quad (16)$$

z_V and z_L are the compressibility factors for each phase. A and B are functions of the temperature, the pressure and the composition^[6].

The perturbed-chain statistical-associating-fluid-theory equation of state: In the third model described by the PC-SAFT equation of state, the molecules are modelled by chains made up of m spherical segments^[7]. The potential of interaction of a segment $u(r)$ is that of Chen^[8].

$$u(r) = \begin{cases} \infty & r < \sigma \\ -\varepsilon & \sigma \leq r \leq \lambda\sigma \\ 0 & r \geq \lambda\sigma \end{cases} \quad (17)$$

where r is the distance between two segments, σ is the effective diameter of a segment, ε the depth of the well of the attraction potential and λ its reduced width fixed at 1, 5. According to this model, a pure substance is characterized by three parameters: the number of segments in a chain m , the diameter of the sphere σ at $T = 0$ and the attraction potential ε . If specific interactions, such as the dipole-dipole electrostatic forces, are not negligible, parameters characterizing association will be added.

The PC-SAFT equation of state is written using the reduced free energy which is composed of two parts: the term corresponding to the energies of translation, rotation and vibration of the molecule and the term due to the molecular interactions; this second term corresponds to the deviations from the perfect gas. It is, thus, written in the reduced form:

$$a = \frac{A}{RT} = a^{id} + a^{res} \quad (18)$$

The free energy, A , is expressed using its canonical variables: temperature T , density ρ and molar compositions x_i of the different components.

The molar free energy of a mixture of perfect gases depends on the properties of its pure components:

$$a^{id} = \frac{A^{id}}{RT} = \sum_{i=1}^c \left(\frac{A_i^{id}}{RT} + x_i \ln x_i \right) \quad (19)$$

For a pure substance it is given by the following general relation:

$$A_1^{id}(T, \rho) = U_0^{id} - TS_0^{id} + \int_{T_0}^T C_v^{id} dT + T \int_{T_0}^T \frac{C_v^{id}}{T} dT + RT \ln \left(\frac{\rho}{\rho_0} \right) \quad (20)$$

We notice that starting from a model of the heat capacity at constant volume C_v^{id} , we can build the fundamental equation of a pure substance at the perfect gas state. $(T_0, \rho_0, U_0^{id}, S_0^{id})$ is an arbitrary state of the perfect gas.

According to the theory of perturbations, the molecular interactions can be divided into a repulsive part and an attractive part. The repulsive contribution is calculated by introducing a reference fluid represented by a rigid chain which spheres have an effective diameter of collision $d(T)$:

$$d(T) = \int_0^\sigma \left(1 - \exp \left[-\frac{u(r)}{kT} \right] \right) dr \quad (21)$$

For the potential of interaction given by equation (1), integration leads to the expression of the effective diameter of collision of component i [8]:

$$d_i(T) = \sigma_i \left[1 - 0.12 \exp \left(-\frac{3\varepsilon_i}{kT} \right) \right] \quad (22)$$

The attractive interactions are treated as being a perturbation of the system of reference. The explicit equation of state in terms of the reduced residual free energy, a^{res} , is the sum of the contribution of the chain of hard spheres hc and the contribution of perturbation $disp$ resulting from the attractive interactions [8]:

$$a^{res} = \frac{A^{res}}{RT} = a^{hc} + a^{disp} \quad (23)$$

If the treated substances would be associated (like water, for example), a term corresponding to the free energy of association $assoc$ is introduced into the equation

$$a^{res} = a^{hc} + a^{disp} + a^{assoc} \quad (24)$$

The contribution of the rigid chain of reference of a c components mixture in the free energy is given by [8]:

$$a^{hc} = \bar{m} a^{hs} - \sum_{i=1}^c x_i (m_i - 1) \ln g_{ii}^{hs} \quad (25)$$

x_i is the molar fraction of component i , m_i is the number of spherical segments in the chain of component i and m is the average number of segments in the mixture. The free energy of the rigid sphere fluid is given by:

$$a^{hs} = \frac{A^{hs}}{RT} = \frac{1}{\xi_0} \left[\frac{3\xi_1\xi_2}{1-\xi_3} + \frac{\xi_2^3}{\xi_3(1-\xi_3)^2} + \left(\frac{\xi_2^3}{\xi_3^2} - \xi_0 \right) \ln(1-\xi_3) \right] \quad (26)$$

and the function of radial distribution of the rigid sphere fluid is:

$$g_{ij}^{hs} = \frac{1}{(1-\xi_3)} + \left(\frac{d_i d_j}{d_i + d_j} \right) \frac{3\xi_2}{(1-\xi_3)^2} + \left(\frac{d_i d_j}{d_i + d_j} \right)^2 \frac{2\xi_2^2}{(1-\xi_3)^3} \quad (27)$$

and ξ_n are defined as follow :

$$\xi_n = \frac{\pi N_{Av}}{6} \rho \sum_{i=1}^c x_i m_i d_i^n; \quad n \in \{0, 1, 2, 3\} \quad (28)$$

The perturbation theory of Barker and Henderson is used to evaluate the attractive part of the molecular interactions. The free energy is written as being the sum of the contributions of first and second order [8]:

$$a^{disp} = \frac{A^{disp}}{RT} = \frac{A_1}{RT} + \frac{A_2}{RT} \quad (29)$$

The two terms of the equation are given respectively by

$$\frac{A_1}{RT} = -2\pi N_{Av} \rho I_1 (\eta, \bar{m}) \overline{m^2 \epsilon \sigma^3} \quad (30)$$

$$\frac{A_2}{RT} = -\pi N_{Av} \rho \bar{m} C_1 I_2 (\eta, \bar{m}) \overline{m^2 \epsilon^2 \sigma^3} \quad (31)$$

The abbreviations C_1 , $\overline{m^2 \epsilon \sigma^3}$, $\overline{m^2 \epsilon^2 \sigma^3}$ and the polynomials for reduced density I_1 and I_2 are available in the literature [8,9].

Conventional mixture rules are used to determine the parameters between a pair of distinct molecules [9]:

$$\sigma_{ij} = \frac{1}{2} (\sigma_i + \sigma_j) \quad (32)$$

$$\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j} (1 - k_{ij}) \quad (33)$$

k_{ij} is a binary interaction parameter introduced in order to rectify the segment-segment interactions of the different chains ($k^{ii} = 0$).

COMPARISON OF THE DIFFERENT APPROACHES

In a first step, several mixtures of alkanes are treated to evaluate the results of each approach. For each mixture we know two of the four variables: the temperature, the pressure, the composition in the liquid phase and that in the vapour phase and we calculate the two others according to the chosen model. The accuracy of each approach is evaluated by calculating the deviation of the calculated variables from the experimental data. The relative errors on temperatures and the pressures and the absolute errors on compositions yield to the evaluation of each method and the choice of the best one which will be taken thereafter as reference.

Next, the distillation column is calculated with the suggested approaches to evaluate the quantity of heat required for the generator which gives an idea on the performance coefficient of the machine.

Calculation of the equilibrium: As an example, Table 1 presents the relative errors on the pressures and the absolute errors on the molar fractions in the vapour phase calculated for the propane-pentane mixture at different temperatures.

$$\text{Relative error on } T = 100 * \frac{(T^{exp} - T^{calc})}{T^{exp}} \quad \text{Relative error on } P = 100 * \frac{(P^{exp} - P^{calc})}{P^{exp}}$$

$$\text{Absolute error on } y_i = 100 * (y_i^{exp} - y_i^{calc})$$

Table 2 illustrates the relative errors on the temperatures and the absolute errors on the molar fractions in the vapour phase calculated for the pentane-octane mixture at different pressures.

The accuracy of the two first models depends on the binary parameters calculated by fitting the experimental data and the nature of these data themselves.

For the majority of the studied systems the errors made on the temperature and the composition are more significant for the first approach. The third approach is more realistic; consequently, it is taken as a reference, later, for the calculation of the parameters of the column and the COP.

Calculation of the column parameters: For ten refrigeration mixture investigated, the absorption machine is simulated to obtain the mass and the energy flows entering and outgoing from the column such as the composition, the rate of the feed and its temperature. The flow rate of the refrigeration vapour and its temperature, the flow rate of the poor solution are determined too and finally the flow rate of the reflux and its composition [1]. These data are injected thereafter into the column simulation program.

We propose, as an example, the study of a machine operating with the c4-c8 mixture, the one of the high performance among the investigated mixtures. The operating parameters of this machine are:

- The cooling fluid of the condenser and the absorber is the air
- High pressure $P_c = 4.8$ bar
- Temperature at the outlet of the evaporator $T_g = 275.15$ K
- Refrigerating power $Q_E = 17.5$ kW
- Temperature at the outlet of the condenser $T_c = 318.15$ K

Table 1: Errors on the pressures and the vapour compositions according to the different approaches for the c3-c5 mixture. ata is Sage, B.H., W.N. Lacey. Ind. Eng. Chem., 32 (1940) 7,992

C3-C5			
T = 360.93 K	NRTL	SRK	PC-SAFT
Relative error on P (%)	9.09	4.92	0.29
Absolute error on y_1 (%)	0.16	0.87	0.08
T = 377.59 K			
Relative error on P (%)	8.77	5.40	0.16
Absolute error on y_1 (%)	1.04	0.67	0.19
T = 394.26 K			
Relative error on P (%)	7.42	6.51	0.98
Absolute error on y_1 (%)	3.40	1.73	0.18
T = 410.93 K			
Relative error on P (%)	8.77	4.22	1.02
Absolute error on y_1 (%)	6.16	2.39	0.12
T = 427.59 K			
Relative error on P (%)	12.66	4.39	0.45
Absolute error on y_1 (%)	7.32	2.51	0.46
T = 444.26 K			
Relative error on P (%)	15.99	3.60	1.70
Absolute error on y_1 (%)	9.35	3.89	1.11
T = 460.93 K			
Relative error on P (%)	22.97	0.79	0.80
Absolute error on y_1 (%)	6.91	1.24	0.22

Table 2: Errors on the temperatures and the vapour compositions according to the different approaches for the c5-c8 mixture. The reference of the experimental data is Chueh, P.L., J.M. Prausnitz, calculated

C5-C8			
P = 0.507 bar	NRTL	SRK	PC-SAFT
Relative Error on T (%)	0.38	0.07	0.21
Absolute Error on y_1 (%)	0.46	0.11	0.35
P = 2.027 bar			
Relative Error on T (%)	1.70	0.12	0.16
Absolute Error on y_1 (%)	1.39	0.30	0.13
P = 3.041 bar			
Relative Error on T (%)	2.39	0.25	0.11
Absolute Error on y_1 (%)	2.18	0.43	0.04
P = 5.068 bar			
Relative Error on T (%)	4.41	0.40	0.01
Absolute Error on y_1 (%)	4.27	0.37	0.14
P = 7.095 bar			
Relative Error on T (%)	6.73	0.40	0.03
Absolute Error on y_1 (%)	4.27	0.20	0.15
P = 11.149 bar			
Relative Error on T (%)	14.28	0.30	0.14
Absolute Error on y_1 (%)	0.07	0.01	0.15

- Composition of the poor solution $x_p = 0.124$
- Temperature at the outlet of the absorber $T_a = 318.15$ K
- Low pressure $P_E = 1.0$ bar
- Composition of the refrigerating vapour $y_F = 0.99$
- Temperature pinch in the precoolers $pin1 = 10$ K
- Temperature pinch in the solution heat exchangers $pin2 = 5$ K

In addition to the COP, the simulation program of the machine gives the state of the mixture in any point of the cycle (the temperature, the pressure, the flow rate and the

Table 3: Calculation of the number of stages, the feed stage the COP and the relative variation of the COP calculated by the three approaches

C3-C5	Qg (kJ.mol ⁻¹)	n	na	COP	δCOP
NRTL-VIRIEL	118.54	6	3	0.148	1.93%
SRK	123.19	6	3	0.142	1.93%
PC-SAFT	120.87	5	3	0.145	
NRTL-VIRIEL	112.50	8	4	0.156	5.39%
SRK	124.36	7	5	0.141	4.67%
PC-SAFT	118.54	6	4	0.148	
NRTL-VIRIEL	91.81	7	4	0.191	5.54%
SRK	109.25	5	3	0.160	11.30%
PC-SAFT	96.93	5	3	0.181	
NRTL-VIRIEL	93.09	3	2	0.188	7.24%
SRK	117.38	3	2	0.149	14.96%
PC-SAFT	99.83	3	2	0.175	
NRTL-VIRIEL	156.90	6	4	0.112	0.71%
SRK	166.19	7	4	0.105	6.32%
PC-SAFT	155.73	6	4	0.112	
NRTL-VIRIEL	85.54	5	4	0.205	2.61%
SRK	101.69	5	3	0.172	13.69%
PC-SAFT	87.75	5	4	0.199	
NRTL-VIRIEL	82.17	5	3	0.213	4.95%
SRK	94.72	4	3	0.185	17.58%
PC-SAFT	78.10	4	3	0.224	
NRTL-VIRIEL	161.55	6	5	0.108	7.12%
SRK	184.79	6	5	0.095	6.33%
PC-SAFT	173.17	6	5	0.101	

composition) and the exchanged heats. The specific parameters of the mass and energy flows managing the column are:

- Rate of the feed = 8.8 mol/s
- Composition of the feed = 0.217
- Temperature of the feed = 407.6 K
- Flow of the refrigerating vapour = 0.95 mol/s
- Temperature of the refrigerating vapour at the head of the column = 337.22 K
- Flow of the poor solution = 7.85 mol/s
- Temperature of the reboiler = 423.15 K
- Flow of the reflux = 0.43 mol/s
- Composition of the reflux = 0.707

These data are transmitted to the simulation program of the distillation column to calculate the total number of stages, to specify the stage where the feed is introduced and the quantities of heat provided to the reboiler and released from the condenser. The compositions of the two phases, the temperatures as well as the molar flows on each stage are also calculated. Table 3 presents some results: the total number of stages n , the feed stage na and the COP. This last is calculated from Q_G ($COP = Q_E/Q_G$). The third approach is taken as reference in the calculation of the relative deviation on the COP

$$(\delta_{COP}^{NRTL} = \left| \frac{COP^{PCSAFT} - COP^{NRTL}}{COP^{PCSAFT}} \right| * 100,$$

$$= * 100, \delta_{COP}^{SRK} = \left| \frac{COP^{PCSAFT} - COP^{SRK}}{COP^{PCSAFT}} \right| * 100).$$

Interpretations: The deviations, on the equilibrium calculation, from the experimental data made with the PC-SAFT equation of state are significantly less than those with the SRK equation of state and the NRTL model.

The calculation of the liquid-vapour equilibrium based on the NRTL model for the description of the liquid phase and the Virial equation of state for the vapour one requires an important experimental database to determine the six NRTL parameters for each considered binary mixture. To have general parameters it is preferable to have various data, i.e. liquid-vapour equilibrium data at different temperatures, mixture enthalpy data and solubility data. With the limited database we have concerning some mixtures the calculated parameters may not describe well the real behaviour at a large interval of temperature.

The SRK equation of state is a suitable model to describe alkane mixtures, generally ideals, especially when we dispose of many experimental data to determine the interaction parameter k_{ij} .

When we have not enough experimental data or these data are not guaranteed, the PC-SAFT equation of state is a very good choice since it offers a realistic description for the both phases and for the mixture. It permits to calculate all the calorimetric properties of the mixture too. This approach seems to be the best and it will be taken as a reference for the simulation of the distillation column and the whole absorption machine later.

The errors made on the calculation of the temperatures and the compositions will affect the calculation of the molar fractions, the flow rates and the quantities of heat exchanged on each stage of the column. This explains the difference of the three approaches in the calculation of the total number of stages, of the position of the feed stage and the quantity of heat provided to the reboiler.

The simulation of the distillation column with the three proposed approaches gives different results concerning Q_G , n and n_a .

The Q_G calculated with the SRK equation of state is generally less than that calculated with the PC-SAFT equation. This is due to the weakness of the model based on the SRK equation. Indeed, this equation describes well the liquid phase as well as the vapour one but it is not a fundamental equation of state, so it doesn't provide a real description of the calorimetric properties of the mixture, specially the enthalpy in our study. This cubic equation of state used in the two phases offers a completely simple description of the system. Unfortunately, a volumetric equation of state does not give a complete description of the system. We do not have any information on the other heating properties of the system (enthalpy, entropy).

The Q_G calculated with the NRTL-Virial approach are generally greater than those calculated with the PC-SAFT equation of state. This may be due to the inaccuracy of the description of the liquid phase illustrated by the six NRTL parameters. This model can describe the behaviour of systems presenting a great deviation from the ideality and can be extended to solutions with several components. In addition, it offers the possibility of representation of the enthalpy of the mixture. On the other hand it presents the disadvantage of requiring a large database to be accurate.

The PC-SAFT equation of state leads to the description of all the properties of a mixture (enthalpy, entropy, volume...) by simple derivation.

The description of the behavior of the mixture using a chosen model affects also the number of the total stages required to accomplish the separation and the position of the feed stage since these two parameters depend on the calculated molar fractions on each stage.

The error made on the modelling of the equilibrium will be amplified during the simulation of the column and other elements of the machine. While passing at the stage of design, we can have a machine which does not take up its duties as expected.

CONCLUSION

To have a realistic simulation of the absorption refrigeration machine, which replies to the industrial requirements, it is necessary to give a detailed attention to the model used to represent the thermodynamic properties at the various points of operation of the cycle.

In this study we study the distillation column, a principal element of the proposed absorption machine. This column is simulated using three different approaches for the modelling of the equilibrium between phases; the first approach is based on the NRTL model for the description of the liquid phase and the Virial equation of state for the vapour one. The second approach is a cubic equation of state, that of SRK. A fundamental equation of state, the PC-SAFT, is the third approach.

Even though the errors made on the modelling of the thermodynamic equilibrium are acceptable, they can generate significant errors on the COP, what we can see with the SRK equation of state and this will affect later the dimensioning and the design of the machine.

The modelling approach may be selected according to the experimental database we dispose, our needs in term of thermodynamic properties and the complexity or the non-ideality of the proposed mixtures. In our study the chosen model is the fundamental equation of state since it doesn't require a large experimental database and it offers a complete description of the mixture.

Some of the proposed alkane mixtures are rather promising refrigerants according to the technical advantages they offer, such as the possibility of the use of solar energy or thermal waste as a heat source at a temperature not exceeding 150°C.

To improve the COP and to reduce the losses of energy, we can consider a modification of the initial configuration of the machine allowing the recovery of the heat released in the partial condenser by the rich solution feeding the distillation column.

NOMENCLATURE

a	reduced free energy
B_{ii}	second coefficient of Viriel de i, $\text{m}^3\text{mol}^{-1}$
COP	coefficient of performance
f_i^V	fugacity in vapour phase, Pa
g^E	fugacity in liquid phase, Pa
g^E	excess free energy, Jmol^{-1}
h_j^L	liquid molar enthalpy on the stage j
h_j^V	vapour molar enthalpy on the stage j
h_j^F	molar enthalpy of feed on the stage j
i	compound of the mixture
n	total number of stages
na	feed stage
$\bar{N}_j^F$	feed molar flow on the stage j
P_i^s	saturation pressure, Pa
Q	heat provided or extracted, kJ.mol^{-1}
Qj	heat provided or extracted from the stage j
R	perfect gas constant
T^{calc}	calculated temperature, K
T^{exp}	experimental temperature, K
V	molar volume, $\text{m}^3\text{mol}^{-1}$
$\bar{v}_{i,L}$	partial molar volume de i, $\text{m}^3\text{mol}^{-1}$
V_i^{*L}	molar volume of liquid component i at saturation, $\text{m}^3\text{mol}^{-1}$

z_{ij}	feed composition on the stage j
γ_i	Greek Symbols activity coefficient of i
φ_i^L	fugacity coefficient of i in liquid phase
φ_i^V	fugacity coefficient of i in vapor phase

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