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Refrigerants: A Review

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Abstract

In the present time refrigeration is a fast growing industry, but refrigeration industry is facing two major problems namely global warming potential (GWP) and ozone depletion potential (ODP) due to refrigerant. Refrigeration and air conditioning are important Social dimension, Economic dimension, Environmental dimension.

Keywords: GWP, ODP, Refrigerants, Ozone

1 INTRODUCTION:

Refrigerants are essential working substances used in refrigeration systems. The performance of refrigeration system largely depends upon the characteristics of the refrigerants. Besides performance issues, there are environmental issues concerning the use of refrigerants. In last few decades, it was discovered that some refrigerants cause ozone layer depletion and global warming, which is a serious hazard to environment. Ozone layer depletion (ODP) and global warming potential (GWP) have become one of the most important global issues. The Montreal protocol (UNEP, 1997) states the phasing out of CFC's and HCFC's as refrigerants that deplete the ozone layer (ODP). The Kyoto protocol (UNFCC, 2011) encouraged promotion of plans for sustainable development and reduction of global warming potential (GWP) including the regulations of HCFCs. Chlorofluorocarbons (CFCs) are the refrigerants which were responsible for both the environmental problems. Ozone layer depletion problem has been almost solved by replacing chlorofluorocarbons (CFCs) by hydro fluorocarbons (HFCs), hydrocarbon (HCs) and some natural refrigerants. However, problem of global warming is still associated with some newer refrigerants. R22 refrigerant was mainly used in air conditioners and deep freezers etc. R22 has ozone depletion potential (ODP) of 0.034. The global warming potential (GWP) of R22 is 1700 and atmospheric life time of 12 years. The replacements of R22 are R407C and 410A having zero ozone depletion potential. Although, R22 has very low ozone depletion potential but high global warming potential. The replacements of R22 are R407C and 410A. The GWP of R407C and R410A are 1600 and 2000 respectively. Since both the refrigerants are blends are unstable and have negligible atmosphere life time. Therefore, search for better alternatives which have zero ozone depletion potential (ODP) and zero or lower global warming potential (GWP) and having low atmospheric life time is still on.

2 THEORY OF REFRIGERANTS:

A refrigerant is a substance or mixture, usually a fluid, used in a heat pump and refrigeration cycle. In most cycles it undergoes phase transitions from a liquid to a gas and back again. Many working fluids have been used for such purposes. Fluorocarbons, especially chlorofluorocarbons, became commonplace in the 20th century, but they are being phased out because of their ozone depletion effects. Other common refrigerants used in various applications are ammonia, sulfur dioxide, and non-halogenated hydrocarbons such as propane.[1]

The ideal refrigerant would have favorable thermodynamic properties, be noncorrosive to mechanical components, and be safe, including free from toxicity and flammability. It would not cause ozone depletion or climate change. Since different fluids have the desired traits in different degree, choice is a matter of trade-off.

The desired thermodynamic properties are a boiling point somewhat below the target temperature, a high heat of vaporization, a moderate density in liquid form, a relatively high density in gaseous form, and a high critical temperature. Since boiling point and gas density are affected by pressure, refrigerants may be made more suitable for a particular application by choice of operating pressures.

3 REFRIGERATION AND AIR CONDITIONING ARE IMPORTANT FOR FOLLOWING POINT OF VIEW:

3.1 Social dimension:

The impact of the refrigeration and air-conditioning sector on the social dimension of sustainable development has numerous facets. The refrigeration sector employs more than 3 million people worldwide particularly in the industrial, commercial and service fields. Refrigeration is indispensable to human life. In the food sector, refrigeration contributes to reducing post-harvest losses and supplying safe, wholesome foods to consumers by enabling perishable foods to be preserved at all stages from production to consumption. In the health sector, refrigeration is employed for vaccine storage; cryo technology is used in surgery, superconductivity in scanners, etc.

3.2 Economic dimension:

From an economic point of view, the role of refrigeration in many industrial processes and in cutting-edge technologies should be stressed. Refrigeration is necessary for the implementation of many current or future energy sources.

Cryogenic processes make it possible to liquefy natural gas which is a more environmentally friendly energy source than other fuels. Many industrial processes could not operate without refrigeration.

3.3 Environmental dimension:

The contribution of refrigeration to the environmental aspect of sustainable development is important as shown by the role of refrigeration technologies in maintaining biodiversity thanks to the cryopreservation of genetic resources (cells, tissues, and organs of plants, animals and microorganisms)in enabling the liquefaction of CO2 for underground storage and in making it possible to envisage the separation of CO2 from fossil fuels in power stations in the future.

3.3.1 Hydroflurocarbon, HFC (R-134a)

HFC R-134a, is used in almost all of the commercial applications as well as for household purposes. The alarming increase in atmospheric concentration ofHFC-134a suggested careful considerations of not over using any single compound for substituting ozone depleting and global warming substances. It must be phased out soon according to Kyoto Protocol due to its high GWP of 1300.Its impact to the environment is far more significant than ozone depletion.

Non-HFC refrigerants developed to replace fluorocarbon refrigerants, the focus is again on natural refrigerants such as ammonia, carbon dioxide.

3.3.2 Carbon dioxide (R-744)

Carbon dioxide was used as a refrigerant before the discovery of CFCs. Carbon dioxide is one of the classic refrigerants that had fallen into almost complete disuse but which is currently making a spectacular comeback, thanks in particular to its very good environmental properties.

Global warming potential of CO2 is 1, it is non-ozone depleting, non-toxic, non-flammable. CO2 operates at a higher pressure than HFC, which means it requires new system design and components. The CO2 refrigerant also has favorable thermo-physical properties such as higher values of density, latent heat, specific heat, thermal conductivity and volumetric cooling capacity, and lower value of viscosity (Ge and Cropper 2009). The automotive industry now is pursuing three primary candidates to replace R-134a in mobile air conditioners, namely carbon dioxide, Hydro-Fluro-Olefin (HFO)-1234yf in direct expansion systems and R-152a in indirect (''secondary loop'') systems employing an intermediate heat transfer fluid. The major objections to the use of carbon dioxide as a refrigerant are its low critical point and its high operating pressure compared with other refrigerants. Nevertheless, carbon dioxide, as a refrigerant, can be used in two distinct ways one as a supercritical refrigerant operating on a trans critical cycle, evaporating in the subcritical region and rejecting heat at temperatures above the critical point in a gas cooler instead of a condenser. A very significant number of developmental efforts are directed towards applications such as automotive air conditioning and heat pumping applications. The high operating pressures of CO2 put different constraints on the design of conventional components such as heat exchangers and compressors and as a low-stage refrigerant in a cascade system using a more conventional refrigerant such as HFC, ammonia or hydrocarbon in the high-temperature stage. Cascade carbon dioxide systems have been in use since 2000 and have developed quickly since 2004. Today more than 130–140 such installations exist in European supermarkets and around 150 are used in agro food processes (freezing) and ice rinks. CO2 is now being adopted as a solution in retail applications (e.g. small commercial applications such as beverage vending machines) and is approaching market application in the field of mobile air conditioning. CO2 is also used as a volatile secondary fluid at low or medium temperatures with pump circulation to avoid trans critical cycles.

3.3.2.1 Benefits of CO2 (R-744) : Carbon dioxide concentration inside the passenger cabin room do not reach critical levels, due to reduced refrigerant charges (\300 g) so it is safe for human beings. It is nontoxic,R-744 is neither flammable nor does any decomposition products harmful to human life and has no health issue in workshops/service places. CO2 itself is cheap and readily available. Carbon dioxide use also is increasing, especially in Europe, for commercial refrigeration both as a refrigerant and in indirect hydrocarbon refrigerants. The potential applications ofCO2 are numerous. One important obstacle to overcome is the cost of the construction of refrigerating equipment suitable for the high pressures involved when CO2 is used (SAE International 2008) (Table 3).CO2 based air conditioning systems are used in industry, but none have been installed in a car, partly owing to the engineering challenges posed by CO2. One of these is the high pressures required in the system, up to 10 times those of fluorocarbon-based systems. Another is the inefficiency of operating trans critically or above a refrigerant's critical temperature (Tc). CO2 has a very low Tc of 31 _C (88 _F).High pressures required by CO2 result in higher ''indirect' 'greenhouse gas emissions (for example, from the tail pipe)than HFO-1234yf. CO2 systems must work harder to make up for the inefficiency of trans critical operation. The cost of redesign of CO2 system is another shortcoming.

Carbon dioxide potential health effects Concentration of CO2 (%) Time Adverse effects17–30 0–60 s Loss of controlled activity, unconsciousness, death[10–15 1–3 min Dizziness, drowsiness, muscle twitching, unconsciousness7–10 1.5–60 min Headache, increased heart rate, shortness of breath, dizziness, sweating rapid breathing7.5 5 min Significant performance decrement6 Several hours Tremors6 \16 min Headache, dyspnea6 1–2 min Hearing and visual disturbances4–5 A few minutes Headache, dizziness, increased blood pressure, uncomfortable dyspnea4–5 4 h Drop in body temperature (1 _C)3 1 h Mild headache, sweating, dyspnea at rest2 Several hours Headache, dyspnea upon mild exertion876 Int. J. Environ. Sci. Technol. (2013) 10:871–880

123Hydro-Fluoro-Olefin (HFO-1234yf)

HFO-1234yf is the leading alternative refrigerant to replace R-134a. It has excellent environmental properties, very low GWP of four, zero ODP, favorable life cycle climate performance (LCCP)(Spatz and Minor 2008), atmospheric chemistry determined and published low toxicity similar to R-134a (Kenji et al.2009). System performance is very similar to R-134a.Excellent COP and Capacity, no glide temperature, the only problem is HFOs are mildly flammable (Shigeo et al. 2009;Kenji et al. 2009). From both internal tests and OEM tests,HFO-1234yf has recently been approved as a class–A2Lrefrigerant by American Society of Heating, Refrigerating and Air Conditioning Engineers (ASHRAE). Despite carbon
dioxide's appeal as a ''natural refrigerant'' and favorable findings in some reported bench and vehicle tests, as a single compound refrigerant, HFO-1234yf offers similar thermo physical properties to R-134a, thus minimizing equipment changes and has met criteria for stability and compatibility. The Society of Automotive Engineers (SAE) validated that HFO-1234yf as safe for use in automotive applications. The critical temperature, critical density and critical pressure were measured by the visual observation of the meniscus disappearance and were determined to be 367.85 K, 478kg/m3, and 3382 kPa, respectively (Tanaka and Higashi2010). After independent review of all toxicology test results, DuPont and Honeywell have concluded that HFO-1234yf is safe to commercialize for use in mobile air-conditioning (MAC). Furthermore, industry risk assessments of various potential exposure scenarios have also concluded

HFO-1234yf is safe for use in MAC applications.HFO-1234yf flammability characteristics are much more favourable than those of hydrocarbon gases. It is far less dangerous than other hydrocarbon refrigerants. HFO-1234yfoffers equivalent or lower toxicity compared to R-134a orR-12 in terms of both human health effects and ecological effects. HFO 1234yf met all key technical customer criteria to be adopted for MAC. Various LCCP evaluations done showing LCCP benefit of HFO-1234yf compared to HFC-134a and CO2 (Spatz and Minor 2008; Minor et al. 2008).HFO-1234yf is not yet a proven entity and despite the fact that it may not be commercialized for at least a year or
two, it is nevertheless promoted by the chemical industry as the alternative to HFC-134a, which the car industry should wait for and switch to. This is effectively blocking the uptake of currently available, safe, environmentally friendly, efficient and low GWP, non-fluorocarbon alternatives such as CO2 mobile air conditioning systems or the commercialization of hydrocarbon MAC systems (SAE International 2008).CO2 manufacturers also argue that, unlike HFO-1234yf,CO2 is proven, safe, natural and sustainable for environmental point of view (Jama-Japia2008; Spatz Mark 2009).In a letter to German OEMs, Greenpeace Germany raises concerns over the chemical's flammability, stating that' 'the claim that HFO-1234yf will be an alternative is not only wrong but also life threatening; the legal consequences not calculable''.

4 THERMODYNAMIC PROPERTIES OF SEVERAL FLUORINATED PROPENE ISOMERS, NAMELY:

R-1225ye(E), R-1225ye (Z), R-1225zc, R-1234ye (E), R-1234yf,R-1234ze (E), R-1234ze (Z), and R-1243zf (the reader can consult ASHRAE (2008) for the naming convention for the fluorinated propene series) (Steven Brown et al. 2010).Results and discussion. There is no ideal refrigerant in the world; so the best approach for presenting evolution and trends of refrigerant Interiors Superior performance in al climates Less effective/efficient in hot climates Safety Safe for use in automotive air conditioning applications with proper mitigation Safe for use in automotive air conditioning applications with proper mitigation Int. J. Environ. Sci. Technol. (2013) 10:871–880 877123is certainly the application approach. The global warming impact of refrigerating plants is about 20 % direct impact due to emissions of fluorinated refrigerants (fluorocarbons)and about 80 % of this impact results from indirect CO2emissions originating in the production of the energy which is used by the plants (generally electricity). Thanks to the Montreal Protocol that was adopted in 1987, 191 countries(as of March 13, 2007) have committed themselves to measures designed to protect the ozone layer. This protocol
calls for the gradual phase-out and total banning of CFCs followed by HCFCs, with a longer time frame for developing countries.

5 CONCLUSIONS:

Refrigerant selection based on a simple approach of 'zero ODP' will have to pay high cost to both global warming and energy efficiency. Use of this single criterion is no longer environmentally acceptable today. The alarming increase in atmospheric concentration of HFC-134a suggested careful considerations of not over using any single compound for substituting ODSs. The use of refrigeration will continue to expand worldwide, especially in developing countries, because it is vital to life. However, the environmental impacts, both on the ozone layer and on global warming are important. The refrigeration sector has already helped to mitigate global warming by applying the Montreal Protocol, also thanks to improved technologies and important international cooperation. The chemical industry is promoting new refrigerant it calls 'Hydro-Fluoro-Olefins' or HFOs. Chemically, HFOs are HFCs, but due to the negative connotations that HFCs have acquired, this new class of chemicals has been marketed under a different name. This is part of a marketing strategy to portray these new HFCs as having a low impact on the climate while glossing over their negative environmental effects. DuPont and Honeywell's advertising point to car manufacturers is that it is a near drop in replacement toHFC-134a and does not require a complete MAC system redesign. CO2 on the other hand, operates at higher pressure so requires a new system with new components and tooling. So selection of proper refrigerant is very important. One can select the particular refrigerant as per the application, the environmental and physiological properties and performance parameters. In this study it is suggested to phase out presently most used refrigerant R-134a considering global warming and to use natural refrigerants such as ammonia, carbon dioxide and hydro carbons in vapour compression refrigeration system for sustainable environment.HFO-1234yf can be used after all its tests are over and found suitable for refrigeration and air conditioning systems. Thermo-electric, magnetic and adsorption refrigeration are all eco-friendly technologies which are receiving more and more attention in the days of increasing energy and environmental problems. Adsorption refrigeration with a short study period can be used only in the condition of near room temperature.

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