Refrigerants – Part 1: Properties and air-conditioning applications

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Abstract

The paper on refrigerants has been divided in two parts. Refrigerants' thermodynamic, physical, chemical, safety – related and environmental properties have been presented and discussed in the first part of the paper. Influence of those properties, which is of the utmost significance on the vapor – compression process efficiency and design has been presented. The design of HVAC system is influenced by the choice of the vapor – compression process, which means that refrigerant choice defines HVAC design as well. Throughout the history, refrigerant development took place due to different reasons, such as safety, stability, durability, economic or environmental issues, thus giving the boost to new research and equipment improvement in terms of safety and efficiency. Recent legislation worldwide and in EU is still not quite completed concerning refrigerant issues. The delicate subject of refrigerants is widely discussed, viewpoints of different parties are opposite, depending on positions and interests, and compliance on that issue is not easy to achieve. In the second part of the paper about refrigerants, past present and future of refrigerants and suitable applications will be discussed, with emphasis on natural refrigerants.

Introduction

Refrigerants are the working fluids used in the counter clockwise thermodynamic working cycles. Depending on temperature levels of the heat source and the heat sink, the application area of the working cycle can be refrigeration, air- conditioning, or heat-pumping. Refrigerant circulates within the refrigeration machine, absorbs the heat from the heat source at lower temperature level and rejects it into the heat sink at higher temperature level. In absorption and mechanical vapor compression systems refrigerants usually pass the phase change, namely evaporation or condensation. Gas refrigeration cycles are also available and phase change of the working fluid in such cycles does not occur. Gas refrigeration cycles are less efficient compared to vapor – compression cycles and will be omitted in the considerations that follow.

The choice of the refrigerant is not only the technical problem, it is subject to lot of interests, public and industrial groups advocate their positions and neutral position in all that multiple source information is not always easy to achieve.

Throughout the history of refrigeration organic and inorganic natural working fluids, chlorofluorocarbons CFCs, hydro chlorofluorocarbons HCFCs, fluorocarbons HFCs have been used and some of them abandoned for certain reasons, such as security, cost or environmental, defining in some way the direction of development of refrigeration and HVAC industry.

The refrigerant issue is becoming more important in present time due to the fact that refrigeration or heat pumping can contribute to better utilization of renewable heat contained in the environment on low temperature level, thus making possible easier design of zero energy buildings.

Refrigerant properties

Refrigerant selection involves compromises between conflicting desirable properties. The working fluid desirable properties are related to thermodynamic and physical properties which lead to efficient cooling or heating factor and effective design of equipment, such as high evaporation heat, high volumetric refrigeration capacity, low temperature at the end of the compression. Other physical properties comprise the favorable position of critical and the freezing point, low specific heat capacity, low specific volume, low viscosity and high thermal conductivity. Desirable chemical and safety properties comprise chemical stability within the working conditions in the refrigeration unit in the presence of used materials and lubricating oil, non-flammability, non-toxicity, good miscibility with oil. If possible, the refrigerant must be odorless, but easy detection in the air is desirable. Safety properties of refrigerants considering flammability and toxicity are defined by ASHRAE standard 34 [1]. Toxicity classification of refrigerants is assigned to classes A or B. Class A signifies refrigerants for which toxicity has not been identified at concentrations less than or equal to 400 ppm by volume, and class B signifies refrigerants with evidence of toxicity at concentrations below 400 ppm by volume. By flammability refrigerants are divided in three classes. Class 1 indicates refrigerants that do not show flame propagation when tested in air (at 101 kPa and 21°C). Class 2 signifies refrigerants having a lower flammability limit (LFL) of more than 0.10 kg/m³ and a heat of combustion of less than 19 000 kJ/kg. Class 3 indicates refrigerants that are highly flammable, as defined by an LFL of less than or equal to 0.10 kg/m³ or a heat of combustion greater than or equal to 19 000 kJ/kg.

Table 1. Safety classification of refrigerants as defined by ASHRAE standard 34.

increasing flammability→	SAFETY GROUP	
higher flammability	A3	B3
lower flammability	A2	B2
	A2L*	B2L*
no flame propagation	A1	B1
	lower toxicity	higher toxicity
	increasing toxicity→	

* A2L and B2L are lower flammability refrigerants with a maximum burning velocity ≤ 10 cm/s.

New flammability class 2L has been added since 2010 denoting refrigerants with burning velocity less than 10 cm / sec.

Desired environmental properties comprise that refrigerants should not affect the ozone layer (the presence of chlorine in the working fluid molecules is not acceptable), that the impact on global warming should be as low as possible and that working fluid decomposition by-products should not have negative effects on the environment.

Some refrigerants (chlorofluorocarbons CFCs and hydro chlorofluorocarbons HCFCs) can affect the ozone layer. Ozone (O_3) is naturally formed in the atmosphere and it absorbs the sun's harmful UV rays. The chlorine contained in CFCs and HCFCs distorts the natural equilibrium of the ozone in the atmosphere and affect its concentration, which, in turn, increases the risk of skin cancer, weakens human immune system leading to diseases, causes the flora and fauna imbalance, plankton depletion and species count decrease.

Another negative effect of HFCs, which belong to the greenhouse gasses (CO_2, CH_4, NO_2, HFCs, PFCs and SF_6) is the global warming. The greenhouse gasses emitted into atmosphere allow the short wave radiation of the Sun passing through, but are less permeable for the long wave radiation of the Earth's surface. This is why the certain amount of energy reaching the surface of the Earth through the atmosphere stays trapped as if in a greenhouse and causes the temperature to rise. This distorts the total energy balance of the Earth and causes dramatic climate change.

The refrigerant impacts on the environment are evaluated with the ozone Depletion Potential (ODP) and the Global Warming Potential (GWP). ODP is expressed as a relative potential of ozone depletion compared to influence of R-11 which has ODP=1. The Global Warming Potential (GWP) is the relative measure of the substance impact on the greenhouse effect in relation to the impact of a kilogram of CO_2. The CO_2 is retained permanently in the atmosphere, which is why the GWP of greenhouse gasses which can have lower lifetime in the atmosphere is calculated over a specific time interval, commonly 20, 100 or 500 years.

Finally, some demands of economic nature, such as low price and good availability are also important for refrigerant selection.

There is no "ideal" working fluid available. Neither one among working fluids has all the required properties and the above – mentioned requirements are fulfilled only partially. When selecting the refrigerant, the device application and temperature range must always be analyzed in order to be able to determine the optimal refrigerant. In technical practice, which is subject to changes over time, priority is always given to certain refrigerants for certain purposes.

Influence of refrigerants on process efficiency

The design and efficiency of the refrigeration equipment depends strongly on the selected refrigerant's properties. Consequently, operational and equipment costs depend on refrigerant choice significantly. Vapor – compression unit consists of compressor, condenser, expansion device and the evaporator, connected with refrigerant pipelines.

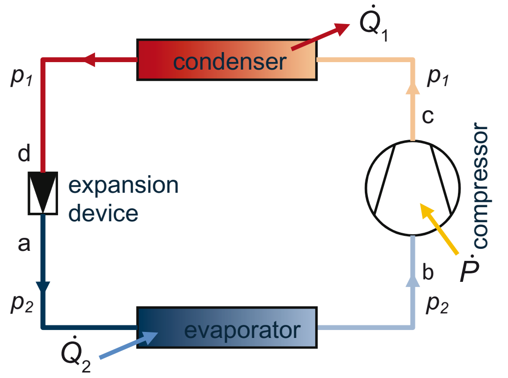

Figure 1. Single-stage compression refrigeration unit schematics.

The basic vapor – compression cycle is considered to be one with isentropic compression, with no superheat of vapor and with no subcooling of liquid (**Figure 2**).

When zeotropic mixtures are used as refrigerants, gliding temperatures influence cycle efficiency as well as system design. An example of the process operating with zeotropic mixture is given on **Figure 3**. Temperature glide appears during evaporation and condensation at constant pressure. Use of counter flow heat exchangers can sometimes help to utilize that temperature glide efficiently, but problems can appear with leakage of refrigerants from such systems as the initial refrigerant composition and thus properties can be disturbed.

The specific compression work w, the specific cooling performance q_2, volumetric refrigerating capacity q_{0v}, the cooling factor COP_2 are calculated for above presented processes as follows:

$$w = h_c - h_b \quad [\text{kJ/kg}], \tag{1}$$

$$q_2 = h_b - h_a = h_b - h_d \quad [\text{kJ/kg}] \tag{2}$$

$$q_{0v} = \frac{q_2}{v_b} = q_2 \rho_b \quad [\text{kJ/m}^3] \tag{3}$$

$$COP_2 = \frac{q_2}{w} = \frac{h_b - h_a}{h_c - h_b} \tag{4}$$

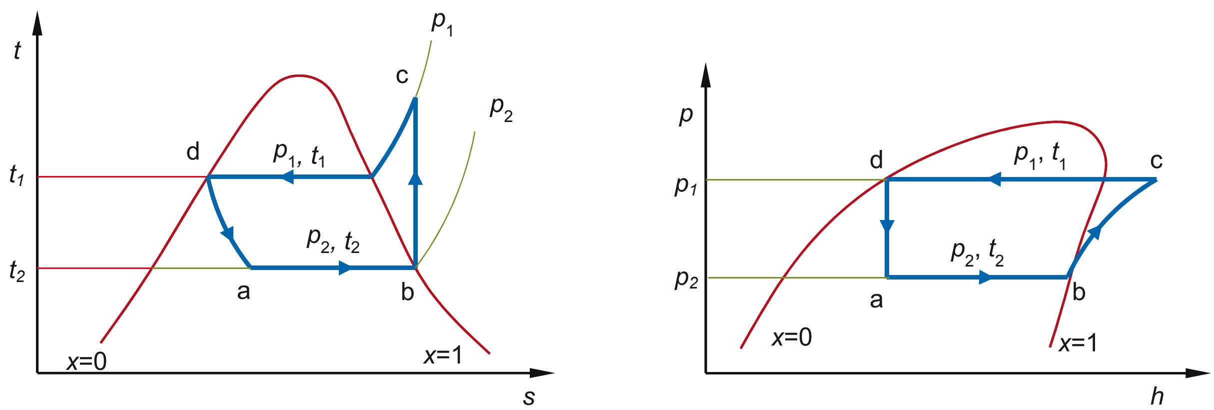

Figure 2. Single-stage vapor - compression subcritical process with a single – component or azeotropic refrigerant in temperature - entropy ***t,s-*** and pressure – enthalpy ***p,h-*** diagrams.

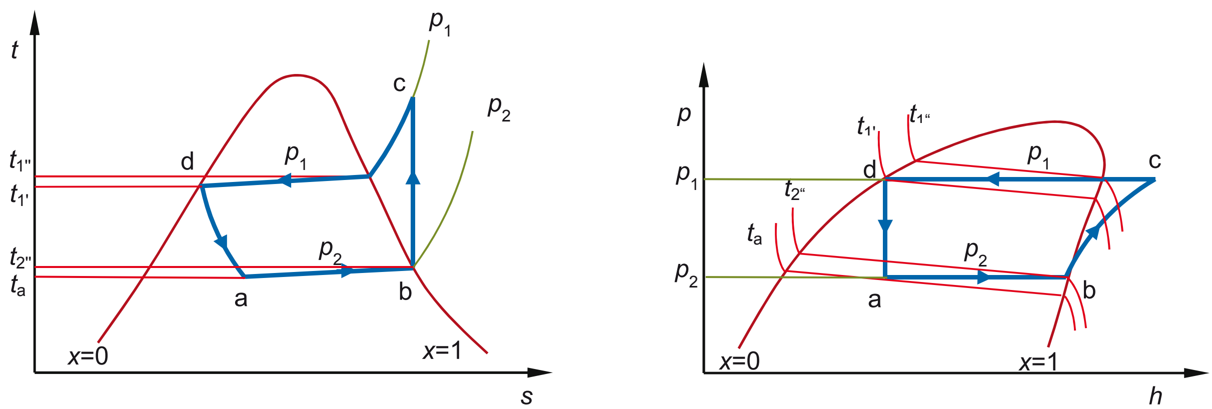

Figure 3. Single-stage vapor – compression subcritical process with a zeotropic mixture refrigerant in temperature – entropy ***t,s-*** and pressure – enthalpy ***p,h-*** diagrams.

The refrigerant mass flow is calculated from the required cooling capacity and the specific cooling performance.

$$\dot{M} = \frac{\dot{Q}_2}{q_2} \quad [\text{kg/s}] \tag{5}$$

The power necessary for the isentropic compression may be calculated as

$$\dot{P}_{is} = \dot{M}\, w \quad [\text{kW}] \tag{6}$$

The effective power on the compressor shaft is bigger and is calculated as

$$\dot{P}_{ef} = \frac{P_{is}}{\eta_{is}} \tag{7}$$

Comparison of different refrigerants gives a good overview of achievable cycle performance for a basic referent cycle. **Table 1** gives comparison for refrigerating reference cycle with evaporation temperature –15°C and condensing temperature +30°C. Cycle data for zeotropic refrigerants in **Table 1** are given for combination of temperatures $t_{2''}$ and $t_{1'}$ [2]. Cycle data are available from different sources, e.g. IIR - Refrigerant cycle data [2], ASHRAE Fundamentals Handbook [3], or can be evaluated from suitable software such as REFPROP [4]. The selection of refrigerants in **Table 2** has been made in order to present the overview of cycle data for historically used natural inorganic refrigerants such as ammonia R-717, carbon dioxide R-744, sulfur dioxide R-764 (which is not in use anymore), chlorofluorocarbons CFCs such as R-11 or R-12 and hydro chlorofluorocarbons HCFCs such as R-22, and azeotropic mixture R-502 which dominated in 20th century and are also phased out. Amongst newly used refrigerants hydro fluorocarbons HFCs R-32 and R-134A are presented as well as zeotropic mixtures of HFCs R-404A, R-407C, R-410A, and azeotropic mixture of HFCs R-507. Finally, natural hydrocarbons HCs R-600A and R-290, together with propylene R-1270 are listed.

As it can be seen from data presented in **Table 2** pressures in the system are temperature – dependent and are different for each particular refrigerant. Evaporation and condensing temperatures are close coupled with corresponding pressures for single – component refrigerants, while for zeotropic mixtures temperature glide appears during the phase change at constant pressure. Pressures influence design and thus equipment costs, but also the power consumption for compression and thus operational costs. Refrigerant transport properties, such as liquid and vapor density, viscosity, thermal conductivity or surface tension, define heat transfer coefficients and consequently temperature differences in heat exchangers thus directly influencing pressures in the system as well as necessary heat transfer surface of heat exchangers. Molecular mass or volumetric refrigerating capacity of some refrigerants influences application of certain compressor types. For example, ammonia systems are not suitable for application of centrifugal compressor due to low molecular mass of ammonia. On the contrary, R-11 with relatively high molecular mass and low volumetric refrigeration capacity represented a good candidate for application of centrifugal compressors. The higher the volumetric refrigeration capacity is, the smaller compressor displacement can be, which results in smaller compressors for refrigerants with high volumetric refrigeration capacities. Excellent example is R-744 with highest volumetric capacity among all the refrigerants presented in **Table 2**. R-744 compressors are smaller compared to compressors for some other refrigerants.

Achievable efficiency of the entire process is in a great deal a consequence of the refrigerant used. For example, R-11 which has been banned since 2006 can produce highest COP among all other refrigerants for the temperature range considered. Effective energy consumption or cooling factor is not equal to the one of the theoretical cycle. Isentropic efficiency η_{is} in equation 7 is also dependent on refrigerant properties. Discharge temperature on the compressor outlet depends on refrigerant and systems pressures, and it must be limited in order to avoid deterioration of oil properties, or even the oil burnout. For the –15/30°C cycle that problem is not so obvious, but when heat pump applications come into consideration, with evaporation temperatures close or significantly lower than 0°C, and condensing temperatures up to 60°C which is approximately upper level of achievable condensing temperatures for most of refrigerants in cycles with a single – stage compression, that can for certain refrigerants result in high temperatures at the end of the compression, which must be avoided by use of modified cycles (e.g. economizer cycle) or different type of the cycle (e.g. two – stage compression). Behavior of some refrigerant during the compression can result in no or low superheating of the vapor at the end of the compression (e.g. R-134A with low superheating, or R-600A where final refrigerant state at the end of the compression can end in saturated area unless proper superheating at the compressor inlet is provided). Systems with such refrigerants are not suitable for utilization of superheated part of vapor heat content in refrigeration cycles with heat recovery for sanitary water

Table 2. Parameters of –15/30°C cycle with different refrigerants.

R number	p_1 bar	p_2 bar	p_1/p_2	q_{0v} kJ/m³	COP_2 –15/30°C	t_c °C
R-717	11,672	2,362	4,942	2 167,6	4,76	99,08
R-744	72,1	22,9	3,149	7979	2,69	69,5
R-764	4,624	0,807	5,730	818,8	4,84	96,95
R-11	1,260	0,202	6,233	204,2	5,02	42,83
R-12	7,437	1,823	4,079	1 273,4	4,70	37,81
R-22	11,919	2,962	4,024	2 096,9	4,66	52,95
R-32	19,275	4,881	3,949	3 420,0	4,52	68,54
R-134A	7,702	1,639	4,698	1 225,7	4,60	36,61
R-404A	14,283	3,610	3,956	2 099,1	4,16	36,01
R-407C	13,591	2,632	5,164	1 802,9	3,91	51,43
R-410A	18,893	4,800	3,936	3 093,0	4,38	51,23
R-502	13,047	3,437	3,796	2 079,5	4,39	37,07
R-507	14,60	3,773	3,870	2 163,2	4,18	35,25
R-600A[1]	4,047	0,891	4,545	663,8	4,71	32,66
R-290	10,79	2,916	3,700	1 814,5	4,55	36,60
R-1270	13,05	3,630	3,595	2 231,1	4,55	41,85

[1] Superheating at compressor suction port 5°C.

heating during the cooling operation. Analyses become more complicated when superheating and subcooling of refrigerant occurs within the cycle. Liquid subcooling and vapor superheating can be intentionally produced by introducing liquid – vapor heat exchanger into the cycle. With heat exchange between the low – pressure vapor and high pressure liquid refrigerant, efficiency increases for certain refrigerants, while for other refrigerants the decrease of efficiency appears.

Finally, pressure drops within heat exchangers and in pipelines connecting refrigeration machine components are essential for system efficiency and are also dependent on refrigerant properties. All presented examples illustrate the fact that refrigerant properties are essential for the refrigeration equipment design and that gives the refrigerant choice the most important position in design of the refrigeration equipment.

Conclusion

Influence of refrigerant properties and refrigeration system design is significant and those properties influence the design of HVAC systems which contain refrigeration subsystems as well. In the future we may expect changes in regulation concerning refrigerants, the construction of systems that are suitable for the use of newly developed and natural refrigerants, the optimization of the system in the sense of compensating the lower efficiency of some refrigerants, but with keeping cost within acceptable limits. ■

Literature

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