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C. Arzano

Electricite de France

D. Clodic

Ecole des Mines de Paris

B. Hivet

Electricite de France

C. Ducruet

Electricite de France

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INFLUENCE OF THERMODYNAMIC PARAMETERS IN A VAPOUR COMPRESSION CYCLE

C. Arzano, D. Clodic*, B. Hivet, C. Ducruet

Electricité de France, Direction des Etudes et Recherches
ADEI Department
Centre des Renardières, B.P. 1
77250 MORET-SUR-LOING
FRANCE
Phone : (+ 33) 1 60 73 60 73
Fax : (+ 33) 1 60 73 64 40

* Centre d'Energétique
Ecole des Mines de Paris
60, Boulevard St Michel
75272 PARIS, Cedex 06
FRANCE
Phone : (+ 33) 1 40 51 92 49
Fax : (+ 33) 1 46 34 24 91

ABSTRACT

The influence of molar heat capacity on a vapour compression cycle is pointed out, through the use of two separate though complementary approaches. The first of these approaches consists in establishing mathematical relationships which characterise the stages of the cycle, such as compression, de-superheating, expansion and subcooling. The second approach uses cycle calculations for nine refrigerants and allows to compare to one another the energetic performances of each, and to analyse the effect of two subcooling modes on these performances. A classification of the studied fluids, based on a synthesis of the two approaches, is proposed.

NOMENCLATURE

Letters	Indices
T : Temperature (K)	NB : Normal boiling point
P : Pressure (Pa)	cr : Critical
C_p : Heat capacity at constant pressure ($\text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$)	K : Condensation
V : Molar volume ($\text{m}^3\cdot\text{mol}^{-1}$)	0 : Evaporation
H : Enthalpy ($\text{kJ}\cdot\text{mol}^{-1}$)	σ : Saturation curve or saturated
S : Entropy ($\text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$)	sb : subcooling
L : Latent evaporation heat ($\text{kJ}\cdot\text{mol}^{-1}$)	vap : vapour
β : Isobaric expansion coefficient (K^{-1})	liq : liquid
	P : at constant pressure
	S : at constant entropy

INTRODUCTION

The selection of a working fluid in a refrigerating machine or a heat pump impacts the performance of the equipment. Accordingly, it seems advisable to compare to one another refrigerants liable to be used under identical conditions. Ammonia, commonly used in refrigerating machines, is today used in heat pumps which condensation pressure may reach up to 4000 kPa (78°C at saturation temperature). The paper below aims at studying the energetic behaviour of ammonia with respect to that of pure fluids used at identical temperature levels.

METHODOLOGY

Two temperature ranges, applicable to agro-food industries, 0°C/55°C and 25°C/75°C, are investigated under this comparison. The fluids showing identical trends in both ranges, results are given for the first one indicated, so as not to make the legibility of illustrations exceedingly complex. The fluids have been selected in the list of the United Nations Program for the Environment // according to two thermodynamic criteria : normal boiling temperature T_{NB} and critical temperature T_{cr} . Thus :

- T_{NB} must be lower than 0°C (to avoid the entrance of air or moisture in the system)
- the reduced condensation temperature must be lower than 0.9 (or the critical temperature higher than 110°C approx.).

Although this choice eliminates HCFC 22 ($T_{cr} = 96.2^{\circ}\text{C}$) and propane ($T_{cr} = 96.8^{\circ}\text{C}$), these two fluids will nevertheless be incorporated into the study.

The software used for calculation of thermodynamic properties not including in its data base all pure fluids which satisfy the conditions above, the work below will finally encompass nine refrigerants : ammonia, propane, isobutane, CFC 12, HCFC 142b and 22, HFC 134a and 152a, and FC 318.

The shape of the saturation curve is studied according to the molar heat capacity, and the role this capacity plays on isentropic compression, de-superheating, isenthalpic expansion and subcooling is analysed. The use of a liquid-vapour exchanger is then studied.

A cycle calculation is then carried out for three configurations, two of which use different subcooling modes. These calculations are made for irreversible adiabatic compression, with the isentropic efficiency (η_{is}) calculated through the following equation, given in /2/ :

$$\eta_{is} = 0.8 - 0.004 * (\tau - 5)^2 - \frac{0.5}{(\tau - 0.3)} \quad (1)$$

(where τ is the ratio pressure).

Pressure drops are neglected and the subcooling values used are 20°C .

THERMODYNAMIC RELATIONSHIPS AND VARIATIONS OF A CYCLE

Saturation curve slopes and molar heat capacity

The shape of the saturation curve and its link to heat capacity have already been studied (/1/, /5/, /6/). In a (T,S) diagram, the saturation curve is studied specifically on the liquid and vapour "side" thanks to the second member of the following equation /6/ :

$$\left(\frac{dS}{dT}\right)_{\sigma} = \frac{C_P}{T} - \left(\frac{\partial V}{\partial T}\right)_P * \left(\frac{dP}{dT}\right)_{\sigma} \quad (2)$$

Slope is always positive on the liquid side but is less important for refrigerants having a "high" molar heat capacity (higher than about $100 \text{ J.mol}^{-1}.\text{K}^{-1}$: "type 2" fluids).

On the vapour side, the slope of the saturation curve is constantly negative for fluids having a low molar heat capacity ("type 1" fluids). In the case of fluids with a more complex molecular structure, thus having a high molar heat capacity, this slope can reverse itself between two points, called "inversion points" /1/ (see Figure 1), where $C_{\sigma, \text{vap}}$, the heat capacity calculated on the saturation curve, cancels out.

The vapour quality at the end of isenthalpic expansion is smaller in "type 1" refrigerants than in "type 2" refrigerants, moreover these latter may cause wet compression.

Slope of the de-superheating isobar

The temperature rise of vapour during compression influences directly the isobaric de-superheating (2-3). The larger the hachured area (3b-2-3), the higher the irreversibilities (Figure 2). Indeed, the slope of the isobar is specific to each fluid and the extent of irreversibilities associated to this superheating varies according to this slope.

The calculation of the slope of the isobar :

$$\left(\frac{\partial T}{\partial S}\right)_P = \frac{T}{C_P(T)} \quad (3)$$

shows that (for $T = T_k$) the slope for ammonia ($4.94 \text{ mol.K}^2/\text{kJ}$) is about twice as large as that for HFC 134a ($2.48 \text{ mol.K}^2/\text{kJ}$) in the $0/55^{\circ}\text{C}$ range (see table 1). Molar exergetic losses are three times higher for ammonia than for HFC 134a during de-superheating.

Overheating during compression

The phenomenon of overheating can be represented by a dimensionless coefficient (ref. /3/), which we call

"overheating coefficient" :

$$\mu_{S, \Delta T} = \frac{\beta VT}{C_{P, \text{vap}}(T)} * \left(\frac{dP}{dT}\right)_{\sigma} \quad (4)$$

It enables to specify the capability of the fluid to heat-up by using the difference between saturated temperatures.

Figure 3 highlights the influence of the vapour heat capacity (calculated at evaporation temperature) on the overheating coefficient.

Among the studied fluids, ammonia has approximately an overheating coefficient twice higher than the other refrigerants studied.

Expansion and subcooling

The quality after isenthalpic expansion varies with the refrigerant. This quality depends not only on the slope of the boiling curve but also, on the operating range (Figure 4).

In order to evidence the irreversibilities which exist during isenthalpic expansion, the quality is expressed according to schematised entropy differences (Figure 4).

$$X = \frac{\Delta S_1 + \Delta S_3}{L_0 / T_0} \quad \text{where } \Delta S_3 \text{ thus represents the difference at reversibility.} \quad (5)$$

Term ΔS_1 represents the vapour generation of an isentropic expansion and depends on the difference between saturated temperatures and on the slope of the saturation curve. The creation of expansion entropy is also shown in Figure 5 and is all the lower as the quality is poor.

The quality obtained through execution of any subcooling can be expressed according to that of the reference cycle :

$$X_{sb} = X - \frac{C_{P,liq}(T_K) * \Delta T_{sb}}{L_0} \quad (6)$$

Equations (5) and (6) highlight the importance of latent heat value. Indeed, the higher the latter, the lower the quality after isenthalpic expansion.

Low molar heat capacity characterises refrigerants having a simple molecular structure. Thus, according to the remarks above, subcooling allows for a reduction of the quality but this improvement is all the higher for the fluids having a high molar heat capacity.

Liquid-vapour exchanger

The use of a liquid-vapour exchanger in a vapour compression cycle has already been studied [3] through comparison between the performance coefficients of both cycles, with (noted with mark ') and without exchanger, the cycles are visible in figure 6 (isentropic compression). This work having been carried out on a refrigerating machine, its results can be easily transposed to a heat pump : the efficiency of the cycle with such an exchanger is obtained when the COP ratio is higher than 1 or, according to thermodynamic parameters :

$$\frac{COP'}{COP} > 1 \Rightarrow \frac{1}{\frac{L_0}{C_{P2,vap}} + (T_{2i} - T_K)} > \frac{V_{1'} - V_1}{V_1(T_{1'} - T_1)} + \frac{T_{1'} - T_1}{T_{2i'} - T_{2i}} \quad (7)$$

This is notably made possible when $L_0 / C_{P2,vap}$ has the lowest possible value, i.e. low latent heat and high vapour heat capacity, ratio already pointed out in equation (6).

Term $\frac{V_{1'} - V_1}{V_1(T_{1'} - T_1)}$ can be likened to the average isobaric expansion coefficient $\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$ during superheating (1 - 1'), and this coefficient appears in equation (4) which characterises the overheating of a refrigerant.

It is then possible to assert that the higher the molar heat capacity of a fluid, the lower its overheating during compression but the higher the quality at the end of isenthalpic expansion. This duality is well illustrated in figure 3. Internal or external subcooling allows to reduce the quality at the end of expansion. These subcooling processes will be all the more efficient as the molar heat capacity of the refrigerant is high.

The mathematical relationships used enable to forecast trends. A comparison between the energetic performances of each refrigerant will now be carried out.

CYCLE CALCULATIONS

These calculations call upon two temperature ranges, 0°C/55°C and 25°C/75°C, and three different structures (figure 6) : a reference cycle (1, 2, 3, 4, 5, 1) and two different subcooling modes : fluid-heat transfert medium exchanger, external subcooling (1, 2, 3, 4', 5', 1), and liquid-vapour heat exchanger, internal subcooling (1', 2', 3, 4', 5', 1, 1').

The relative performance of the refrigerants is analysed through calculation of the coefficient of performance and of the volumetric heating capacity :

$$\text{COP}_{\text{cal}} = \frac{\text{energy available on heating side}}{\text{work of compressor}}$$

$$\text{VHC} = \frac{\text{energy available on heating side}}{\text{suction volume}}$$

and of relative exergetic losses :

$$\frac{\text{Exergetic loss}}{\sum_{\text{all components}} \text{Exergetic losses}}$$

The results obtained are indicated in table 2 and in figures 7 and 8.

Main findings

- External subcooling always leads to improve cycle performances.
- Internal exchanging via a liquid-vapour heat exchanger generates different effects on energetic performances depending on the refrigerant :
 - no improvement with HCFC 22 and HFC 152a,
 - reduction of performance with ammonia,
 - improvement of performance with all the other studied fluids.

The use of subcooling allows a reduction of exergetic losses during isenthalpic expansion. With the internal heat exchanger, this reduction is more important than the increase of the de-superheater losses for all fluids except ammonia.

- The study of COP_{cal} and VHC of the three cycles by means of figure 7 leads to various remarks :
 - improvement of performances is higher with external subcooling than with internal subcooling,
 - ammonia, HCFC 22 and propane show better energetic performances (COP_{cal} and VHC) with the cycle involving external subcooling, as well as for the reference cycle in the case of ammonia,
 - the COP_{cal} of HCFC 142b, of HFC 134a and 152a and of isobutane is higher than that of ammonia with the cycle involving external subcooling,
 - the COP_{cal} of ammonia with the reference cycle is higher than the COP_{cal} of the fluids with the cycle including a liquid-vapour exchanger, except for HCFC 142b.

Under the simulation conditions selected, one can conclude that ammonia used in a cycle without liquid-vapour exchanger shows better energetic performances than the other refrigerants studied in the same case or when a liquid-vapour exchanger is used. Moreover, for technological reasons, it is inadvisable to use a liquid-vapour exchanger with ammonia. Indeed, in the reference cycle, discharge temperatures reach 167°C and 164°C for the 0°C/55°C and 25°C/75°C ranges respectively, which already requires the use of a compressor cooling system.

CONCLUSIONS

- The study of mathematical relation-ships allows to indicate the trends of behaviour of a fluid in a vapour compression cycle based on the knowledge of its molar heat capacity. Moreover, the equations obtained point out an interesting aspect : the reduction of the quality by means of an subcooler is not identical between the refrigerants studied within an identical operating range, and this inequality benefits fluids with high quality.
- The specific study of use of a liquid-vapour heat exchanger shows that such a system is not necessarily favorable to all fluids, notably those showing high overheating upon compression.
- Cycle calculations confirm the results obtained through the thermodynamic relation-ships (Figure 8) on the influence of the heat capacity of the refrigerant. Use of external subcooling always improves performance but this improvement is higher with fluids having high molar heat capacity. Use of a liquid-vapour heat exchanger may improve or degrade energetic performances depending on the refrigerant, but the relative variation of COP_{cal} versus molar heat capacity is identical with both subcooling modes (Figure 8) :
 - use of a liquid-vapour heat exchanger is :
 - * favorable to fluids FC 318, HFC 134a, R 600a, R 290, CFC 12 and HCFC 142b,
 - * useless for HFC 152a and HCFC 22,
 - * inadvisable for ammonia, since leading to degraded performances.
 - the COP_{cal} of HFC 152a and HCFC 142b is close to that of ammonia but the good volumetric heating capacity of the latter may make it more attractive to use.

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Table n°1 : Influence of molar heat capacity on different evolution of the cycle

°C/55°C Fluids	Cp _{vap} (T ₀) kJ/mol.K	Desuperheating	Compression	Expansion
		Isobaric slope (mol.K ²)/kJ	Overheating coefficient	X _{vap}
CFC 12	0.078	3.11	1.649	0.358
HCFC 22	0.062	3.34	2.011	0.342
HCFC 142b	0.081	3.26	2.074	0.315
HFC 134a	0.091	2.48	1.669	0.402
HFC 152a	0.068	3.50	2.291	0.321
FC 318	0.154	1.72	1.210	0.542
R290	0.081	2.76	1.370	0.399
R600a	0.094	2.69	1.647	0.377
R717	0.046	4.94	3.690	0.211

Table n°2 : Energetic comparison of the cycles

°C/55°C Fluids	Elementary cycle		External subcooling		Internal subcooling	
	VHC MJ/m ³	COP _{cal}	VHC MJ/m ³	COP _{cal} -COP _{cal} COP _{cal}	VHC MJ/m ³	COP _{cal} -COP _{cal} COP _{cal}
CFC 12	3.14	3.49	3.62	0.15	3.27	0.028
HCFC 22	5.16	3.44	5.89	0.14	5.20	0.002
HCFC 142b	1.75	3.73	1.98	0.13	1.81	0.023
HFC 134a	3.10	3.44	3.67	0.18	3.28	0.046
HFC 152a	3.08	3.66	3.49	0.13	3.12	0.012
FC 318	1.20	3.08	1.57	0.31	1.45	0.148
R290	4.26	3.29	5.02	0.18	4.50	0.045
R600a	1.69	3.54	1.97	0.17	1.80	0.056
R717	6.02	3.76	6.47	0.07	5.71	-0.050

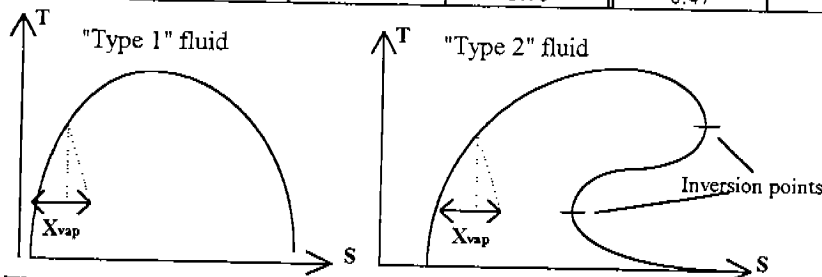


Figure n°1 : Simple representation of the shape of the (T,S) saturation boundary for two types of fluids

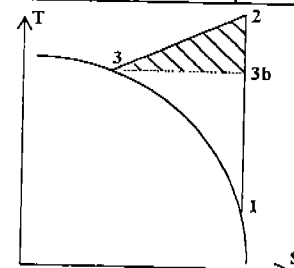


Figure n°2 : De-superheating corner in the (T,S) space.

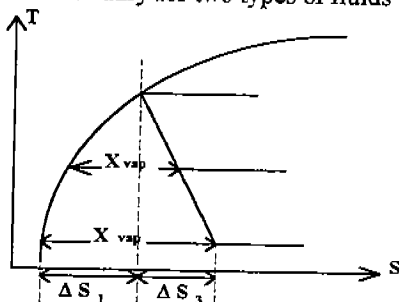


Figure n°4 : Influence of the saturated temperature difference on the quality, representation according to entropies.

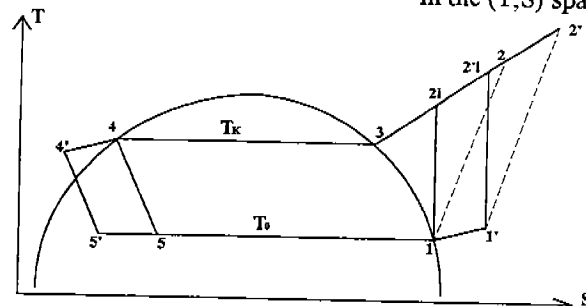


Figure n°6 : Heat pump cycles with isenthalpic expansion and isentropic or irreversible adiabatic compression.

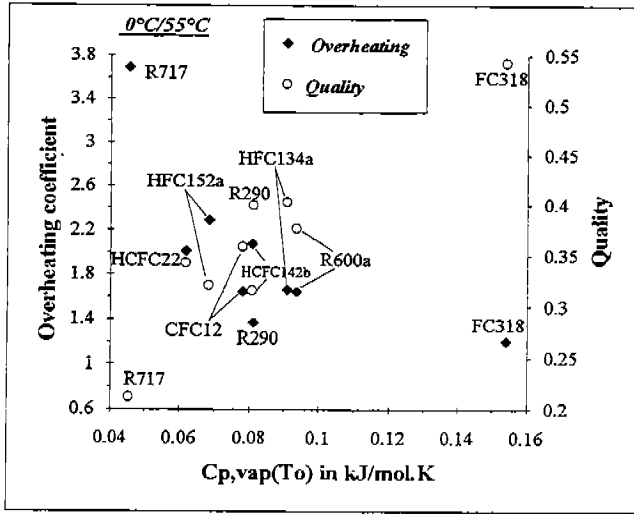


Figure 3 : Influence of molar heat capacity on the evolutions of a vapour compression cycle

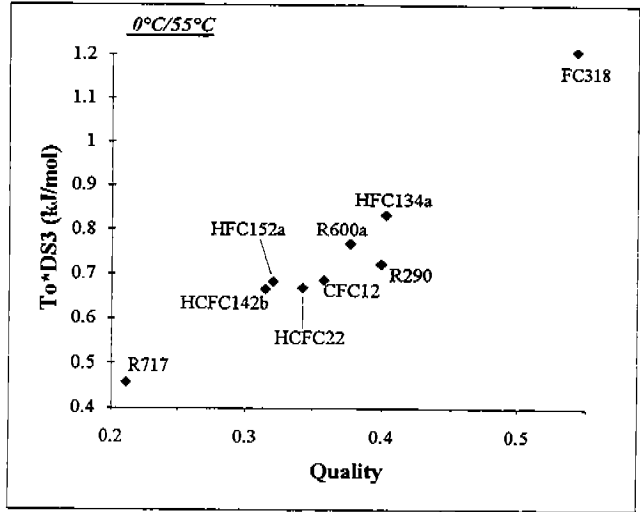


Figure 5 : Created entropy at isenthalpic expansion

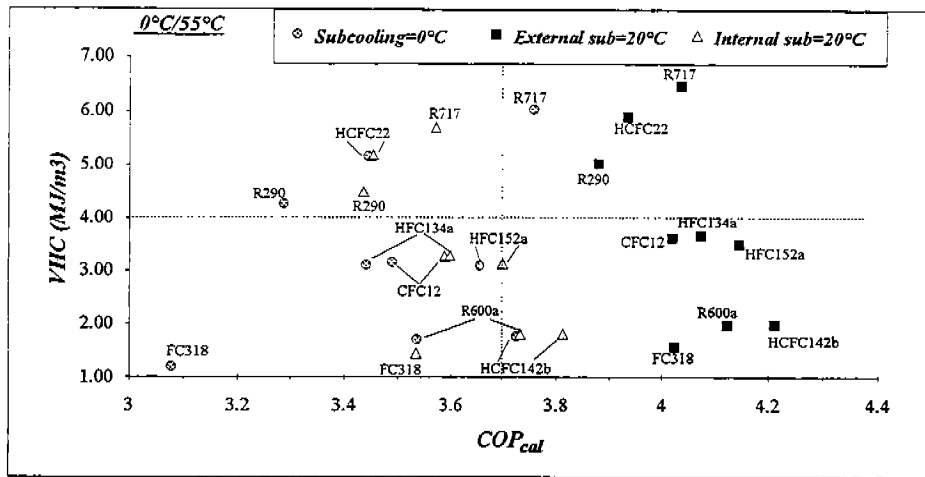


Figure 7 : Energetic performances at 0°C/55°C for the 3 studied cycles

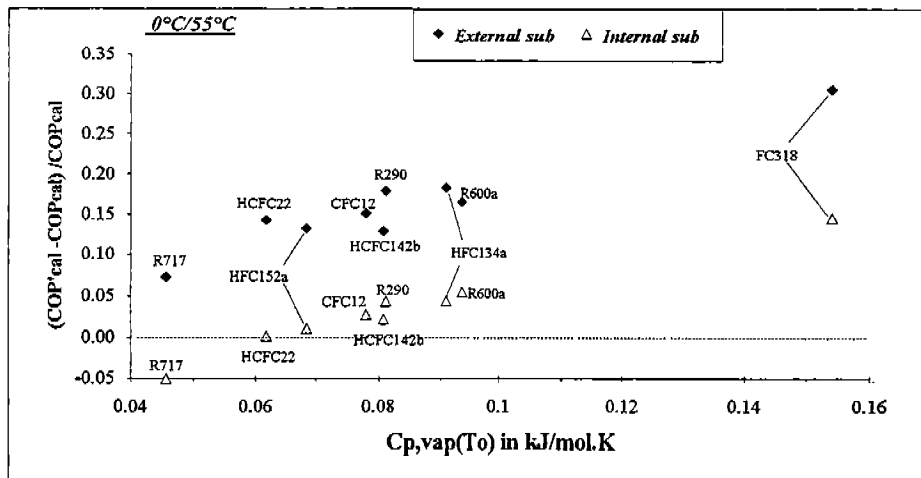


Figure 8 : COP variation versus vapour heat capacity