

Modeling of the Use of Hydrocarbons in Absorption Refrigeration Machine

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The present work considered the modeling of a refrigeration absorption machine with either air or water cooling at 25 and 35°C, respectively to test binary hydrocarbon mixtures as working fluids, namely n-propane and n-butane as refrigerants and n-heptane, n-octane, n-decane as absorbents.

The calculations consisted of mass and heat balances over the main machine parts and also on the vapor-liquid phase equilibria using thermodynamics models like the NRTL and the UNIFAC for the activity coefficients predictions in the liquid phase and the virial and Peng-Robinson equations of state for the fugacity coefficients in the vapor phase.

Coefficients of performance (COP) values of 0.632 and 0.6 were obtained for the mixtures n-C₃H₈/n-C₁₀H₂₄ and n-C₄H₁₀/n-C₁₀H₂₄, respectively.

The results showed the great reliability of the NRTL model compared to the UNIFAC which was characterized by some limitations due to the approximations induced by the group contribution concept.

Through this study one can measure how difficult is to choose the most appropriate model to calculate the enthalpies for the different involved streams.

The systems achieving the best performances *i.e.* n-C₃H₈/n-C₁₀H₂₄ and n-C₄H₁₀/n-C₁₀H₂₄ are non toxic and can be regarded as competitors of Ammonia.

1. Introduction

Despite being flammable, Hydrocarbons have shown good refrigerant properties. This has encouraged the use of refrigeration absorption machines operating with alkane binary mixtures as working fluids. This has also been motivated by the fact that these hydrocarbons have no negative impact on the environment and can be considered as good alternatives to replace vapor compression machines which are known to be great electrical energy consumers. However and comparatively to the vapor compression based processes, only few works on the use of alkane mixtures in absorption machines are reported in the literature and one can cite the work carried out by Chekir et al. (2006). The global behaviour and the performances of an absorption machine operating with mixtures of light alkanes have been considered by Dardour et al. (2011-2012).

Consequently the present work deals with the test of binary fluid mixtures consisting of alkane compounds as refrigerants, like propane and n-butane, considered as relatively volatile and less volatile like n-heptane, n-octane, n-decane as absorbents.

2. The refrigeration machine

2.1. Modeling of the refrigeration machine

Referring to Figure 1 which shows the different compartments of the considered refrigeration machine, the coefficient of performance (COP) which is defined as the ratio of the refrigerating effect Q_E over the external energy supplied ($Q_B + W_P$) (Duminil, M. BE 9735-9), can be expressed as:

$$COP = \frac{h_{10} - h_9}{(h_7 - h_4) + f(h_4 - h_3) + f(h_2 - h_1)} \quad (1)$$

with f denoting the recirculation rate.

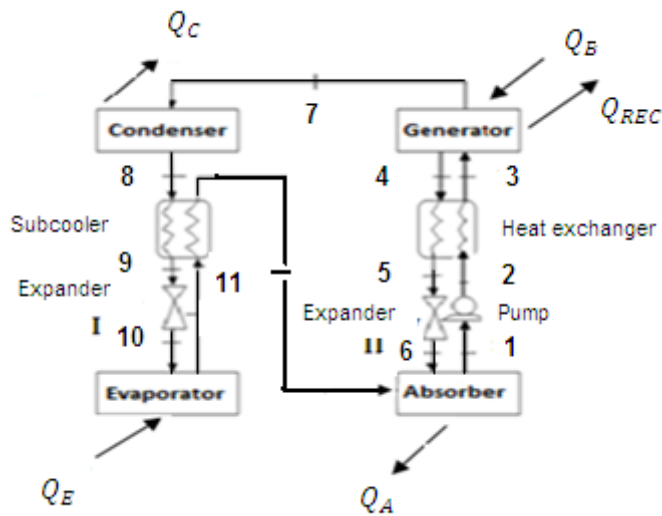


Figure 1. The refrigeration unit, Chekir et al. (2006)

2.1.2. Enthalpy calculations

The enthalpy of n components mixture is expressed as:

$$h = \sum_{i=1}^n x_i \bar{h}_i \quad (1)$$

where h is the molar enthalpy of the mixture, x_i is the mole fraction and \bar{h}_i is the partial molar enthalpy of component calculated as follows:

$$\bar{h}_i = h_i^* - RT^2 \left(\frac{\partial \ln f_i}{\partial T} \right)_{P, N_i} \quad (2)$$

with h_i^* the molar enthalpy of pure component i at temperature T and at perfect gas state and can be calculated as follows:

$$h_i^* - h_0^* = \int_0^T C_p^0(T) dT \quad (3)$$

with h_0^* a constant chosen so that the liquid molar enthalpy at saturation is zero at 0°C and $C_p^0(T)$ is the gas specific heat of component i usually given as a polynomial function of T .

The relationship shown by Equation 2 is valid for both liquid and vapor phases. However for the liquid phase the term $-RT^2 \left(\frac{\partial \ln f_i}{\partial T} \right)_{P, N_i}$ represents the molar excess enthalpy, h^E and may not be negligible compared to the case of a vapor phase.

2.1.2a Enthalpy of vapor phase

The vapor mixture enthalpy can be expressed as follows:

$$h^V = \sum_{i=1}^n y_i \bar{h}_i^V = \sum y_i h_i^* + \left(B^M - T \frac{dB^M}{dT} \right) P \quad (4)$$

With B^M the mixture second Virial coefficient expressed in (m^3/mole) and h^V in (J/mol), y_i vapor fraction of component i , \bar{h}_i^V Partial molar enthalpy of mixture in vapor state, h_i^* molar enthalpy of pure component i at temperature T and at a perfect gas state.

2.1.2b Enthalpy of liquid phase

The liquid mixture enthalpy can be expressed as follows:

$$h^L = \sum x_i \bar{h}_i^L = \sum x_i h_i^* + h^E + \sum x_i \left[-T(B_{ii} + RT/P - V_i^s) \frac{dP_i^s}{dT} + \left(B_{ii} - T \frac{dB_{ii}}{dT} \right) P_i^s + \left(V_i^s - T \frac{dV_i^s}{dT} \right) (P - P_i^s) \right] \quad (5)$$

with h^E the molar excess enthalpy expressed as:

$$h^E = -RT^2 \sum x_i \frac{\partial \ln \gamma_i}{\partial T} \quad (6)$$

with x_i the molar liquid fraction, V_i^s the molar volume at saturation (m^3/mole), B_{ii} the second Virial coefficient and P_i^s the saturation pressure in Pa, all of component i.

2.1.3. Vapor-liquid phase equilibria

Vapor- liquid phase equilibria taking place in the evaporator, absorber, condenser and generator of the refrigeration unit, at constant temperature and pressure have also to be calculated. Usually this is performed according to the isofugacity criteria:

$$f_i^{(v)} = f_i^{(l)} \quad (7)$$

with $f_i^{(v)}$ and $f_i^{(l)}$ the fugacities in the vapor and the liquid phases, respectively

Explicitly Equation 7 can be expressed as:

$$\phi_i y_i P = \gamma_i x_i f_i^{0L} \exp\left(\frac{P_i^s}{RT}\right)$$

where for a component i, ϕ_i is the fugacity coefficient, y_i and x_i are the vapor and liquid mole fractions, respectively, v_i^s is still the molar volume at saturation ($\text{m}^3 \text{mol}^{-1}$), γ_i is the activity coefficient, R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T temperature of the system (K), P pressure (Pa), and f_i^{0L} is the fugacity of pure components i at zero pressure (Pa.) and is expressed as:

$$f_i^{0L} = P_i^s \phi_i^s \exp\left(-\frac{v_i^s P_i^s}{RT}\right) \quad (9)$$

P_i^s is the pressure at saturation.

The volume at saturation for a pure component was calculated using Rackett's correlation given by Reid et al. (1987). For the pure liquid vapor pressure estimation Lee Kesler's correlation was used Reid et al. (1987). A thermodynamic model was adopted for the fugacity coefficient determination in the vapor phase using the Virial and Peng-Robinson equations of state for pressures below and above 5 bar, respectively. The UNIFAC described by Reid et al. (1987) and NRTL by Renon et al. (1971) models were chosen for the calculation of the activity coefficient in the liquid phases.

3. Results and discussion

3.1. Operating conditions

- The considered condensation pressures were in the range of 0.3 to 1.7 MPa where as the evaporation pressures did not exceed 0.5 MPa as used by Chekir *et al.*(2006).
- The considered refrigeration machine used water at 7°C, had a power of 17.5 kW and the temperature at the evaporator exit was of 2°C. The driving temperature was $T_g \leq 150^\circ\text{C}$ (with air cooling) and $T_g \leq 130^\circ\text{C}$ (with water cooling).
- The cooling of the absorber and the condenser was performed according by means of air or water cooling at 35°C or 25°C, respectively.
- The condensation and the absorption temperatures were assumed above the cooling medium by 12 to 15°C when air was used and by 5°C when water was used Jacquard (1999).
- The liquid solutions exiting from the condenser and the absorber were subcooled by 4K.
- The exit temperatures from the absorber and the condenser were 45 and 30°C for air and water cooling, respectively;
- The liquid solution and the refrigerant vapor exiting from the generator were saturated ;
- The liquid solution and liquid-vapor heat exchangers were assumed adiabatic with thermal pinch points of 5 and 10 K, respectively.

3.2. Vapor-liquid phase equilibria

Vapor- liquid phase equilibria for the considered different systems were calculated in different compartments of the machine using the above relevant equations and sample results are shown in Figure 2 for $n-C_3/n-C_{10}$ system at constant pressure and temperature and where the obtained curves are showing typical shapes, confirming the reliability of the results.

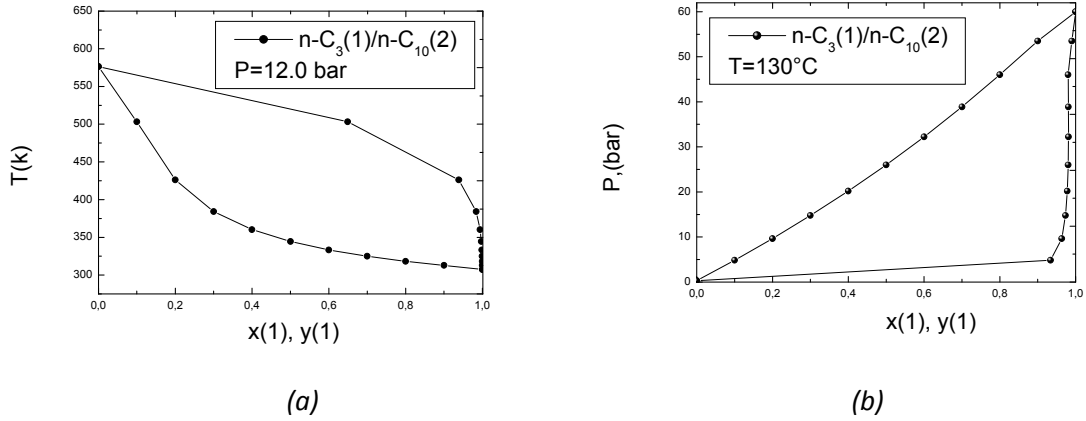


Figure2: Sample vapor-liquid phase equilibria for the $n-C_3/n-C_{10}$ (a) at generator constant pressure, (b) at generator constant temperature

3.3 COP calculations

3.3.1. Enthalpy calculation results

The molar enthalpies of the different liquid and vapor streams obtained from Equations 4-6 are shown in the following Figure 3:

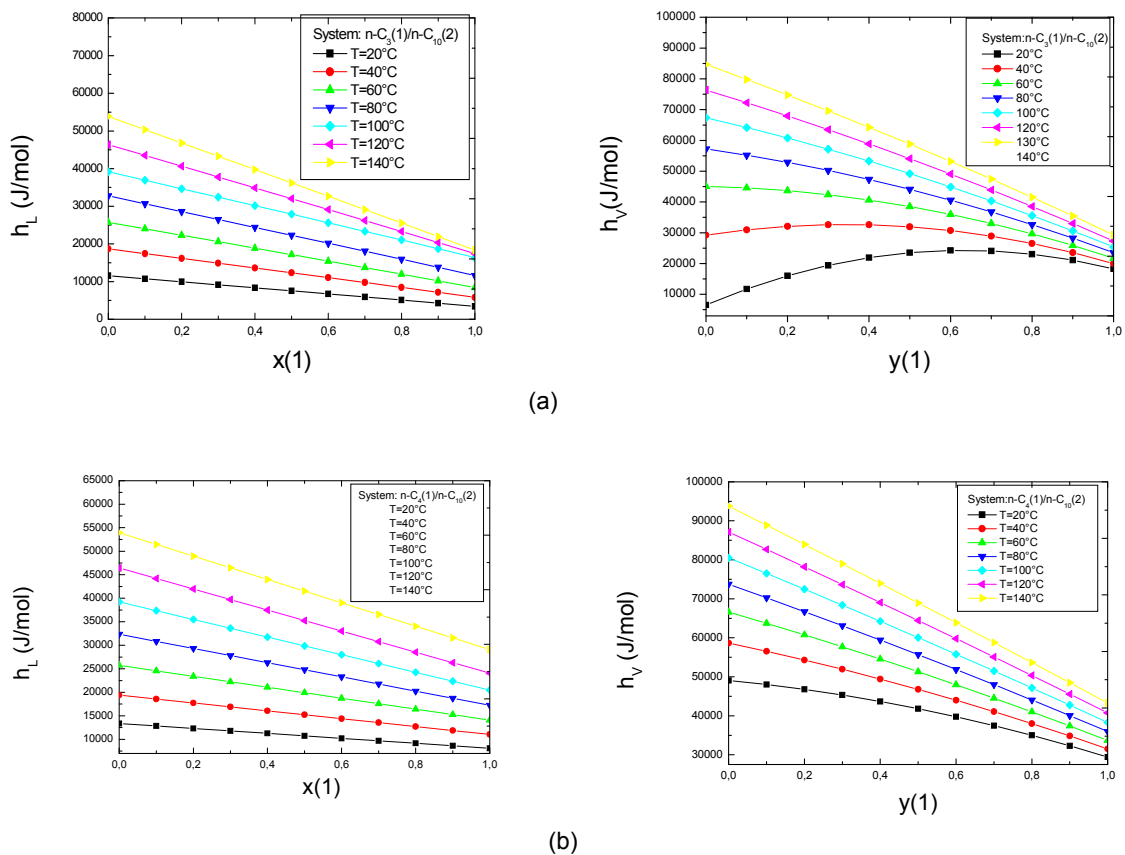


Figure.3- Liquid and vapor molar enthalpies variations with refrigerant molar fraction (a) $C_3/n-C_{10}$, (b) $C_4/n-C_{10}$

These enthalpy values were used to calculate the COP of the absorption refrigeration machine using Equation 1 and the results for both cases with air and water cooling are shown in Tables 1 and 2 are of the same order of magnitude as values reported from the literature Chekir et al. (2006), Dardour et al. (2011) and Dardour. (2012).

Table 1: Machine performance using the proposed refrigerant binary mixtures with air cooling

Binary system	P_C (MPa)	P_E (MPa)	T_E (K)	COP	COP
				From (Chekir et al. 2006)	from This work
C_3H_8/C_7H_{16}	1.664	0.460	423.15	0.356	0.350 ^a
C_3H_8/C_8H_{18}	1.664	0.470	423.15	0.332	0.340 ^a
C_4H_{10}/C_8H_{18}	0.480	0.100	423.15	0.372	0.410 ^b

^a Using NRTL and Peng-Robinson equation of state; ^b Using UNIFAC and Virial equation of state

Table 2: Machine performance using the proposed refrigerant binary mixtures with water cooling

Binary system	P_C (MPa)	P_E (MPa)	T_E (K)	COP	COP	COP
				from Chekir et al. (2006)	from Dardour. (2012)	from This work
C_3H_8/C_7H_{16}	1.073	0.440	403.15	0.599	0.39	0.415 ^a
C_3H_8/C_8H_{18}	1.073	0.440	403.15	0.634	0.49	0.530 ^a
C_4H_{10}/C_8H_{18}	0.282	0.095	403.15	0.623	0.38	0.454 ^b
$C_3H_8/C_{10}H_{24}$	1.2	0.500	403.15			0.632 ^a
$C_4H_{10}/C_{10}H_{24}$	0.325	0.100	403.15			0.616 ^b

^aUsing NRTL and Peng-Robinson equation of state; ^b Using UNIFAC and Virial equation of state

It can be noted that for the first two systems with Decane as the absorbent, air cooling would not be possible when adopting the same conditions and assumptions mentioned above. However for the case of water cooling, COP values of 0.66 (Chekir et al. (2006)) and 0.6 (Dardour. (2012)) were obtained with ammonia as reported in the literature. These values are very close to the ones of 0.632 and 0.616, obtained in the present work.

Figure 4 shows the variations of the COP with the generator temperature at conditions fixed in section 3.1 for the two binary systems, with water cooling and a driving temperature not exceeding 130°C.

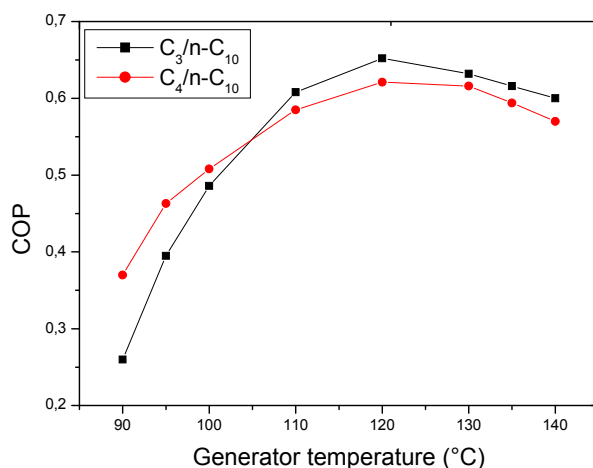


Figure 4. COP variations with generator temperature for $n-C_3/n-C_{10}$, $C_4/n-C_{10}$ systems with water cooling

The two curves exhibited the same trend with the highest COP values at the same temperature of 120°C. Figure 5a & b present the COP variations with the evaporation pressure P_E for both systems *i.e.* $n-C_3/n-C_{10}$ and $n-C_4/n-C_{10}$ where it can be seen that the maximal values for the first one are within the pressure range of [4.8-5.0] bar and at low pressure of 1 bar for the second.

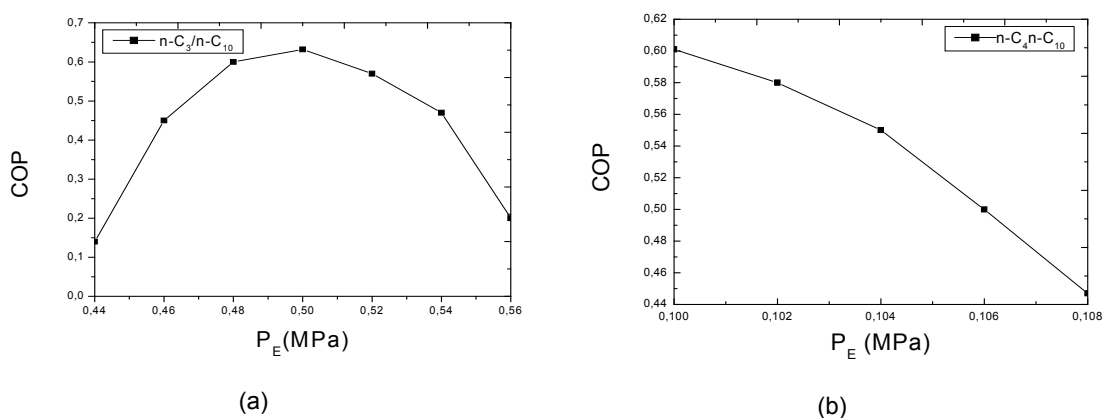


Figure 5: COP variations with evaporator pressure for a) $n\text{-C}_3/n\text{-C}_{10}$ b) $n\text{-C}_4/n\text{-C}_{10}$ systems with water cooling

4. Conclusion

This study showed the importance of the choice of the model to calculate the required different stream enthalpies at different absorption cycle points. In fact the results showed the limitations of the UNIFAC model comparatively to the NRTL which described more accurately the behavior of the different fluid mixtures, particularly in the liquid phases at different operating conditions of temperature and pressure.

The best achieved performances at the fixed conditions were those when using the mixture $n\text{-C}_3\text{H}_8/n\text{-C}_{10}\text{H}_{24}$ reaching a COP of 0.632 followed by the $n\text{-C}_4\text{H}_{10}/n\text{-C}_{10}\text{H}_{24}$ with 0.60. These systems can then easily compete with Ammonia and have also the advantage to be non toxic.

The UNIFAC model did predict accurately enough the vapor-liquid phase equilibria when used along with the Virial equation of state, for binary systems where n -butane was the refrigerant and which had critical temperatures greater than the prevailing driving temperature. However the predictions of the binary mixtures enthalpies were poor in contrary to the NRTL model which better predicted the excess molar enthalpies and the enthalpies at different points of the refrigeration absorption machine, and this at different fixed operating conditions of temperature and pressure.

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