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TERNARY MIXTURES AS LONG TERM ALTERNATIVE REFRIGERANTS FOR R12 AND R134A – A REVIEW

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ABSTRACT

As per Montreal protocol, R134a has been suggested as an alternate refrigerant to R12. R134a is not miscible in mineral oil. Alternatively synthetic oils are recommended. As R134a can cause high global warming, its usage needs to be controlled as per the Kyoto protocol. On the other hand Hydro Carbon refrigerants do have flammability issues and safety standards that limit the usage of pure HC refrigerants in domestic appliances. Because of the above factors, safe conversion of existing R134a refrigerators with environmentally friendly refrigerants is of utmost importance in Refrigeration and Air-conditioning sector. This paper presents a review of present status of alternative refrigerants.

KEYWORDS: Refrigerants, Global Warming, Ternary Mixture, Propane, Isobutane, R134a

INTRODUCTION

A refrigerant is a substance or mixture, undergoes phase transitions from a liquid to a gas and back again. Many working fluids have been used for such purposes. Fluorocarbons, especially CFCs, 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.

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.

A chlorofluorocarbon (CFC) is an organic compound that contains only carbon, chlorine, and fluorine, produced as a volatile derivative of methane, ethane, and propane. They are also commonly known by the DuPont brand name Freon. The most common representative is dichlorodifluoromethane (R-12 or Freon-12). Many CFCs have been widely used as refrigerants, propellants (in aerosol applications), and solvents. Because CFCs contribute to ozone depletion in the upper atmosphere, the manufacture of such compounds has been phased out under the Montreal Protocol, and they are being replaced with other products such as hydrofluorocarbons (HFCs).

As per Montreal protocol, R134a has been suggested as an alternate refrigerant to R12. R134a is not miscible in mineral oil. Alternatively synthetic oils are recommended. As R134a can cause high global warming, its usage needs to be controlled as per the Kyoto protocol. On the other hand Hydro Carbon refrigerants do have flammability issues and safety standards that limit the usage of pure HC refrigerants in domestic appliances.

R. S. Agarwal [1], have conducted experiments to evaluate the substitute for R12 with the HC mixture of R290/R600a (50%/50%) and R134a/R600a. Thermodynamic properties of these mixtures needed for the analysis have been computed using REFPROP. The HC blend consumes 12% less energy than R134a/R600a.

M. A. Hammad [2] has experimentally investigated the performance parameters of a domestic refrigerator with four ratios of R290, R600 and R600a are used as possible alternative replacements to the R12. The proposed alternative refrigerants have the advantage of being locally available, economical and of an environmentally friendly nature. An unmodified R12 domestic refrigerator was charged and tested with each of the four hydrocarbon mixtures that consist of 100% R290, 75% R290/19.1%R600/5.9%R600a, 50%R290/38.3%R600/11.7%R600a and 25%R290/57.5%R600/17.5%R600a. The investigated parameters are the refrigeration effect, energy consumption of the power and. The results show that the hydrocarbon mixture with 50%r290/–38.3% butane–11.7% isobutane is the most suitable alternative refrigerant which has COP 2.7% higher than the R12.

Bilal A. Akash[3] has conducted performance tests on the performance of liquefied petroleum gas (LPG) as a possible substitute for R12 in domestic refrigerators. LPG is obtained from the local market with the composition of about 30% propane, 55% n-butane and 15% isobutane by mass fraction. The refrigerator which is initially designed to work with R12 is used to conduct the experiment for LPG. Various mass charges of 50, 80 and 100 g of LPG were used during the experimentation. The results show that LPG compares very well to R12. The COP was higher for all mass charges at evaporator temperatures lower than -15^{0}C. Overall, it was found that a mass charge of 80 g of LPG had the best results when used in this refrigerator. The condenser was kept at a constant temperature of 47^{0}C. Cooling capacities were obtained and they were in the order of about three to fourfold higher for LPG than those for R12

S. Joseph Sekhar [4], has developed drop in substitutes for R12 with R134a and HC blends. HC refrigerants do have inherent problems in respect of flammability. R134a is neither flammable nor toxic. But HFCs are not compatible with mineral oil and the oil change is a major issue while retrofitting. The experimental analysis has been carried out in a 165 liter R12 domestic refrigerator retrofitted with the ternary mixture of 91%R134a/4.032%R290/4.968%R600a without changing the mineral oil. Its performance, as well as energy consumption, is compared with the conventional one. It has been found that the new mixture could reduce the energy consumption by 4 to 11% and improve the actual COP by 3 to 8% from that of R12.

The author carried out the experiments with the same mixture in a walk in cooler, operating with an open type compressor with mineral oil as lubricant. Tests were conducted with the alternative mixture as well as with R12 for the realistic comparison. It is observed that the mixture has better performance, resulting in 28.6% less energy consumption than R12. The enhancement in COP was 6 to 10%. With the same mixture tests were extended to low temperature and medium temperature systems of deep freezer and visi cooler respectively. The oil miscibility of the new mixture with mineral oil was also studied and found to be good. The R134a/HC mixture that contains 9% HC blend (by weight) has better performance resulting in 10 to 30% and 5 to 15% less energy consumption than R12 in medium and low temperature system, respectively.

Gurumurthy Vijayan Iyer et. al. (2006), has experimentally investigated drop in replacement for R12 refrigerant with the ternary mixture of R290/R600/R600a with the mass fraction of 50%/38.3%/11.7%. To conduct experiments on ternary mixture same unmodified R12 refrigerator were used. With similar operating conditions ternary mixture shows an improvement in COP by 2.7%. After 5000 hours of continuous running of the refrigerator with the ternary mixture no problems have been encountered with the condenser, compressor and evaporator in addition, no degradation of lubricating oil could be detected.

Rafael Quintero Ricardo [5], has developed a drop in replacement for R12 with zeotropic mixture of R290/R600/R600a with the mass fraction of 65%/25%/10%. The author carried out the theoretical analysis with the REFPROP software; experiments were conducted on 220 liters capacity, single evaporator domestic refrigerator. The energy consumption of the alternative refrigerant was 9.6% greater than R12 and ice making time was increased by 10% than R12.

Man-Hoe Kim [6] has assessed the performance of a hydrocarbon refrigerant, R600a, as an alternative to R12 in a 215 liters domestic refrigerator. A theoretical analysis was performed with REFPROP and tests were conducted with R600a. All the tests were performed in a temperature controlled room at 30±1°C. The test results showed that the energy efficiencies and the cooling speeds with R600a were improved by 1 to 11% and 3 to 10%, respectively, compared to R12.

T.S. Ravikumar [7] reported that R134a is used in place of R12. However, to avoid synthetic oil and to use the conventional mineral oil as lubricant, R134a is mixed with the commercially available hydrocarbon blend, (45.2% R290 and 56.8% R600a) in the proportion of 91% and 9%, respectively by mass. The mass of hydrocarbons used is well below the safe limit of 150 grams. This new mixture R134a/R600a/R290 is tested in the air-conditioning system of a passenger car 'on road' in the true running conditions and compared with the results that has been obtained with R12. The cool down performance was better than R12 under varying speed and varying ambient conditions, system performance under severe accelerating conditions and bumper-to-bumper traffic conditions. The test results show that the new blend can be a promising substitute for the existing R12 systems and overcome the issue of change of lubricating oil.

It is clear from the above paragraphs that various authors have tried for a suitable alternative for R12 from open literature it is quite evident that identifying a suitable alternative for R12 attempted from various quarters at different angles. Even though R134a has been identified as a substitute in the context of retrofitting R12 systems issues of change of lubricating oil and lower COP values for the same cooling capacity. Also global warming is quite serious, as per the Kyoto protocol there is a necessity to decrease the greenhouse gases including R134a. Pure hydrocarbons are not drop in replacements for R12 refrigerators due to mismatch in saturation characteristics. A zeotropic mixture of hydrocarbons of 50%R290/ 50%R600a was identified as drop in replacement for R12 with little modification of changing the length of capillary. The drawback of the hydrocarbon mixture is flammable. Thus it is needless to say that R12 phase out demands a better alternative refrigerant.

The reduction in chlorofluorocarbon (CFC) and hydro chlorofluorocarbon (HCFC) production and the scheduled phase out of these ozone depleting refrigerants require the development and determination of environmentally safe refrigerants for use in refrigerators, heat pumps, water chillers and air conditioners.

Suresh Bhakta Shrestha [8] has studied the performance of R290 and R600a mixtures in VCR systems for heating, and simultaneous heating and cooling applications in comparison with R134a, R114 and R236ea. R290 offers large pressure difference usually more than 18 bar, an allowable limit for reciprocating compressors. It offers discharge temperature comparable with that of R134a. R290 is not suitable for high temperature heat pumps due to its lower critical temperature. R290 is not suitable to retrofit into systems designed for R134a and R236ea. Pure R600a is also not suitable for retrofit condition due to its high pressure ratios. At 50%R290 and 50%R600a has favorable pressure chrematistics can be used as drop in replacement for R134a.

Somchai Wongwises [9] has conducted experiments to substitute R134a in a domestic refrigerator with hydrocarbon mixtures of R290, R600 and R600a. A 239 liter capacity refrigerator initially designed to work with R134a were chosen in the experiment. The pressure and temperature at the entry and exit of the compressor, compressor power readings were taken for the analysis. The alternative refrigerant mixtures used are divided into three groups: the mixture of three hydrocarbons, the mixture of two hydrocarbons and R134a and the mixture of two hydrocarbons. The experiments are conducted with the refrigerants under the same no load condition at a surrounding temperature of 25^0C. The results show that 60%R290/40%R600 is the most suitable alternative refrigerant to R134a. Somchai Wongwises has experimentally investigated the performance of hydrocarbon mixtures to replace R134a in automotive air conditioners. The hydrocarbons investigated are R290, R600 and R600a. The air conditioner, with a capacity of 3.5 kW driven by a Diesel engine, is charged and tested with four different mass fractions of HC mixtures. The experiments are conducted at the same ambient conditions. The temperature and pressure of the refrigerant at every major position in the refrigerant loop, humidity of air and refrigerant mass flow rate, engine speed and torque are recorded and analyzed. The parameters investigated are the refrigeration capacity, the compressor power and the COP. The results show that 50%R290/40%R600/10%R600a is the better substitute for R134a among the considered HC mixtures.

M. Fatouh [10], have studied the possibility of using hydrocarbon mixtures as working fluids to replace R134a in domestic refrigerators has been evaluated through a simulation analysis. The performance parameters COP, cooling capacity, compressor power, discharge temperature, pressure ratio and mass flow rate of the refrigerant were studied over a wide range of evaporator and condenser temperatures −35 to -10^0C and 40 to 60^0C respectively for various working fluids such as R134a, propane, commercial butane and R290/R600a/R600 mixtures with various propane mass fractions.

The results showed that pure propane could not be used as a drop in replacement for R134a due to mismatch in saturation characteristics, leads high operating pressures and low COP. R600 yields many desirable characteristics but requires a compressor change. The COP of the domestic refrigerator using a ternary hydrocarbon mixture with propane mass fractions from 0.5 to 0.7 is higher than that of R134a. Comparison among the selected working fluids confirmed that the average refrigerant mass flow rate of the R290/R600 mixture is 50% lower than that of R134a. Also, the results indicated that R134a and the R290/R600 mixture with 60% R290 mass fraction have approximately the same values of saturation pressure, compressor discharge temperature, condenser heat load, input power and cooling capacity. However, the pressure ratio of the hydrocarbon mixture with 60% propane is lower than that of R134a by about 11.1%. Finally, the reported results confirmed that the R290/R600a/R600 mixture with 60% propane is the best drop in replacement for R134a. M. Fatouh investigated a drop in substitute for R134a in a single evaporator domestic refrigerator with a total volume of 0.283 m^3 with Liquefied petroleum gas (LPG) of 60% propane and 40% commercial butane. To optimize the performance of the refrigerator tests were conducted with different capillary lengths and different charges of R134a and

LPG. Experimental results of the refrigerator using LPG of 60g and capillary tube length of 5 m were compared with those using R134a of 100g and capillary tube length of 4 m. Pull-down time, pressure ratio and power consumption of LPG refrigerator were lower than those of R134a by about 7.6%, 5.5% and 4.3%, respectively. Also, actual COP of LPG refrigerator was higher than that of R134a by about 7.6%. Lower on-time ratio and energy consumption of LPG refrigerator by nearly 14.3% and 10.8%, respectively, compared to those of R134a refrigerator were achieved. In conclusion, the proposed LPG is drop in replacement for R134a, to have the better performance, optimization of capillary length and refrigerant charge was needed.

M. Mohanraj [11], have studied experimentally the drop in substitute for R134a with the environment friendly, energy efficient hydrocarbon (HC) mixture consists of 45% HC290 and 55% R600a at various mass charges of 50g, 70g and 90g in domestic refrigerator. The experiments were carried out in 165 liters domestic refrigerator using R134a with

POE oil as lubricant. The performance characteristics such as COP, energy consumption, pull down time and compressor discharge temperature of HC mixture are measured and compared with R134a. During the experimentation the ambient temperature is maintained at 30 ± 2^0C. The results showed that the higher COP of 8.82%, 11.42% and 12.67% respectively for -15^OC evaporator temperature and 45^OC condensing temperature.

The discharge temperatures of HC mixtures are found to be lower than R134a by 13.76%, 6.42% and 3.66% for 50g, 70g and 90g respectively. The power consumption of HC mixture at 50g and 70g are lower by 10.2% and 5.1% respectively and 90g has higher power consumption by 1.01%. The percentage reduction in pull down time is 18.36%, 21.76% and 28.57% for 50, 70 and 90g mass charges respectively compared to R134a. The HC mixture because of its high energy efficiency will also reduce the indirect global warming. In conclusion HC mixture of 70g is found to be an attractive alternative to R134a in 165 liters domestic refrigerator. Apart from the flammability the hydrocarbon mixtures are found to be best long term alternative option for R134a.

M. A. Sattar [12], investigated and compared the performance of the refrigerator using R600a, R600 and a ternary mixture of mixture of R290/R600a/R600 as refrigerants with the R134a. The effects of evaporator and condenser temperatures on COP, refrigerating effect, compressor power and heat rejection ratio were investigated. The results show that the compressor consumed 3% and 2% less energy than that of R134a at 28°C ambient temperature when R600a and R600 was used as refrigerants respectively. The energy consumption and COP of hydrocarbons and their blends shows that hydrocarbon can be used as refrigerant in the domestic refrigerator. The COP and other result obtained from the experiments show a positive indication of using HC as refrigerants in domestic refrigerator.

K.Mani [13], has conducted tests on a VCR system with HC mixture of R290/R600a as drop in replacement for R12 and R134a. Base line tests were carried out with R12 and R134a. Experimental results showed that the refrigerant R290/R600a had 19.9% to 50.1% higher cooling capacity than R12 and 28.6% to 87.2% than R134a.The refrigerant R134a showed slightly lower cooling capacity than R12. The mixture R290/R600a consumed 6.8% to 17.4% more energy than R12. The refrigerant R12 consumed slightly more energy than R134a at higher evaporating temperatures. The COP of R290/R600a mixture increases from 3.9% to 25.1% than R12 at lower evaporating temperatures and 11.8% to 17.6% at higher evaporating temperatures. The refrigerant R134a showed slightly lower coefficient of performance than R12. The discharge temperature and discharge pressure of the R290/R600a mixture was very close to R12. The R290/R600a with the mass fraction of 68%/32% has considered as a drop in replacement refrigerant for R12 and R134a.

M. Mohanraj [14], experimental investigation was carried out to investigate a drop in replacement for R134a with the binary mixture of 45.2%R290/54.8%R600a in a 200 liter single evaporator domestic refrigerator. Tests were carried out at different ambient temperatures (24, 28, 32, 38 and 43^0C), cycle ON/OFF tests were carried out at 32^0C ambient temperature. The results showed that the HC mixture has lower energy consumption; pull down time and ON time ratio by about 11.1%, 11.6% and 13.2% respectively, with 3.25 to 3.6% higher COP. The discharge temperature of HC mixture was found to be 8.5 to 13.4 K lower than that of R134a. The overall performance has proved that the above hydrocarbon refrigerant mixture could be the best long term alternative to R134a.

Ching-Song Jwo[15] have investigated the substitute for R134a with the zeotropic mixture of 50%R290/50%R600a. The experiments used a 440 liters capacity domestic refrigerator as test facility, which originally works with 150g R134a refrigerant. Tests were conducted by varied mass of hydrocarbon mixture. The results show that refrigerating effect is improved by using 50%R290/50%R600a. Moreover, the total consumed energy is saved 4.4% and applied mass of refrigerant is reduced 40%.

CONCLUSIONS

It is clear from the above paragraphs that various authors have tried for a suitable alternative for R134a. It has been observed that the energy consumption of R12 appliances tend to increase while they are retrofitted with R134a. These days, the concern for the greenhouse warming has never been greater, Thus, in 1997 the Kyoto protocol was agreed by many nations calling for the reduction in emissions of greenhouse gases including HFCs (R134a). Pure hydrocarbons are not drop in replacements for R134a refrigerators due to mismatch in saturation characteristics. Zeotropic mixture of 50%R290/50%R600a can be used as drop in replacements for R134a refrigerator by adjusting the capillary length and optimizing the refrigerant charge, but the hydrocarbons have the flammability factor.

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