Study and Comparative Analysis of Selection of Eco-Friendly Refrigerants and Possible Refrigerants by Mixing Them: A Review

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Abstract— There are many kind refrigerants, which are used to transfer heat from low temperature reservoir to high temperature reservoir by using vapour compression refrigeration system. There are various obstacles faced in working of different refrigerants due to their environmental impact (CFC, HCFC), toxicity (NH3), flammability (HC) and high pressure (CO2) which makes them more hazardous than other working fluids according to safety and environmental issues. Keeping in mind the present scenario of climatic change and demand comfort of modern human age the researcher and inventors must have to be take a steps on all possible ways to protect/prevent or save the earth and its environment in terms of global warming effect. Refrigerants are one of the reasons which contribute the change in temperature by exchanging heat to the environment so our efforts should also be focused on the use of possible natural refrigerants replacements at lesser cost and at low potential effect on environment. As there is large no. of natural refrigerants are available with varying nature of their thermodynamic properties, chemical properties and its stability so it is possible to find better mixture of natural refrigerants by using these refrigerants at different proportion of composition to get the better heat absorbing substance at lesser cost so that the performance of VCRS system can be improved/optimized in terms of COP, other environmental hazards (ODP & GWP) and can be used for future replacement refrigerants.
Keywords: Eco-friendly Refrigerants, VCRS, COP, Replacement Refrigerants, Mixture Refrigerants

I. INTRODUCTION

As there is nothing hidden about the use of refrigerants, its contribution to increase the entropy of universe and its harmful effects producing capacity to the nature and on there living things in terms of global warming and ozone layer depleting potential. The EU (European Union) F-gas regulation has taken effect from January 1, 2015. The regulation implies or applied an HFC (hydro fluoro carbon) phase-down from 2015 to 2030 by means of bans on high GWP refrigerants.

A. *Refrigerants and Selection Criterion:*

The working substance that flows through a refrigerator and is capable of absorbing heat from the source (which is at a lower temperature) and dissipate the same to the sink (which is a higher temperature than the source) either in the form of sensible heat (as in case of air refrigeration) or in the form of latent heat (as in the case of vapor Refrigeration) is called a refrigerant. A working fluid in a compression refrigeration system must satisfy a number of requirements that can be divided into two groups:

1) The refrigerant should not cause any risk of injuries, fire or property damage in case of leakage.
2) The chemical, physical and thermodynamic properties of the refrigerant must suit the system and the working conditions at a reasonable cost.

It is not possible to fulfill all the requirements above at the same time. The most important criterion is chemical stability within the refrigeration system. All the other criteria are meaningless if the refrigerant decomposes or reacts with the materials used in the system. However, the chemical criterion can also be a problem. When a refrigerant is emitted to the atmosphere, it should not be so stable that it can exist indefinitely. The ideal refrigerant would be totally stable in use within the system, but would decompose easily in the atmosphere without the formation of any harmful substances. The thermodynamic and transport properties determine the performance of the refrigeration system. The pressure should be neither too high nor too low. A pressure below atmospheric is undesirable, because air can then be sucked into the system, resulting in problems such as inert gases in the condenser or ice plugs in the expansion valve. The latent heat multiplied by the vapor density gives an estimate of the capacity of a refrigeration system. A refrigerant with a high pressure gives a higher capacity, but a refrigerant with a low critical pressure compared with the pressure in the system leads to a low coefficient of performance (COP). This tradeoff between high capacity and high efficiency must be considered when choosing the refrigerant. Another desired criterion is that the specific heat should be small compared to the latent heat of vaporization, in order to achieve small losses in the expansion device.

Oil is normally present in a refrigeration system, and the interaction between the oil and the refrigerant must be considered. High oil solubility is used in hermetic compressors, but immiscible oils are normally used when the working fluid is ammonia.

In addition to being toxic or explosive and thereby dangerous to people's health, there are other problems associated with refrigerants. Environmental aspects are increasingly being taken into consideration. Refrigerants can thus also be ranked according to their impact on the stratospheric ozone layer (the Ozone Depletion Potential, ODP) or as greenhouse gases (the Global Warming Potential, GWP).

B. *Ozone Depletion Potential (ODP):*

Refrigerants containing chlorine or bromine contribute to the breakdown of the ozone layer the reaction is as follows:

$$Cl + O_3 \rightarrow O_2 + ClO$$

However, the CIO molecule is unstable. It breaks down and reacts with ozone molecules (in accordance with the equation above) repeatedly until a more stable compound is created. The ODP is the ratio of the impact on ozone of a chemical compared with the impact of a similar mass of CFC-

11 (R11). Thus, the ODP of CFC-11 is 1.0 by definition. Other CFCs and HCFCs have ODPs ranging from 0.01 to 1.0. The halons have ODPs ranging up to 10. Carbon tetrachloride has an ODP of 1.2, and methyl chloroform's ODP is 0.11. HFCs have zero ODP because they do not contain chlorine.

C. Global Warming Potential, GWP:

Due to their stability in the atmosphere, CFCs as well as HCFCs and HFCs are often very effective greenhouse gases. The GWP factor is used to reflect their impact on global warming. The GWP is the ratio of the warming caused by a substance to the warming caused by a similar mass of carbon dioxide. Thus, the GWP of CO2 is 1.0 by definition. CFC-12 has a GWP of 8500, while CFC-11 has a GWP of 5000. Various HCFCs and HFCs have GWPs ranging from 93 to 12100. Water, a substitute in numerous end-uses, has a GWP of 0. When using GWP values from different sources, it is important to consider that the values may differ due to different integration times or calculation models.

Another measurement of the impact on global warming is the TEWI value (Total Environmental Warming Impact). This includes not only the direct impact of any release of the refrigerant (GWP), but also the impact during the generation and use of primary energy in the system.

D. Mixture of Refrigerants:

A refrigerant mixture consists of two or more components. The extent to which these dissolve in the compressor oil varies for the different components. In systems where the refrigerant charge is small in comparison to the oil volume, this difference in solubility may lead to problems. For example, if a mixture has a small percentage of one component that dissolves more readily in the oil than the other components, this will influence the physical properties and thereby the system performance.

A refrigerant may be either a pure compound or a mixture (blend) of two or more refrigerants. Examples of pure refrigerants are R12, R22 and R134a. Examples of mixtures are R502, R404A and R407C. A mixture can behave either as a pure refrigerant (azeotropic mixtures), or differently (non-azeotropic, or zeotropic, mixtures).

E. Azeotropic Mixture:

Although it contains two or more refrigerants, at a certain pressure an azeotropic mixture evaporates and condenses at a constant temperature. Because of this, azeotropic mixtures behave like pure refrigerants in all practical aspects.

F. Zeotropic mixtures:

Zeotropic mixtures have a gliding evaporation and condensing temperature. When evaporating, the most volatile component will boil off first and the least volatile component will boil off last. The opposite happens when gas condenses into liquid this results in a gliding evaporation and condensing temperature along the heat transfer surface. In practice, the saturation temperature at the inlet of the evaporator will be lower than at the outlet. In the condenser, the saturation temperature at the inlet will be higher than at the outlet.

II. Research Objectives

The aim of this study is to provide a detailed insight into the characteristics of robust mechanism for preparing a new eco-friendly mixture of refrigerant as a replacement of R-134a even though ODP is zero but GWP is high as about 1300, proposed a new scheme which applies hybrid approach using different highly eco-friendly refrigerant mixture. The scheme is robust against existing methodology using other alternative refrigerant.

III. Literature Review

R. Cabello, E. Torrella and J. Navarro-Esbri [1], have analyzed the performance of a vapour compression refrigeration system using three different working fluids (R134a, R407c and R22). The operating variables are the evaporating pressure, condensing pressure and degree of superheating at the compressor inlet. They analyzed that the power consumption decreases when compression ratio increases with R22 than using the other working fluids.

B.O. Bolaji et al [2] investigated experimentally the performances of three ozone friendly Hydrofluorocarbon (HFC) refrigerants R12, R152a and R134a. R152a refrigerant found as a drop in replacement for R134a in vapour compression system.

B.O. Bolaji [3] discussed the process of selecting environmental-friendly refrigerants that have zero ozone depletion potential and low global warming potential. R23 and R32 from methane derivatives and R152a, R143a, R134a and R125 from ethane derivatives are the emerging refrigerants that are nontoxic, have low flammability and environmental-friendly. These refrigerants need theoretical and experimental analysis to investigate their performance in the system.

James M. Calm [4], has studied the emission and environmental impacts of R11, R123, R-134a due to leakage from centrifugal chiller system. He also investigated the total impact in form of TEWI and change in system efficiency or performance due to charge loss. He also summarized the methods to reduce the refrigerant losses by the system like design modifications, improvement in preventive maintenance techniques, use of purge system for refrigerant vapour recovery, servicing and lubricant changing in system.

Samira Benhadid-Dib and Ahmed Benzaoui [5], have showed that the uses of halogenated refrigerants are harmful for environment and the use of "natural" refrigerants become a possible solution. Here natural refrigerants are used as an alternative solution to replace halogenated refrigerants. The solution to the environmental impacts of refrigerant gases by a gas which contains no chlorine no fluorine and does not reject any CO2 emissions in the atmosphere. The researchers showed that emissions have bad effects on our environment. They also concerned by a contribution to the reduction of greenhouse gases and by the replacement of the polluting cooling fluids (HCFC).

Eric Granryd [6], has enlisted the different hydrocarbons as working medium in refrigeration system. He studied the different safety standards related to these refrigerants. He showed the properties of hydrocarbons (i.e. no ODP and negligible GWP) that make them interesting refrigerating alternatives for energy efficient and environmentally friendly. But safety precautions due to flammability must be seriously taken into account.

Y. S. Lee and C. C. Su [7], have studied the performance of VCRS with isobutene and compare the results with R12 and R22. They used R600a about 150 g and set the refrigeration temperature about 4 °C and -10 °C to maintain the situation of cold storage and freezing applications. They used 0.7 mm internal diameter and 4 to 4.5 m length of capillary tube for cold storage applications and 0.6 mm internal diameter and 4.5 to 5 m length of capillary tube for freezing applications. They observed that the COP lies between 1.2 and 4.5 in cold storage applications and between 0.8 and 3.5 in freezing applications. They also observed that the system with two capillary tubes in parallel performs better in the cold storage and air conditioning applications, whereas that with a single tube is suitable in the freezing applications.

Mao-Gang He, Tie-Chen Li, Zhi-Gang Liu and Ying Zhang [8], have analyzed that the R152a/R125 mixture in the composition of 0.85 mass fraction of R152a has a similar refrigeration performance with the existing refrigerant R12.Experimental research on the main refrigeration performances of domestic refrigerators was conducted, under the different proportions and charge amounts, when R152a/R125 is used to substitute R12 as a drop-in refrigerant. The experimental results indicate that R152a/R125 can be used to replace R12 as a new generation refrigerant of domestic refrigerators, because of its well environmentally acceptable properties and its favorable refrigeration performances. Ki-Jung Park,

Taebeom Seo and Dongsoo Jung [9], have analyzed performances of two pure hydrocarbons and seven mixtures composed of propylene, propane, R152a, and di methylether were measured to substitute for R22 in residential air-conditioners and heat pumps at the evaporation and condensation temperatures of 7 °C and 45 °C, respectively. Test results show that the coefficient of performance of these mixtures is up to 5.7% higher than that of R22. Whereas propane showed 11.5% reduction in capacity, most of the fluids had a similar capacity to that of R22. For these fluids, compressor-discharge temperatures were reduced by 11–17 °C. For all fluids tested, the amount of charge was reduced by up to 55% as compared to R22. Overall, these fluids provide good performances with reasonable energy savings without any environmental problem and thus can be used as long-term alternatives for residential air-conditioning and heat-pumping applications.

A. Baskaran, and P. Koshy Mathews [10], a performance analysis on a vapour compression refrigeration system with various eco-friendly refrigerants of HFC152a, HFC32, HC290, HC1270, HC600a and RE170 were done and their results were compared with R134a as possible alternative replacement. The results showed that the alternative refrigerants investigated in the analysis RE170, R152a and R600a have a slightly higher performance coefficient (COP) than R134a for the condensation temperature of 50^{o}C and evaporating temperatures ranging between -30^{o}C and 10^{o}C.Refrigerant RE170 instead of R134a was found to be a replacement refrigerant among other alternatives.

K. Mani and V. Selladurai [11], have analyzed a vapour compression refrigeration system with the new R290/R600a refrigerant mixture as drop-in replacement was conducted and compared with R12 and R134a. The VCRS was initially designed to operate with R12.The results showed that the refrigerant R134a showed slightly lower COP than R12. The discharge temperature and discharge pressure of the R290/R600a mixture was very close to R12. The R290/R600a (68/32 by wt %) mixture can be considered as a drop-in replacement refrigerant for R12 and R134a.

A.S. Dalkilic and S. Wongwises [12], have studied the performance on a VCRS with refrigerant mixtures based on R134a, R152a, R32, R290, R1270, R600 and R600a was done for various ratios and their results are compared with R12, R22 and R134a as possible alternative replacements. The results showed that all of the alternative refrigerants investigated in the analysis have a slightly lower COP than R12, R22, and R134a for the condensation temperature of 50 °C and evaporating temperatures ranging between −30 °C and 10 °C. Refrigerant blends of R290/R600a (40/60 by wt. %) instead of R12 and R290/R1270 (20/80 by wt. %) instead of R22 are found to be replacement refrigerants among other alternatives.

Vincenzo La Rocca and Giuseppe Panno [13], have analyzed and compared the performance of a vapour compression refrigerating unit operating with R22, and with three new HFC fluids, substituting the former according to Regulation No 2037/2000. Here the plant working efficiency was first tested with R22 and then with three new HFC fluids: R417a, R422a and R422d. It is analyzed that the performance with the new tested fluids did not result as efficient as when using R22.

Vincenzo La Rocca and Giuseppe Panno [14], have analyzed and compared the performance of a vapour compression refrigerating unit operating with R22, and with three new HFC fluids, substituting the former according to Regulation No 2037/2000. Here the plant working efficiency was first tested with R22 and then with three new HFC fluids: R417a, R422a and R422d. It is analyzed that the performance with the new tested fluids did not result as efficient as when using R22.

Minxia Li, Chaobin Dang and Eiji Hihara [15], have investigated that Hfo1234yf has been proposed for mobile air-conditioners due to its low GWP and performance comparable to that of R134a. However, its performance is inferior to that of R410a. This makes it difficult to be applied to residential air-conditioners. In order to apply the low GWP refrigerant to residential air-conditioners, refrigerant mixtures of Hfo1234yf and R32 are proposed, and their flow boiling heat transfer performances were investigated at two mass fractions (80/20 and 50/50 by mass %) in a smooth horizontal tube with an inner diameter of 2 mm. The results showed that the heat transfer coefficients of the mixture with an R32 mass fraction of 20% were 10–30% less than those of pure Hfo1234yf for various mass and heat fluxes. When the mass fraction of R32 increased to 50%, the heat transfer coefficients of the mixture were 10–20% greater than those of pure Hfo1234yf under conditions of large mass and heat fluxes.

IV. CONCLUSIONS

In this paper, after detailed study of survey paper, news report analysis of climatic change and awareness of use of refrigerants on VCRS it is found that chemical refrigerants are creating a serious impact on environment by using the existing CFC, HCFC and R134a refrigerants in terms of global warming, ODP etc. As there is a large no. of natural refrigerants are available and by blending them with certain ratio to create possible eco-friendly refrigerants. The above mentioned harmful existing refrigerants must be replaced with the possible natural alternative refrigerants. The main conclusions of this paper can be summarized as follows.

- Out of the given natural refrigerants it is possible to obtained the new mixture alternate refrigerants by blending these refrigerants.
- By mixing these refrigerants it possible to obtained better refrigerants properties.
- The performance of VCRS may be enhanced by using these alternate refrigerants.

V. FUTURE SCOPE

Keeping in mind the present scenario of climatic change and demand comfort of modern human age the researcher and inventors must have to be take a steps on all possible ways to protect/prevent or save the earth and its environment in terms of global warming effect. Refrigerants are one of the reasons which contribute the change in temperature by exchanging heat to the environment so our efforts should also be focused on the use of possible natural refrigerants replacements at lesser cost and at low potential effect on environment.

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