Past, present and future perspectives of refrigerants in air-conditioning, refrigeration and heat pump applications

IOAN SÂRBU, EMILIAN STEFAN VALEA
Department of Building Services Engineering, Polytechnic University Timisoara
Piata Bisericii, no. 4A, 300233 Timisoara, ROMANIA
ioan.sarbu@ct.upt.ro, emilian.valea@ct.upt.ro

Abstract: The paper presents a study of refrigerants and some issues relating to their environmental impacts in HVAC&R equipment. They are treated aspects of the environmental pollution through the working fluids of the air-conditioning, refrigeration and heat pump systems, and a new strategy in using refrigerants in accordance with the international legislation is described. Additionally, this study presents the refrigerant development throughout the history and discusses the selection of refrigerants adapted to each utilisation based on the thermodynamic and -physical properties. Influence of those properties, which is of the utmost significance on the vapour-compression process efficiency and design are also presented. Finally, a comparative analysis of the total equivalent warming impact (TEWI) for possible substitutes of refrigerant R22 used in various air-conditioning, heat pump and refrigeration systems is performed.

Key-Words: Pollution, environmental protection, cooling, refrigerants, ecological substitutes.

1 Introduction

Environmental pollution represents a major risk for all life on our planet (men, flora, fauna), because it consists not only of the local noxious effects of different pollutants but also the imbalances produced on a large scale over the entire planet.

The term “pollutant” appoints each solid, liquid or gaseous substance, microorganisms, sounds, vibrations, all kind or combination of radiations, that modifies the natural state of environment.

Environmental protection represents the fundamental condition of the society’s sustainable development, a priority purpose of national interest that is realized in institutional frame where the legal norms authoresses the development of activities with environmental impact and exert the control upon these.

The purpose of environmental protection is to maintain the ecological balance, to maintain and improve the natural factors, to prevent and control pollution, the development of natural values, to assure better life and work condition for the present and future generations and it refers to all actions, means and measures undertaken for these purpose.

One of the minor components of atmosphere, the ozone has a special importance in maintaining the ecological balance. It is distributed in principal between the stratosphere (85-90%) and troposphere. Any perturbation of the atmospheric ozone concentration (it varies between 0 and 10 ppm, depending on the regions) has direct and immediate effect upon life.

For most of the states the problems of forming and maintaining the earth’s ozone layer, represents a major priority. In this context during the last 30 years, the European Union has adopted a large number of laws and regulations concerning environmental protection to correct the pollution effects, frequently by indirect directives, through imposition of the levels of allowable concentrations by asking for government collaboration, programs and projects for the regulation of industrial activities and productions. The Alliance for Responsible Atmospheric Policy is an industry coalition and leading voice for ozone protection and climate change policies, which maintains a brief summary of the regulations for some countries [5].

Refrigerants are the working fluids used in the counter clockwise thermodynamic working cycles [37]. They absorb heat from one area, such as an air-conditioned space, and reject it into another, such as outdoors, usually through evaporation and condensation. These phase changes occur both in absorption and mechanical vapour compression systems, but not in systems operating on a gas cycle using a fluid such as air.

Vapour compression-based systems are generally employed in refrigeration, air-conditioning and heat pump units operating with halogenated refrigerants. The international protocols (Montreal and Kyoto) restrict the use of the halogenated refrigerants in the vapour compression-based refrigeration systems. As per Montreal Protocol 1987, the use of CFCs was completely stopped in most of the nations. However, HCFCs refrigerants can be used until 2040 in developing nations and developed nations should phase out by 2030 [29]. To meet the global demand in refrigeration and air-conditioning sector, it is necessary to look for long-term alternatives to satisfy the objectives of international protocols. From the environmental, ecological and health point of view, it is urgent to find some better substitutes for HFC refrigerants [21]. HC and HFC refrigerant mixtures with low environment impacts are considered as potential alternatives to phase out the existing halogenated refrigerants.

In this paper are treated aspects of the environmental pollution through the working fluids of the air-conditioning, refrigeration and heat pump systems, and a new strategy in using refrigerants in accordance with the international legislation is described. Additionally, this study presents the refrigerant development throughout the history and discusses the selection of refrigerants adapted to each utilisation based on the thermo-dynamic and -physical properties. Influence of those properties, which is of the utmost significance on the vapour-compression process efficiency and design are also presented. Finally, a comparative analysis of the total equivalent warming impact (TEWI) for possible substitutes of refrigerant R22 used in various air-conditioning, heat pump and refrigeration systems is performed.

2 Action of refrigerants upon environment

2.1 Flammability and toxicity

Refrigerant selection involves compromises between conflicting desirable thermo-physical properties. A refrigerant must satisfy many requirements, some of which do not directly relate to its ability to transfer heat. Chemical stability under conditions of use is an essential characteristic. Safety codes may require a non-flammable refrigerant of low toxicity for some applications. The environmental consequences of refrigerant leaks must also be considered. Cost, availability, efficiency, and compatibility with compressor lubricants and equipment materials are other concerns [10]. Safety properties of refrigerants considering flammability and toxicity are defined by ASHRAE standard 34 [6]. Toxicity classification of refrigerants is assigned to classes A or B (Table 1). 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/m^3 and a heat of combustion 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/m^3 or a heat of combustion greater than or equal to 19,000 kJ/kg.

Table 1. Safety classification of refrigerants

Flammability	Safety code	
	lower toxicity	higher toxicity
higher flammability	A2	B2
lower flammability	A2L	B2L
no flame propagation	A1	B1

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

Desired environmental properties comprise that refrigerants should not affect the ozone layer 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.

2.2 Environmental impact

Minimising all refrigerant releases from systems is important not only because of environmental impacts but also because charge losses lead to insufficient system charge levels, which in turn results in suboptimal operation and lowered efficiency.

Working fluids escaped through leakages from refrigeration equipments, during the normal operating (filling, empting) or accidental (damages), gathers in significant quantities in high levels of the atmosphere (stratosphere). There, through catalytically decompounding they deplete the ozone layer that normally is filtering the ultraviolet sun radiations, dangerous for living creatures and plants on earth. Stratospheric ozone depletion has been linked to the presence of chlorine and bromine in the stratosphere. In addition, refrigerants contributed to the global warming of atmosphere, as gases with greenhouse effect.

The average global temperature is determined by the balance of energy from the sun heating the earth and its atmosphere and of the energy radiated from the earth and the atmosphere into space. Greenhouse gases (GHGs), such as CO_2 and water vapour, as well as small particles trap heat at and near the surface, maintaining the average temperature of the Earth's surface at a temperature approximately 34 K warmer than would be the case if these gases and particles were not present (greenhouse effect).

Global warming is a concern because of an increase in the greenhouse effect from increasing concentrations of GHGs attributed to human activities. Thus, the negative environmental impact of the working fluids, especially the effect of halogenated refrigerants on the environment, can be synthesised by two effects [7]:

– depletion of the ozone layer;

– contribution to global warming at the planetary level via the greenhouse effect.

The measure of a material's ability to deplete stratospheric ozone is its *ozone depletion potential* (ODP), a relative value to that of R11, which has an ODP of 1.0.

The global warming potential (GWP) of a GHG is an index describing its relative ability to collect radiant energy compared to CO_2, which has a very long atmospheric lifetime. Therefore, refrigerants will be select so that the ozone depletion potential will be zero and with a reduced GWP.

Concerning the polluting action upon the environment, for atmospheric ozone, as presented through the Montreal Protocol [36] and the subsequent amendments, as well as for the greenhouse effect according to the Kyoto Protocol [16], refrigerants can be classified as follows:

– having strong destructive action on the ozone layer and with significant amplification of the greenhouse effect upon the earth (Chlorofluorocarbons-CFCs);

– having reduced action on the ozone layer and with moderate amplification of the greenhouse effect (Hydro-chlorofluorocarbons-HCFCs);

– being harmless to the ozone layer, with less influence upon the greenhouse effect (Hydrofluorocarbons-HFCs);

– being harmless to the ozone layer, with very less or even no influence upon greenhouse effect (carbon dioxide (CO_2), natural hydrocarbons (HCs), and ammonia (NH_3) respectively).

A second influence of refrigerants upon the environment, as previously mentioned, guided to a new classification of refrigerants according to their contribution to global warming. Comparison of this specific contribution to the greenhouse effect is performed even for R11 (the most noxious even from the point of view of ODP) as well as for CO_2. Halogenated refrigerants is categorised in the undesirable position 3 (14%) between the greenhouse gases, which could be explained by their great absorption capacity of infrared radiation.

In the case of refrigeration and heat pump systems, although supplementary to the direct action to the greenhouse effect because of the refrigerants leakage in atmosphere, it must be considered even the indirect action to global warming by the CO_2 quantity released during the production of the drive energy for system is obviously greater than the associated direct action [33]. While the refrigerant quantity increases in the system, the effect of direct action rises. The environmental impact of an HVAC&R system is due to the release of refrigerant and the emission of greenhouse gases for associated energy use. The *total equivalent warming impact* (TEWI) is used as an indicator for environmental impact of the system for its entire lifetime. TEWI is the sum of the direct refrigerant emissions, expressed in terms of CO_2 equivalents, and the indirect emissions of CO_2 from the system's energy use over its service life [15].

The life-cycle climate performance (LCCP) of an HVAC&R system includes TEWI and adds the effects of direct and indirect emissions associated with manufacturing the refrigerant. The analysis of the TEWI index for refrigeration systems operating with different refrigerants (R22, R134a, R404A, R717, R744) indicated that the direct effect generated by CO_2 is negligible compared with the other refrigerants [13]. The indirect effect generated by CO_2 is significant because of the high condensation pressures that determine the large amount of energy consumption and in consequence the maximum value of TEWI for CO_2.

Environmentally preferred refrigerants have:

– low or zero ODP;

– relatively short atmospheric lifetimes;

– low GWP;

– ability to provide good system efficiency;

– appropriate safety properties;

– ability to yield a low TEWI or LCCP in system.

In Table 2 is listed the environmental properties of refrigerants [32]. Because HFCs do not contain chlorine or bromine, their ODP values are negligible and represented by 0 in this table. Ammonia, HCFCs, most HFCs, and HFOs have shorter atmospheric lifetimes than CFCs because they are largely destroyed in the lower atmosphere by reaction with OH radicals. A shorter atmospheric lifetime generally results in lower ODP and GWP values.

Table 2. Environmental properties of refrigerants

Group	Refrigerant	ODP	GWP (R11=1)	GWP (CO_2=1)	Atmospheric lifetime [years]
0	1	2	3	4	5
CFC	R11	1	1	4000	50…60
	R12	1	2.1…3.05	10600	102…130
	R113	0.8-1.07	1.3	4200	90…110
	R114	0.7-1.0	4.15	6900	130…220
	R12B_1	3-13	–	1300	11…25
	R13B_1	10-16	1.65	6900	65…110
HCFC	R21	0.05	0.1	–	<10
	R22	0.055	0.034	1900	11.8
	R123	0.02	0.02	120	1.4…2
	R142b	0.065	0.3…0.46	2000	19…22.4
HFC	R23	0	6	14800	24.3
	R32	0	0.14	580	6…7.3
	R125	0	0.58…0.85	3200	32.6
	R134a	0	0.28	1600	14…15.6
	R143a	0	0.75…1.2	3900	55…64.2
	R152a	0	0.03…0.04	140	1.5…8
HFO	R1234yf	0	–	<4.4	0.029
NH_3	R717	0	–	0	<0.02
CO_2	R744	0	–	1	>50
Azeotropic mixtures	R500(R12/R152a)	0.63-0.75	2.2	6000	–
	R501(R12/R22)	0.53	1.7	4200	–
	R502(R22/R115)	0.3-0.34	4.01…5.1	5600	>100
	R507(R125/R143a)	0	0.68	3800	–
Near azeotropic mixtures	R404A(0.44R125/0.52R143a/ 0.04R134a)	0	0.6…0.94	3750	–
	R410A(0.5R32/0.5R125)	0	0.5	1890	–
	R428(0.775R125/0.2R134a/0.019R600a/0.006R290)	0	–	3500	–
	FX40(0.1R32/0.45R125/0.45R143)	0	0.6	3350	–
Zeotropic mixtures	R407A(0.2R32/0.4R125/0.4 R134a)	0	0.14…0.45	1920	–
	R407B(0.1R32/R0.7R125/0.2R134a)	0	0.1…0.5	2560	–
	R407C(0.23R32/0.25R125/0.52R134a)	0	0.29…0.37	1610	–
	R417A(0.466R125/0.5R134a/0.034R600)	0	–	2300	–
	R422A(0.851R125/0.115R134a/0.034R600a)	0	–	3100	–
	R424(0.505R125/0.47R134a/0.009R600a/0.01R600/0.006R60)	0	–	2400	–
	R427A(0.15R32/0.25R125/0.1R143a/0.5R134a)	0	–	2100	–

2.3 Historical overview on refrigerants

Beginnings of mechanical refrigeration, starting from early 19th century are characterized by use of natural refrigerants. In 1834 Perkins proposed ethyl ether as the working fluid in his patent of the vapour-compression refrigeration system. By that time ammonia (R717), sulphur dioxide (R764) and carbon dioxide (R744) had been isolated and were available for use as well. First machine working with NH_3 was designed by Linde in 1876. In 1862 Lowe developed a CO_2 refrigeration system. Methyl chloride was used for the first time as a refrigerant in 1878. Most of those early refrigerants were flammable, toxic or both [9].

The most utilised halogenated refrigerants are the family of chemical compounds derived from the hydrocarbons (HC) (methane and ethane) by substitution of chlorine (Cl) and fluorine (F) atoms for hydrogen (H), whose toxicity and flammability scale according to the number of Cl and H atoms. The presence of halogenated atoms is responsible for ODP and GWP. During the last century, the halogenated refrigerants have dominated the vapour compression-based systems due to its good thermodynamic and thermo-physical properties.

The second generation of refrigerants, CFCs replaced classic refrigerants in early 20th century. Refrigerants as CFCs (R12, R11, and R13) have been used since the 1930s because of their superior safety and performance characteristics. However, their production for use in developed countries has been eliminated because it has been shown that they deplete the ozone layer [5]. The CFCs and HCFCs represented by R22 and mixture R502 dominated the second generation of refrigerants [9].

The HCFCs also deplete the ozone layer, but to a much lesser extent than CFCs. HCFCs production for use as refrigerants is scheduled for elimination by 2030 for developed countries and by 2040 for developing countries [29].

Therefore, the traditional refrigerants (CFCs) were banned by the Montreal Protocol because of their contribution to the disruption of the stratospheric ozone layer [27]. The Kyoto Protocol listed HCFCs as being with large GWPs.

With the phasing out of the use of CFCs, chemical substances such as the HCFCs and the HFCs, were proposed and have been used as temporary alternatives.

The HFCs do not deplete the ozone layer and have many of the desirable properties of CFCs and HCFCs. They are being widely used as substitute refrigerants for CFCs and HCFCs. The HFC refrigerants have significant benefits regarding safety, stability and low toxicity, being appropriate for large-scale applications.

A major contribution against the climate changes has the European Union through regulations regarding some fluorinated gases with green house effect and it is a real support in the emission reducing resulted from these fluorinated gases all over Europe. All regulations establish a high protection level of the environment as well as an inside market for equipments containing fluorinated gases and for the members involved in this activities.

3 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. Vapour-compression system (Fig. 1) consists of compressor, condenser, expansion valve and evaporator, connected with refrigerant pipelines.

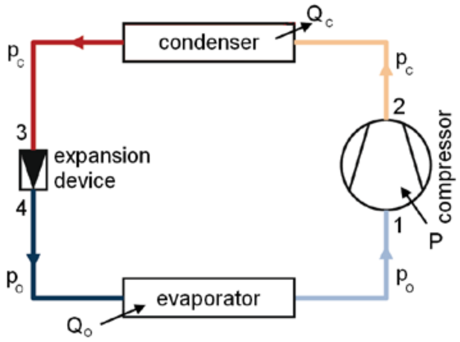

Fig. 1 Schematic of single-stage compression refrigeration system

The basic vapour-compression cycle is considered to be one with isentropic compression, with no superheat of vapour and with no subcooling of liquid (Fig. 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 in Figure3.

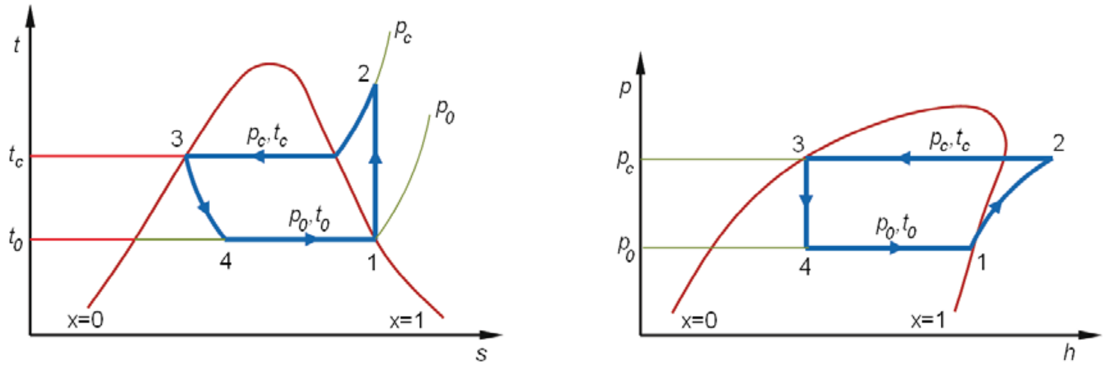

Fig. 2 Single-stage vapour-compression process with a single component or azeotropic refrigerant in *t-s* and *p-h* diagrams

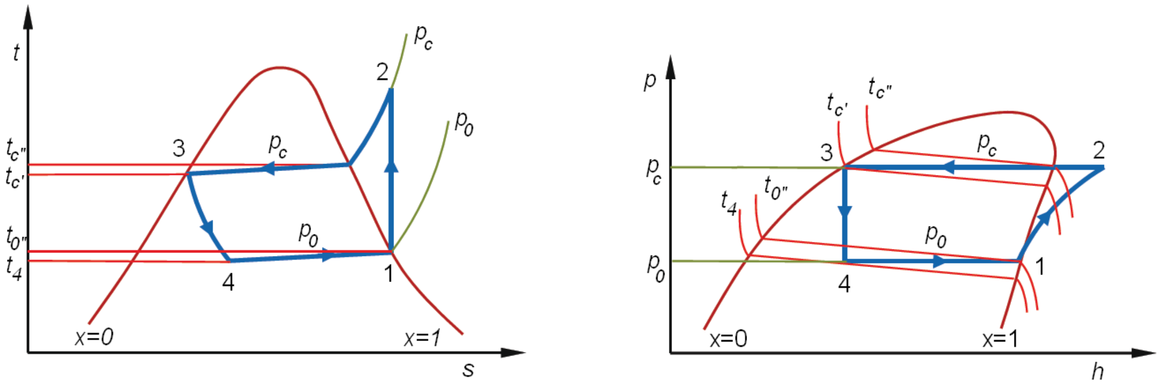

Fig. 3 Single-stage vapour-compression process with zeotropic mixture refrigerant in *t-s* and *p-h* diagrams

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, in kJ/kg, the specific cooling power q_0, in kJ/kg, volumetric refrigerating capacity q_{0v}, in kJ/m^3, the coefficient of performance COP are calculated for above presented processes as follows:

$$w = h_2 - h_1 \tag{1}$$

$$q_0 = h_1 - h_4 = h_1 - h_3 \tag{2}$$

$$q_{0v} = \frac{q_0}{v_1} = q_0 \rho_1 \tag{3}$$

$$COP = \frac{q_0}{w} = \frac{h_1 - h_4}{h_2 - h_1} \tag{4}$$

The refrigerant mass flow rate m, in kg/s, is calculated from the required cooling capacity Q_0 and the specific cooling power q_0:

$$m = \frac{Q_0}{q_0} \tag{5}$$

The power necessary for the isentropic compression P_{is}, in kW, may be calculated as:

$$P_{is} = mw \tag{6}$$

The effective power P_{ef} on the compressor shaft is bigger and is calculated as:

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

where η_{is} is the isentropic efficiency.

Comparison of different refrigerants gives a good overview of achievable cycle performance for a basic referent cycle [28]. Table 3 gives comparison for refrigerants reference cycle with evaporation temperature t_0=–15 °C and condensation temperature t_c=+30 °C.

Cycle data are available from different sources [7, 8], or can be evaluated from suitable software such as REFPROF [23].

The selection of refrigerants in Table 3 has been made in order to present the overview of cycle data for historically used natural inorganic refrigerants such as R717, R744, r764 (which is not in use anymore), CFCs such as R11 or R12 and HCFCs such as R22, and mixture R502. Amongst newly used refrigerants HFCs R32 and R134a are presented as well as zeotropic mixtures of HFCs R404A, R407C, R410A, and azeotropic mixture of HFCs R507. Finally, natural hydrocarbons R600a and R290, together with propylene R1270 are listed.

Table 3. Parameters of –15/30 °C cycle with different refrigerants

Refrigerant	p_0 [bar]	p_c [bar]	p_c/p_0 [–]	q_{0v} [kJ/m^3]	COP [–]	t_2 [°C]	Safety code
0	1	2	3	4	5	6	7
R717	2.362	11.672	4.942	2167.6	4.76	99.08	B2L
R744	22.90	72.10	3.149	7979.0	2.69	69.50	A1
R764	0.807	4.624	5.730	818.8	4.84	96.95	B1
R11	0.202	1.260	6.233	204.2	5.02	42.83	A1
R12	1.823	7.437	4.079	1273.4	4.70	37.81	A1
R22	2.962	11.919	4.024	2096.9	4.66	52.95	A1
R32	4.881	19.275	3.949	3420.0	4.52	68.54	A2L
R134a	1.639	7.702	4.698	1225.7	4.60	36.61	A1
R404A	3.610	14.283	3.956	2099.1	4.16	36.01	A1
R407C	2.632	13.591	5.164	1802.9	3.91	51.43	A1
R410A	4.800	18.893	3.936	3093.0	4.38	51.23	A1
R502	3.437	13.047	3.796	2079.5	4.39	37.07	A1
R507	3.773	14.600	3.870	2163.2	4.18	35.25	A1
R600a	0.891	4.047	4.545	663.8	4.71	32.66	A3
R290	2.916	10.790	3.700	1814.5	4.55	36.60	A3
R1270	3.630	13.050	3.595	2231.1	4.55	41.85	A3

As it can be seen from data presented in Table 3, pressures in the system are temperature-dependent and are different for each particular refrigerant. Evaporation and condensation temperatures are close coupled with corresponding pressure 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 vapour density, viscosity, and thermal conductivity 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, NH_3 systems are not suitable for application of centrifugal compressor due to low molecular mass of ammonia. 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. Good example is R744 with highest volumetric capacity.

Achievable efficiency of the entire process is in a great deal a consequence of the refrigerant used. Effective energy consumption or COP 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 t_2 depend on refrigerant and systems pressures, and it must be limited in order to avoid deterioration of oil properties, or even the oil burnout. Behaviour of some refrigerant during the compression can result is no or low superheating of the vapour at the end of the compression (e.g. R134a with low superheating, or R600a 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 vapour heat content in refrigeration cycles with heat recovery for sanitary water heating during the cooling operation [28].

Pressure drop within heat exchangers and in pipelines connecting refrigeration machine components are essential for system efficiency and are also dependent of refrigerant properties.

4 Replacement of non-ecological refrigerants

After the finding that CFCs, HCFCs and some other human-produced compounds deplete the ozone layer, most countries agreed to the 1997 Kyoto Protocol [16] which calls for the reduction of the emissions of, among others, carbon dioxide (CO_2) and two groups of refrigerants, i.e., hydrofluorocarbons (HFCs) and per-fluorocarbons (PFCs). The production of these refrigerants was regulated even earlier, since 1987 under the Montreal Protocol [36]. Countries, trade associations and companies are increasingly adopting regulations and voluntary programs to minimise these releases and, hence, minimise potential environmental effect while continuing to allow use of these refrigerants.

In response, more environmentally friendly refrigeration systems have been investigated in recent years [3, 4, 11, 22, 26, 35, 40]. Two aspects are of particular concern, namely the use of ecological (environmentally friendly) refrigerants and the energy consumption issue.

Because the thermodynamic and thermo-physical proprieties of refrigerants influences the energetically performances of the system and while exerting an environmental impact, they must be carefully analysed and taken into account during the conception and design of the cooling systems.

The CFC refrigerants of R11 and R12 were substituted by simpler compound refrigerants R123 (HCFC) and R134a (HFC) with a reduced or even zero impact on the depletion of the ozone layer [1, 22]. This alternative is attractive because the substitutes have similar properties (temperature, pressure) with the replaced ones [30] and the changes that occur directly on the existing installations are realised with minimum of investments. Additionally, the substitution of R123 or R11 refrigerants with R22 or R134a, having molecular masses lower by 50%, leads to reduced dimensions of the refrigeration equipment by 25-30% [39].

For other refrigerants, no simple compound fluids, for example for R502, could be replaced with a mixture of R115 (CFC) and R22 (HCFC) or in some cases only with R22, which is a fluid for temporary substitution. However, all these compounds are considered to be greenhouse gases [11]. As a response to these concerns, even more ecological refrigerants, mainly R1234yf [19] and natural refrigerants [20, 25], particularly CO_2 and NH_3, have been proposed as substitutes.

Very limited pure fluids are having suitable properties to provide alternatives to the existing halogenated refrigerants. The mixing of two or more refrigerants provides an opportunity to adjust the properties, which are most desirable. The three categories of mixtures used in refrigeration and air-conditioning applications are azeotropes, near azeotropes (quasi-azeotropes) and zeotropes [12].

Azeotropic mixture of the substances is the one which cannot be separated into its components by simple distillation. The azeotropic mixtures are having boiling points that are lower than either of their constituents. An azeotropic mixture maintains a constant boiling point and acts as a single substance in both liquid and vapour state. Azeotropic refrigerant mixtures are used in low temperature refrigeration applications.

The objective with near azeotropic mixtures is to extend the range of refrigerant alternatives beyond single compounds.

Zeotropic refrigerant mixtures are blends of two or more refrigerants that deviate from perfect mixtures. A zeotropic mixture does not behave like a single substance when it changes state. Instead, it evaporates and condenses between two temperatures (temperature glide). The phase change characteristics of the zeotropic refrigerant mixture (boiling and condensation) are non-isothermal. Zeotropic substances have greater potential for improvements in energy efficiency and capacity modulation. Figure 4 presents the strategy concerning the refrigerants.

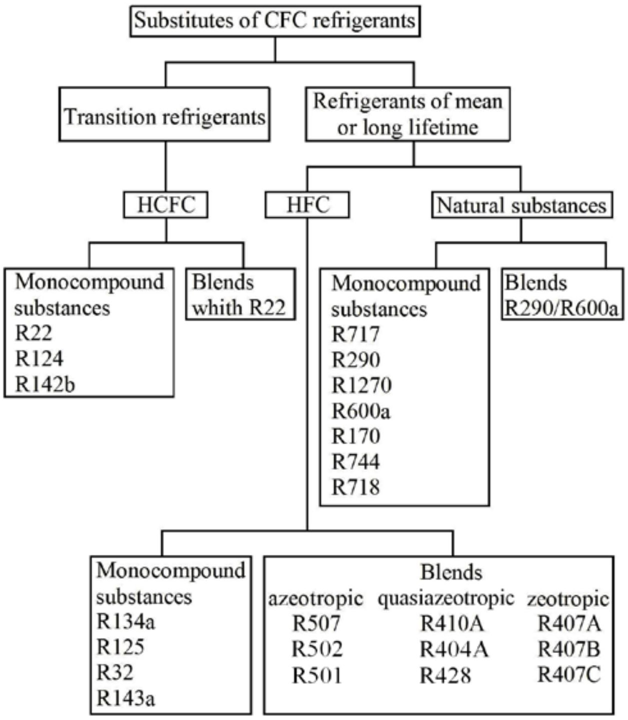

Fig. 4 Strategy concerning the refrigerants

Possible substitutes for R22 are the pure refrigerants R134a, R290, R600a, R152a, the refrigerant mixtures R507, R404A, R410A, R417A, R422A, R424A, R427A, R428A, and the natural refrigerants (R717, R744) [18, 34].

None of these substances can efficiently substitute R22, presenting a specific cooling power or a different saturation pressure, restricted application and specially demands in the installation design.

In new installations, for certain applications, R134a is a good substitute, having a reduced delivering compressor pressure and temperature, but also an inferior specific cooling power being necessary a greater cylinder of the compressor.

The HFC zeotropic blends are considered substitutes for a short period. NH_3 (R717) is the only substitute for R22 having zero GWP. Therefore, between the natural fluids, the NH_3 is the best substitute for R22, having favourable thermodynamic proprieties, a high heat transfer coefficient (3-4 times superior to R22) and a COP similarly good for many applications, especially industrial ones, with great cooling powers [24]. NH_3 is cheap and ecological (ODP=0, GWP=0). However, the NH_3 has high toxicity (class B) and mild flammability. This refrigerant is under the 2L flammability class [6].

Carbon dioxide (R744) is a possible substitute for all refrigerants, being used even by low and high temperatures (cascade system, commercial cooling and air-conditioning). It is accessible, has a low cost and doesn’t impact upon ozone, while his heating potential is negligible. His low critical temperature involves the use in supercritical cycles.

CO_2 has been used in European supermarkets to a significant extent, but it is inherently inefficient in use compared to R22 except when used in cascade with another refrigerant. The working pressure required for the CO_2 system is much higher than that for the R134a system. High working pressure and high isothermal compression coefficient are some issues that should be considered. Subcritical carbon dioxide systems are less efficient than ammonia systems, and trans-critical systems are even less efficient. It will be difficult to justify the use of CO_2 as a general substitute for R22 except in cool and temperate regions.

In Table 4 are presented the principal thermodynamic proprieties of CO_2 and other natural refrigerants [7, 8].

Table 4. Thermodynamic proprieties of principal natural refrigerants

Property	Carbon dioxide (R744)	Ammonia (R717)	Water (R718)	Propane (R290)	Isobutene (R600a)
0	1	2	3	4	5
Molecular mass [g/mol]	44	17	18	44.1	58.1
Critical temperature [°C]	30.98	132.4	374	96.8	135
Critical pressure [bar]	73.75	113.5	221	44.1	36.5
Normal boiling point [°C]	–37.00	–33.5	100	–42.2	–11.7
Freezing point [°C]	–56.57	–77.9	0	–187.1	–159.6
Adiabatic compression index	1.7015	1.400	–	1.140	1.110
Compression ratio (–15/35 °C)	3.147	5.72	–	4.21	–
Volumetric refrigerating volumetric capacity [kJ/m^3]	4922	2156.4	–	450	130

5 Environmental impact analysis of possible substitute for R22

The TEWI index is comparatively analyzed [17] for three types of cooling system operating using above mentioned refrigerants, as follows:

– air-conditioner with a cooling power of 10.55 kW (t_i=25 °C, t_e=35 °C);

– liquid cooler with an air-cooled condenser having a refrigeration power of 11.3 kW ($t_{cold\ water\ in/out}$=7/12 °C, t_e=35 °C);

– refrigerator/freezer with direct and indirect evaporation and an air-cooled condenser for cold storage (refrigeration space with t_i=0 °C and freezing space with t_i=–20 °C and t_e =35°C), with refrigeration power of 11.3 kW.

TEWI is defined as the sum of refrigerant emissions expressed in terms of CO_2 equivalents (direct effect), and CO_2 emissions from the system's energy use over its service life (indirect effect) [31].

For the calculation of the TEWI index, the following equation has been used [2]:

$$\mathrm{TEWI} = nl\mathrm{GWP} + M(1-\alpha_{rec})\mathrm{GWP} + n\beta E \quad (1)$$

where:

$$E = P_t \tau \quad (2)$$

in which: n is the life of the system, in years (10 years); l is the annual leakage rate in the system (3-8%); GWP is the global warming potential of refrigerant for a period of 100 years; M is the refrigerant charge, in kg; α_{rec} is the refrigerant recycling factor (0.70-0.85%); β is the CO_2 emission factor (0.41435 for Romania); E is the annual energy consumption, in kWh; P_t is the compressor power, in kW; τ is the system running time per year, in h (610 h/year).

The performance of refrigeration systems is determined based on energy indicators of these systems. The COP can be calculated as follows:

$$\mathrm{COP} = \frac{E_u}{E_c} \quad (3)$$

where E_u is the cooling usable energy and E_c is the consumed energy by system.

Also, energy efficiency ratio (EES), in British thermal unit per Watt-hours (Btu/(Wh)), is defined by equation:

$$\mathrm{EER} = 3.413\mathrm{COP} \quad (4)$$

where 3.413 is the transformation factor from Watt to Btu/h.

The comparative analysis was performed for a refrigerant vapour superheat of 5 K and an isentropic efficiency of 0.8.

The mass flow rate corresponding to each refrigerant was determined considering the compressor displacement being constant during operation, for the refrigerant and the evaporation temperature change. The consumed electric power in the system was determined as a sum of electric powers consumed by compressor, fans and circulation pumps (for direct evaporation system).

The following values were calculated: refrigerant mass flow rate (m), refrigeration power (Q_0), consumed electric power (P_e) and energy efficiency ratio (EER). These values, corresponding to the above-mentioned operating modes, are summarised in Table 5, from which it is observed that under the same operating conditions of the system, the mass flow rates have different values depending on the refrigerant used. Additionally, it is found that with decreasing evaporation temperature, the mass flow rate for the same refrigerant decreases. This decrease is due to this increase in the specific volume.

For an indirect evaporation system, the total electric power values are reduced compared with the direct evaporation system, although the evaporation temperature decreases. This trend is explained by the fact that the refrigerant mass flow rate decreases more compared to the increase of the specific mechanical work.

The TEWI index variation is summarised in Table 6. The obtained results indicate that possible substitutes for refrigerant R22 can be grouped into three categories:

a) with deviations of approx. 2% (R417A, R407C, R427A, R424A);

b) with deviations of approx. 30-45% (R134a, R410A, R290, R600a, R152a);

c) with deviations of approx. 50-70% (R507, R404A, R428A, R422A).

For substitutes involved in the b) and c) groups, their use is not recommended because the plant will operate with a significant decrease of refrigeration power. The use of such substitutes is possible only if some changes in the components of the installation are made.

6 Conclusions

Scientific research based on mono-compound substances or mixtures, will lead to find adequate substitutes for cooling applications, that will be ecological (ODP=0, reduced GWP), non-flammable and non-poisonous, but also with favourable thermodynamic properties.

Table 5. Characteristics of air-conditioning, refrigeration, and freezing systems

Refri-gerant	Air-conditioning system								Refrigeration system								Freezing system							
	Direct cooling				Liquid cooler				Direct evaporation				Indirect evaporation				Direct evaporation				Indirect evaporation			
	m [kg/s]	Q_0 [kW]	EER [-]	P_t [kW]	m [kg/s]	Q_0 [kW]	EER [-]	P_t [kW]	m [kg/s]	Q_0 [kW]	EER [-]	P_t [kW]	m [kg/s]	Q_0 [kW]	EER [-]	P_t [kW]	m [kg/s]	Q_0 [kW]	EER [-]	P_t [kW]	m [kg/s]	Q_0 [kW]	EER [-]	P_t [kW]
0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
R22	0.061	9.8	8.0	1.71	0.059	9.0	6.6	1.69	0.049	7.3	2.7	3.10	0.044	6.4	2.4	3.11	0.030	4.3	2.5	2.08	0.024	3.3	2.2	1.87
R134a	0.080	12.0	10.0	1.68	0.077	10.9	7.3	1.81	0.033	4.3	3.5	1.61	0.026	3.3	3.1	1.45	0.018	2.2	2.4	1.29	0.015	1.8	2.1	1.21
R290	0.032	9.2	9.8	1.41	0.032	8.8	8.3	1.38	0.025	6.2	3.5	2.15	0.021	5.1	3.1	2.05	0.015	3.5	2.4	1.83	0.012	2.8	2.1	1.71
R600a	0.051	14.4	10.3	1.87	0.049	13.6	8.7	1.89	0.010	2.4	3.7	1.02	0.008	1.9	3.2	0.97	0.005	1.2	2.5	0.86	0.004	1.0	2.2	0.81
R152a	0.050	12.6	10.4	1.89	0.049	11.8	8.5	1.72	0.019	4.3	3.8	1.52	0.016	3.5	3.4	1.43	0.011	2.3	2.7	1.25	0.009	1.9	2.4	1.17
R407C	0.061	10.1	7.8	1.78	0.059	9.3	6.1	1.84	0.056	8.3	2.6	3.62	0.047	6.8	2.2	3.42	0.033	4.6	2.3	2.33	0.027	3.7	2.1	2.17
R404A	0.070	7.8	6.7	1.64	0.068	6.9	4.9	1.74	0.071	6.7	2.2	3.45	0.061	5.6	1.9	3.33	0.042	3.6	1.9	2.21	0.036	2.9	1.7	2.05
R410A	0.050	7.8	7.2	1.56	0.049	7.2	5.7	1.59	0.070	10.1	2.4	4.65	0.059	8.3	2.1	4.40	0.041	5.6	2.3	2.77	0.034	4.6	2.1	2.54
R507	0.071	8.2	7.0	1.65	0.068	7.3	5.1	174	0.075	7.7	3.2	2.77	0.063	6.4	2.1	3.43	0.045	4.3	2.2	2.34	0.037	3.5	1.9	2.15
R417A	0.060	7.7	6.0	1.76	0.058	6.9	4.6	1.82	0.048	5.5	3.2	2.08	0.039	3.9	2.5	1.94	0.026	2.6	2.0	1.69	0.022	2.1	1.8	1.58
R422A	0.100	10.1	7.4	1.84	0.094	8.7	5.2	2.02	0.073	6.4	2.8	2.72	0.063	5.1	2.3	2.55	0.045	3.3	1.7	2.34	0.037	2.7	1.2	2.54
R424A	0.054	9.7	8.1	1.67	0.062	8.8	6.2	1.75	0.041	5.3	3.2	2.02	0.042	5.2	2.5	2.42	0.022	2.5	1.7	1.82	0.020	2.2	1.6	1.73
R427A	0.063	7.9	8.2	1.43	0.051	7.2	6.3	1.48	0.046	6.3	6.0	1.43	0.037	4.9	2.9	2.06	0.024	3.2	4.7	1.06	0.021	2.6	4.2	0.99
R428A	0.101	11.6	9.6	1.68	0.095	10.2	6.6	1.88	0.069	6.9	4.8	1.82	0.066	6.3	2.9	2.53	0.033	3.0	2.0	1.86	0.026	2.2	1.7	1.69

Table 6. TEWI index for analyzed systems

Refrigerant	Air-conditioning system			Refrigeration system			Freezing system		
	Direct cooling	Liquid cooler	Variation [%]	Direct evaporation	Indirect evaporation	Variation [%]	Direct evaporation	Indirect evaporation	Variation [%]
0	1	2	3	4	5	6	7	8	9
R22	6712.14	6593.167	–1.77	10936.271	10758.251	–1.66	7649.71	6867.16	–10.23
R134a	6592.85	6825.870	3.53	6030.105	5418.592	–11.29	4780.63	4504.75	–5.77
R290	3576.38	3493.949	–2.30	5428.709	5184.069	–4.72	4626.12	4315.25	–6.74
R600a	4737.29	4790.571	1.12	2584.504	2460.577	–5.04	2187.29	2046.10	–6.45
R152a	4418.23	4477.189	1.33	3966.865	3745.511	–5.91	3282.83	3055.91	–6.91
R407C	6841.98	6926.828	1.24	12422.319	11607.347	–7.02	8344.42	7731.60	–7.34
R404A	9918.05	9970.406	0.53	17192.790	16081.480	–6.91	11754.72	10760.23	–8.46
R410A	6309.27	6327.940	0.29	16227.552	15116.969	–7.35	10222.35	9354.25	–8.49
R507	10046.62	10096.46	0.49	15943.355	16618.822	4.06	12355.41	11238.14	–9.04
R417A	6746.13	6823.021	1.14	8245.918	7572.605	–8.89	6486.09	6047.81	–6.76
R422A	9598.11	9817.999	2.29	12459.793	11529.942	–8.07	9993.82	10089.46	0.96
R424A	7578.52	7666.723	1.16	8892.173	9950.639	10.64	7434.57	7093.74	–4.58
R427A	6613.22	6650.369	0.56	7765.200	8885.685	12.61	5718.89	5354.30	–6.38
R428A	11365.36	11508.68	1.26	12202.633	13793.359	11.53	9660.66	8755.44	–9.37

A possible solution is the use of inorganic refrigerants (NH_3, CO_2) and hydrocarbon refrigerants (propane, isobutene, ethylene, propylene) for industrial applications, in air-conditioning or food and household cooling. Because the hydrocarbon refrigerant presents a high risk of flammability and explosion, these substances will not be often used as refrigerants comparative with CO_2 or NH_3. On other advantage of these two substances represents the fact that they were used for a long time as refrigerants.

The European Partnership for Energy and Environment considers the HFC refrigerants as the best alternative for the refrigerant CFC and HCFC in most of the applications. The HFC refrigerants allow the use energetically efficient applications, offering significant benefits comparing with the existent alternatives. In average over 80% of the gases with green house effect used in cooling equipments have the indirect emissions as sources. The high energy efficiency resulted by the use of HFC refrigerants balances in a great measure the global warming potential.

The TEWI index values computed for all the three analyzed installation types are lower for indirect evaporation than direct evaporation. Maximal deviation of 20% is obtained for refrigeration system.

The decrease of evaporation temperature by 15 K for refrigeration and freezing systems determine TEWI index decrease by 15-37%. Direct effect of TEWI index represents 33-60% from total value for most of analyzed refrigerants. Minimal values are for R290, R600 and R152. The direct effect of these refrigerants is of 2%.

There are cases with more options for an alternative refrigerant and the problem is to choose the economical variant. The replacement of some refrigerants with other non-polluting influences the operating conditions of the cooling installations, by a rapid degradation of components made from elastomers [7, 24] or plastic materials [10], or it is necessary to replace mineral oils with some other oils adequate to the new refrigerants. Some problems of materials endurance and compatibility can be solved only during many testing, but the estimation of energetically performances and expenses that results by modification of operational characteristics when replacing the refrigerant can be solved with numerical modelling.

A new concept in the implementation of refrigeration systems is now imposed: it must be tightly constructed, with refrigerants having a reduced atmospheric warming potential but with a performance that is as energetically efficient as possible.

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