THE IMPORTANCE OF HIGH PURITY HYDROCARBONS IN SMALL REFRIGERATION AND HEAT PUMP UNITS

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SUMMARY

The results are summarized of a work activity at DIME in the framework of the numerous initiatives in refrigeration for the use of hydrocarbon refrigerant gases as one of the possible solutions to the problem of the environmental impact of inverse cycle plants, by means of new "green" refrigerants and high performance refrigerators.
The research is focused on R600a (isobutane) and R290 (propane) refrigerants in the field of domestic refrigerators (R600a with cooling power up to 500W) and small heat pump systems (R290 with heating power of the order of 1.5 - 5kW), for small domestic hot water (DHW) units and electric heating of small residential units.

INTRODUCTION

Along with other natural refrigerants, hydrocarbons were used in refrigeration from the mid 1800s through to the 1930s. Due to their low environmental impact, hydrocarbons have been regaining popularity since the years 1990. They are now a common alternative to fluorocarbons in a number of applications of vapour compression refrigeration systems, from small scale items such as domestic refrigerators (using very low electrical power, of the order of 100 to 500W) to use on a large scale in chemical and petrochemical plants.

Although the use of these refrigerants is therefore well known, there are very few studies concerning the importance of their purity on the performance of the refrigeration plants and on the advantages of their use, compared to fluids of lower quality and purity, typical of "raw" refinery gases [1]. Several advantages are indeed expected from the use of hydrocarbons as a refrigerant fluid, such as:

- i) zero ozone depletion potential (ODP=0),
- ii) very low global warming potential (GWP<20, only 3 for R600a),
- iii) excellent thermodynamic properties, leading to high energy efficiency (and therefore very low total equivalent warming impact, (TEWI),
- iv) good compatibility with components,
- v) low needed charges, allowing smaller heat exchangers and piping dimensions.

Possible safety problems due to flammability have been progressively solved, and higher charge values are expected to be possible in the near future. Hydrocarbon refrigerants include a number of products including R290 (propane), R600a (isobutane), R1150 (ethene/ethylene), R1270 (propene/propylene), R170 (ethane) and various blends of these products. Limiting however the analysis to small charge (that is small scale refrigerators), the research is here focused on R600a (isobutane) and R290 (propane) refrigerants. The reference fields are domestic refrigerators (R600a with cooling power up to 500W) and small heat pump systems (R290 with heating power of the order of 1.5 - 5kW), for small domestic hot water (DHW) units and electric heating of small residential units.

The investigation here presented, based on market studies and on an in-depth thermodynamic analysis, is focused on the effects of impurities (other hydrocarbons, water, non-condensable gases such as air, nitrogen, oxygen), and demonstrates how the presence of impurities can lead to relevant performance losses (COP), down to -10% and in special worst cases even -40%. An accurate control of the purity of the hydrocarbon therefore has a great importance, especially for the examined reference market, in which very low construction costs and the absence of re-filling during the life cycle of the plant make it particularly important to start with a practically pure refrigerant, with high-quality standards. Such standards are recommended in well know suggestions by AHRI [2] and DIN norms #8960 [3].

THE THERMODYNAMIC ANALYSIS

Thermodynamic calculations refer to the very basic refrigeration cycle shown in Figure 1, qualitatively represented with reference to the pure fluid R600a in the well-known pressure-enthalpy thermodynamic plane.

Given the purpose of the study (which aims exclusively at the effects of the properties and the degree of purity of the refrigerant charge introduced into the system), the simulation of other many important devices commonly used to improve plant performance (sub-cooling, regeneration, continuous speed regulation of the compressor, and so on) has been neglected. Indeed, considering these auxiliary devices would result in an unnecessary complication of thermodynamic calculations, without adding anything in terms of information on the effects induced by the thermodynamic properties of the fluid with which the filling of the system is made at the beginning of the operative life (the "charge").

These properties are strongly influenced by the composition of the hydrocarbons used and by the presence of impurities and non-condensable gases (water, air,…). All the fluid thermodynamic properties were calculated by means of mixture theory and REFPROP database [4].

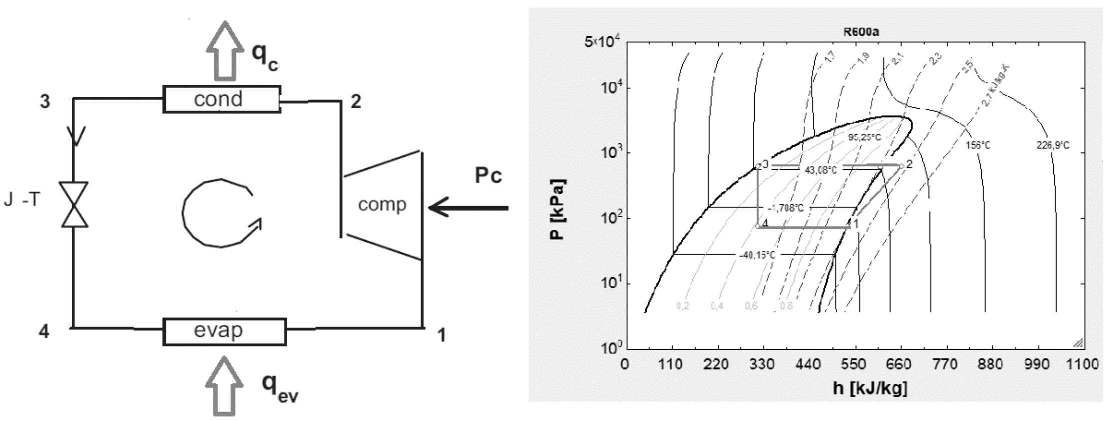

Figure 1. The basic refrigeration cycle used in this paper and the corresponding p-h diagram for R600a (Tc=45°C, Tev=-15°C).

The analysis did fully consider all the possible aspects of hydrocarbon contaminants including hydrocarbon mixtures, water and non-condensable gases and the applications for domestic refrigerators (T_c=45°C, T_{ev}=-15°C) and heat pump devices (T_c=55°C and T_{ev}=5°C). The presence of small percentages of other hydrocarbons (up to 2% in mass) shown very little effects (COP variations less than 0.1%). As the presence of water is to be avoided anyway, only non-condensable gases were studied much more in details.

It is well known that the presence of non-condensable gases such as air, nitrogen, oxygen decreases the performance of refrigeration and heat pump systems.

Table 1B of the AHRI700-2017 standards [2] recommends limit values of 0.5% by weight. The presence of air and other non-condensable gases is also limited to 1.5% in volume, in the standard conditions of 25 ° C and hydrocarbon in liquid phase.

These gases would mainly separate from the hydrocarbon and accumulate in the condenser (due to the high temperatures and pressures), thus determining a much higher weight fraction during the heat exchange process. Given that in the condenser there is a large fraction of liquid, both in the two-phase part and in the sub-cooling zone, the importance of non-condensable gases assumes a particularly significant effect on the condenser. The typical values of the charge fraction present in the condenser vary from 30% to 60%, depending both on the type of system and size, but as a mean for small capacity appliances 50% of the total charge is in the condenser. For this reason, the non-condensable gas concentration in the condenser about the double of the percentage in the fluid charge.

There are two main effects caused by the presence of non-condensable gases, which negatively affect the performance of the condenser:
1) Modification of the condensation curves
2) Deterioration of the conditions of heat exchange at the condenser

The first issue is the most important and translates in the strong deformation of the condensation line (even of evaporation, but this has little or no effect), as shown in Fig. 2

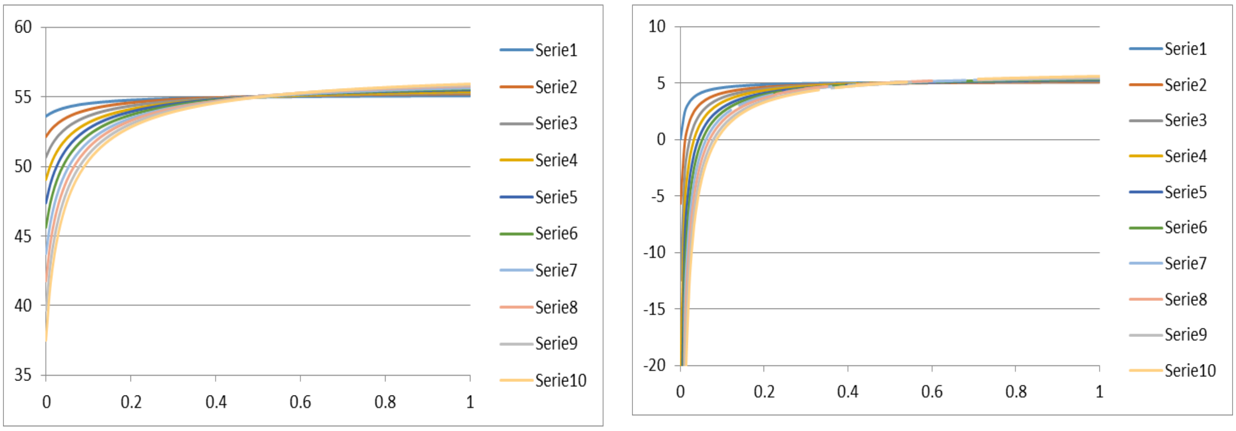

Figure 2. Typical quality-temperature condensation (left) and evaporation (right) isobaric curves for R290, with variable mass concentrations of non condensable gases (serie1=0.1%, serie10=1%). The corresponding phase transition pressures vary from 19.1 to 19.7 bar (condenser) and from 5.53 to 5.7 bar (evaporator) respectively.

This deformation, especially at the end of condensation, that is, with very low quality values, leads to a significant decrease in temperature, giving rise to two different possible effects:

a - If the working temperature at the condenser is not changed, it is impossible to reach the complete condensation at the condenser outlet, with consequent expansion in a two-phase zone and a reduction in the useful effect. This limit condition must be avoided and will therefore not be taken into consideration.
b - Complete condensation to saturated liquid line will take place only with an increase in working temperature (and consequently pressure) at the condenser. The increase in pressure forces the compressor to work with a greater compression ratio and therefore an increase in energy consumption, with a reduction in COP.

RESULTS

The tables of Figure 3 show the effect due to the modification of condensation curves (case #1), evidencing a very strong reduction in performance even for very low % of non condensable gases (less then 1000ppm).

R600a +N_2 (Ta=20 °C, T_eva=-10)

T_{cond} [°C]	COP_F	ppm w/w	% w	%w cond.	ΔCOP_F
35	2.36	100	0.01%	0.02%	-3.0%
		500	0.05%	0.1%	-13.5%
		1000	0.1%	0.2%	-
		5000	0.5%	1.0%	-
		10000	1.0%	2.0%	-
45	1.8	100	0.01%	0.02%	-1.8%
		500	0.05%	0.1%	-9.7%
		1000	0.1%	0.2%	-
		5000	0.5%	1.0%	-
		10000	1.0%	2.0%	-

R290 +N_2 (Ta=20 °C, T_eva=0)

T_{cond} [°C]	COP_{PC}	ppm w/w	% w	%w cond.	ΔCOP_{PC}
45	3.3	100	0.01%	0.02%	-0.49%
		500	0.05%	0.1%	-2.25%
		1000	0.1%	0.2%	-5.2%
		5000	0.5%	1.0%	-11.3%
		10000	1.0%	2.0%	-17.5%
55	2.71	100	0.01%	0.02%	-0.28%
		500	0.05%	0.1%	-1.6%
		1000	0.1%	0.2%	-3.4%
		5000	0.5%	1.0%	-12.8%
		10000	1.0%	2.0%	-20.1%

Figure 3. CASE 1- Performance (COP) reduction in refrigeration and heat pump applications for R600a and R290, as a function of non condensable gases amount, in the range 0.01% to 1%. The refrigeration mode is particularly penalized (often the plant cannot work properly), but also the heat pump mode reaches COP reductions of the order of -20%

Also the analysis of case 2) (deterioration of the heat transfer conditions at the condenser) gave similar results, showing COP reductions of the order of -2% for increments of 0.5% in weight of non condensable gases in the hydrocarbon refrigerant.

CONCLUSIONS

The results here presented prove that the recommendation AHRI700-2017 represents an important and recommended standard regarding the purity of the refrigerant fluids (including the hydrocarbons here examined) and should be considered mandatory. Purities of the used hydrocarbon refrigerant as high as 99.5% are suggested. Furthermore, maximum limits of humidity (10ppm) and total non-condensable gases (175ppm) are recommended. These characteristics are hardly guaranteed by a refinery product, but they represent the rule for the high-purity and high-quality standards in post-processing of hydrocarbon gases.

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