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S. Devotta
National Chemical Laboratory; India

S. Gopichand
National Chemical Laboratory; India

COMPARATIVE ASSESSMENT OF SOME FLAMMABLE REFRIGERANTS AS ALTERNATIVES TO CFC12*

S. Devotta** and S. Gopichand
Chemical Engineering Division
National Chemical Laboratory
Pune 411 008, India

* NCL Communication No: 5380
** Author to whom all correspondence should be addressed.

ABSTRACT

The theoretical performance of some flammable refrigerants, namely, propane (HC290), butane (HC600), isobutane (HC600a), cyclopropane (HCC270), HFC152a and HCFC142b have been comparatively assessed as alternatives to CFC12. This has been done for a range of evaporating temperatures by using some standard refrigeration parameters like pressure ratio, specific compressor displacement, theoretical Rankine coefficient of performance, shaft per ton of refrigeration. Cyclopropane (HC270), which would require smaller compressors than CFC12 and may offer superior energy performance, appears to be a potential candidate. If a suitable weighting is to be given for non-flammability and experience, then HFC152a is perhaps a better alternative.

The paper also discusses the need for the assessment of flammable fluids and the implications of using these fluids as alternatives to CFC12.

NOMENCLATURE

$(COP)_{RR}$	Rankine coefficient of performance, dimensionless
P	pressure, MPa
(PR)	pressure ratio, dimensionless
Q_{EV}	specific refrigerating effect, kJ kg^{-1}
(SCD)	specific compressor displacement, m^3 MJ^{-1}
T	temperature, ^oC or K
W	shaft power per ton of refrigeration, kW $(TR)^{-1}$

Subscript

C	critical
CO	condensing/condenser
EV	evaporating/evaporator

INTRODUCTION

There is a growing evidence that the stratospheric ozone layer is depleting faster than originally assessed. Therefore, there is an impending need to phase out CFCs earlier than that prescribed by the Montreal Protocol. CFC12 is used extensively with reciprocating compressors, e.g. in domestic appliances like refrigerators, water coolers, freezers etc. using small hermetic types, in medium size air-conditioners using semi-hermetic and open types, and in automobiles with open types. In some large size centrifugal chillers CFC12 is used to some extent. HFC134a is considered to be the primary candidate to replace CFC12. However, there are other concerns such as global warming, energy efficiency, cost etc. Some of the countries have volunteered to phase out CFCs earlier even before any revision of the Montreal Protocol schedule. The total process of identification of a new refrigerant, synthesizing and manufacturing initially in required quantities for performance trials, developing the required compatible materials, testing for long term toxicological effects, and finally the hardware optimisation would require at least about ten years. This is also compounded by the risk factor that the exercise may fail ultimately if one of the steps in the development processes is not successful. Therefore, many developed countries do not have adequate time to consider any new alternatives.

Developing Countries Some of the developing countries are following the developed countries because either they are totally dependent on import of refrigerants and related hardware or their main market is export oriented (e.g.) Brazil, Mexico, Singapore. There is another category in which the countries are either self reliant both in the manufacture of refrigerants and related hardware or not very much export oriented e.g. India and China. Most developing countries are also short of funds to initiate the activities on the CFC substitutes. There is also a concern that the substitutes like HFC134a, the technology of which is significantly expensive, may not be really a long term substitute from the GWP point of view. Some of these alternatives could be included in future revisions of Montreal Protocol or in a possible Climate Change Convention. Country like India cannot afford double changes, one with a short term substitute and another with a long term substitute in the horizon. Most of the developing countries have not taken any cognisance of transitional fluids like HCFCs for this reason. The developing countries have additional period of ten years at their disposal. Therefore, one has to look at various fluids with an open mind and assess the merits and demerits of the possible alternatives before making a final choice.

ALTERNATIVES TO CFC12

Desirable Characteristics Any alternative to CFC12 has to possess the desirable characteristics of refrigerants, viz., thermodynamic efficiency, non-toxicity, non-flammability, thermal and chemical stability, compatibility, and low cost. In addition to the above, there are other environmental acceptability factors such as negligible or preferably zero Ozone Depletion Potential (ODP), relatively low Global Warming Potential (GWP). Therefore, any substitute should not only perform efficiently with reliability as long as it is within the refrigeration system but also be harmless and benign to creatures as well as to the environment, should it leak out of the system. These constraints obviously limit the boundary within which thermodynamic screening could be performed. Most of the searches for alternatives had excluded flammable fluids, in spite of their zero ODPs and low GWPs, with the contention that flammable fluids are not safe to be used as refrigerants. Global environmental concern can have an over-riding weighting over localised risks. Therefore, among the attributes which have to be necessarily satisfied one could relax the rigidity on flammability limits and attempt an objective assessment of some of the flammable fluids.

Flammable Fluids as Alternatives A flammable fluid does not pose as much risk as toxic fluids. Manufacture, storage, handling and transport of toxic fluids all pose a greater threat to the lives than flammable fluids. HCFC123, which has AEL of 10 ppm, is considered to be near drop-in substitute for CFC11, which has a TLV of 1000 ppm. The standards to use HCFC123 in centrifugal chillers were revised accordingly. Use of flammable fluids in air-conditioning and refrigeration systems is not something new. The general expert opinion is that in the past flammable refrigerants including propane (HC290), isobutane (HC600a) and butane mixtures (HC600 and HC600a) were used even in domestic refrigerating equipment. Therefore, the safety requirements might not be prohibitive and can be managed with the current technologies (Kuijpers, 1989). Ammonia is still used in absorption refrigeration systems. It should be recognised that the use of flammable fluids in a domestic appliances does increase the risk. Therefore, all possible means of minimising the risk must be attempted through appropriate design and operation of the system. Grob (1989) and Lemoff (1989) have dealt in detail the implications of using flammable fluids in refrigerator freezers. Lemoff (1989) has shown, using the U.S. statistics on the breakdown of kitchen fires, that refrigerators in general form a small percentage of about 1 per cent as the heat source.

Flammability If flammable fluids are used the risk would obviously increase depending on the flammability limits. The flammability of a fluid is gauged by the lower explosion limit (LEL) and upper explosion limit (UEL). LEL and UEL are the maximum and minimum concentration of a gas in air (expressed in volume %) which when ignited would lead to flame propagation throughout the vapour-air mixture with or without the continued application of the source of ignition. The difference between LEL and UEL is known as the flammability limits. LEL is considered to be a more significant factor. The higher the value of LEL the easier it is to avoid the formation of a flammable mixture, in case of any leakage from the system (Grob, 1989). The LEL and UEL values for the fluids, taken from Bretheric (1979), are presented in Table 1.

Safety Aspects The use of flammable fluids would pose many challenges and solutions may have to be borrowed from other areas. A lot of details on safety aspects of could be derived from the experience of aerosol industries which had successfully switched over to LPG as the propellant although they also initially experienced some problems. The experience of handling and storage of propane and LPG for domestic uses has given adequate experience. About 150 gms of a flammable refrigerant in a domestic refrigerator would probably pose less risk than about 10 kg of LPG in a cylinder in a kitchen. There are many ways by which the various concerns on the use of flammable fluids may be addressed and mitigated. i) There are possibilities of reducing the charge in a refrigeration system by some suitable changes in the heat exchangers and piping lay out. Such an approach in a refrigerator would substantially reduce the risk of possible explosions. ii) Improved design and materials should be used to minimise the chances of leaks (e.g.) thicker wall tubes and better joints. iii) Any leakage from the system should be quickly dispersed or diluted so that fluid-air ratio does not reach the flammable limits. iv) An alarm system could be provided to warn if there is any gas leak either by suitably odorising the gas as in the case of LPG or by providing a gas detector alarm. Special gas detector and alarm system have to be developed as most of the detectors currently used are halogen detectors and also the alarm should not be a source for ignition. v) Any source of ignition with in an appliance like refrigerator, should be avoided (e.g) bad insulation in a hermetic compressors can lead to sparks. Any electrical switch within the refrigerator should be avoided. This is particularly important if the leakage is within the refrigerator.

COMPARATIVE ASSESSMENT

The aim of the study is to comparatively assess some compounds which are flammable, as alternatives to CFC12, using some standard refrigeration performance parameters as the scale. For this assessment, propane (HC290), butane (HC600), isobutane (HC600a), cyclopropane (HCC270), HFC152a and HCFC142b have been chosen based on the boiling point as the primary screening factor.

The operation of a refrigeration system approximates to the Rankine cycle. The useful assessment parameters are pressure ratio

(PR), specific compressor displacement (SCD), ideal Rankine coefficient of performance $(COP)_{RR}$, shaft power per unit of refrigeration W. The procedure for the calculation of these parameters from saturation property data of a fluid has been detailed in an earlier communication (Devotta and Gopichand, 1992). The thermodynamic data, except for HCC270, were taken from ASHRAE Handbook 1988 Fundamentals. Properties for HCC270 were generated by a specially developed programme by Devotta and Pendyala (1992) using some basic properties like normal boiling point, critical properties and structural details as the input parameters. The programme was tested for HFC134a to predict the required derived data with normal boiling point as the only input parameter along with the structural data. These results were compared with those derived from the data of Mclinden et al. (1989). The agreement of all the derived data was within 5 per cent. The prediction improved marginally with critical temperature and critical pressure as additional input parameters with the error reducing to 4 per cent. There is some degree of uncertainty in the reliability of the derived results, yet this approach broadens the scope for long term substitutes. As and when more reliable data become available, these calculations can be further refined. The details of this method and the error analysis will be presented in an independent paper.

For a tropical country like India, the usual design conditions for low temperature applications like refrigerators and freezers are $T_{CO} = 55^{o}C$ and $T_{EV} = -23^{o}C$. The high condensing temperature is used as the cooling is done by convective heat transfer with air. Some comparative performance data for the conditions of $T_{CO} = 50^{o}C$ and $T_{EV} = -15^{o}C$, conditions closer to tropical, are presented in Table 1 and in Figures 1 - 4. These results could still be a guideline for systems operating with low condensing temperature operations like industrial refrigeration and air-conditioning.

RESULTS AND DISCUSSION

The ODPs of all the fluids considered are zero except that of HCFC142b which has an ODP of 0.06. HCFC142b can only be considered as a transitional fluid. Also, all of them have much lower GWPs than CFC12.

From operational point of view, the evaporating pressures for HC600a, HCFC142b and HC600 are below atmospheric which means that the evaporator for these fluids will be working under vacuum. This is a serious problem as this can lead to air ingression into the system. For fluids with very low LEL, there is a possibility of forming a flammable mixture within the hermetic system. Therefore, a good care must be exercised to ensure that air does nor get ingressed into the system. The condensing pressure of HC290 is considerably high compared to CFC12. This implies that the system will be operating at a relatively higher pressure than the normal conditions and the tubings have to be thicker. This is particularly important for flammable fluids to avoid rupture of the tubes leading to leakage of flammable gases leading to a hazardous situation. From flammability view point, all the hydrocarbons have relatively high flammabilities.

Figure 1 is a plot of pressure ratio (PR) against evaporating temperature T_{EV} for a condensing temperature of $50^{o}C$. For identical conditions, compared to that for CFC12, the pressure ratios for HC600 are much higher but the values for HCC270 are very close. Typically for $T_{EV} = 50^{o}C$, $T_{EV} = -15^{o}C$, HC600 requires the highest (PR) of 8.82 while HC290 the least value of 5.89. HCC270 requires a (PR) of 6.51 which is very close to 6.66 for CFC12. This means that the volumetric efficiency of the compressor operating with HC600 will be the least while with HC290 it is likely to be the best.

The variation of (SCD) with evaporating temperature T_{EV} is shown in Figure 2. For the typical condition, HCC270 requires the least

(SCD) of 0.679 m3 MJ-1 and HC600 requires the highest displacement of 2.586 m^3 MJ $^{-1}$. The specific compressor displacement for HFC152a is the closest to CFC12. While HCFC142b, HC600 and HCC600a all require fairly larger compressor sizes, HC290 and HCC270 require relatively small compressors than CFC12 and therefore, may not be suitable for domestic refrigerator applications. Manufacturing of cylinders for HFC152a will be simpler than for HC290 and HCC270 owing to their low volume.

Figure 3 shows the variation of theoretical Rankine coefficient of performance $(COP)_{RR}$ with evaporating temperature. For the condition of T_{EV} = -15°C and T_{CO} = 50°C, the coefficients of performance vary between 2.7 and 3.23 with the lowest value corresponding to HC600a and the highest to HCC270. From energy point of view, perhaps HCC270 offers the best choice. If some weightings are given for the flammability factor for lower risk, ODP and GWP, then HFC152a is perhaps a better choice.

Variation of shaft power W required per ton of refrigeration is plotted against T_{EV} in Figure 4. For identical conditions, the shaft power decreases in the order of HC290, HC600a, CFC12, HC600, HCFC142b, HCC270 and HFC152a. The shaft power requirement is the lowest for R152a with 1.04 kW $(TR)^{-1}$ and the highest for HC290 and HC600a with about 1.3 kW $(TR)^{-1}$.

The use of hydrocarbon fluids, particularly propane, is likely to increase in the sectors where they are already used with the required safety measures, e.g. petroleum and petrochemical industries.

Cyclopropane (HCC270), which would require smaller compressors than CFC12 and may offer superior energy performance, appears to be a potential candidate. However, HCC270 would require a very small compressor for domestic appliances and this may be a limiting factor. There is no experience of handling HCC270 in refrigeration and air-conditioning systems. There is no published report on any experimental assessment of this fluid. It would require many toxicological and risk assessments before one could suggest the use of cyclopropane in refrigeration systems.

If a suitable weighting is to be given for non-flammability and experience, then HFC152a is perhaps a better alternative than cyclopropane. The American House-hold Appliances Manufacturers (AHAM) have identified HFC152a one of the potential alternatives to CFC12 in domestic refrigeration. The toxicity of HFC152a is already being studied under international consortia efforts under Alternative Fluorocarbon Environmental Acceptability Studies (AFEAS). HFC152a is commercially manufactured and the technology and the cost may be relatively inexpensive. Some preliminary experiments have shown that, from energy point of view, the performance of a domestic refrigerator-freezer is better with HFC152a than with CFC12 (Tan and Ge, 1990). A recent comparative experimental assessment of HFC134, HFC134a and HFC152a in an 0.51 m^3 automatic defrost refrigerator-freezer under retrofit conditions by Vineyard (1991) has indicated that there is likely to be some energy penalties of the order of 7 per cent with these fluids with respect to CFC12. The type of oil also had affected the overall system performance. The chemical stability of HFC152a is not likely to be a limiting condition in refrigeration application. Temperatures well above those realized in refrigeration compressors and systems may be required for thermal decomposition.

CONCLUSION

HFC152a and cyclopropane appear to be potential alternatives to CFC12. The use of flammable fluids in a domestic appliances does increase the risk and would pose many challenges. Therefore, all possible means of minimising the risk must be attempted. There is a need to formulate new safety standards to address the use of flammable fluids. With the current level of advances and technology, it may be possible to use flammable fluids with much less risk. The published reports on the performance of refrigerator freezers using HFC152a have been encouraging and no adverse effects with respect to safety have been reported. Still the system and compressor manufacturers have not considered HFC152a favourably. The evaluation of HFC152a by US-EPA may answer some of the concerns.

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Refrigerant	HC290	CFC12	HFC152a	HCC270	HC600a	HCFC142b	HC600
Molecular formula	$CH_3CH_2CH_3$	CCl_2F_2	CH_3CHF_2	$-CH_2CH_2H_2-$	$CH(CH_3)_3$	CH_3CClF_2	$CH_3CH_2CH_2CH_3$
Mol.wt, kg $kmol^{-1}$	44.1	120.91	66.05	42.08	58.13	100.5	58.13
T_C, ^oC	96.8	111.8	113.3	124.7	135.0	137.1	152.0
P_C, MPa	4.25	4.11	4.52	5.49	3.65	4.25	3.8
N.B.P, ^oC	-42.1	-29.8	-24.2	-32.85	-11.7	-9.3	-0.5
P_{EV}, MPa	0.291	0.183	0.153	0.207	0.089	0.082	0.056
P_{CO}, MPa	1.713	1.217	1.182	1.344	0.6893	0.687	0.495
Q_{EV}, kJ kg^{-1}	221.7	95.9	209.2	321.4	217.9	143.9	249.2
W, kW $(TR)^{-1}$	1.265	1.24	1.04	1.087	1.298	1.152	1.204
(SCD), m^3 MJ^{-1}	0.696	0.953	0.935	0.679	1.859	1.744	2.586
(PR)	5.897	6.66	7.74	6.51	7.76	8.37	8.82
$(COP)_{RR}$	2.79	2.83	3.03	3.235	2.708	3.05	2.918
ODP	0.0	1.0	0.0	0.0	0.0	0.06	0.0
GWP relative to to CO_2	3	7300	140	-	3	1600	3
LEL/UEL vol %	2.2/9.5	NF	3.2/18.0	2.4/10.4	1.9/8.5	9.0/14.8	1.9/8.5

Table 1. Comparative data for CFC12 and some flammable refrigerants for T_{CO} = 50^oC and T_{EV} = -15^oC

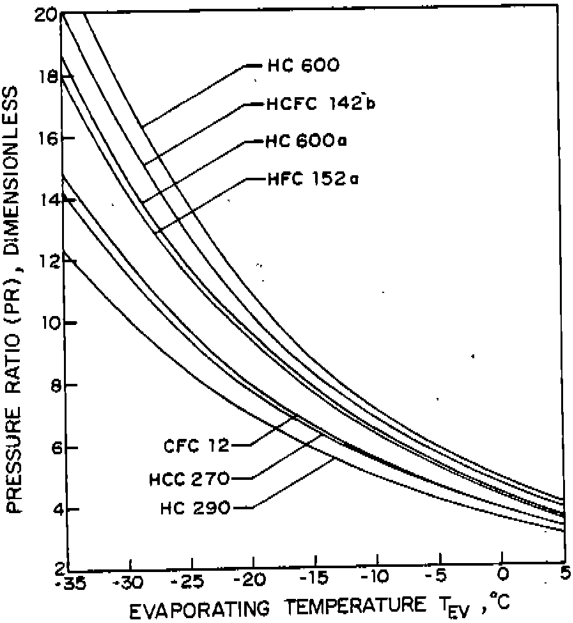

FIG. 1 : (PR) AGAINST T_{EV} FOR T_{CO} = 50°C

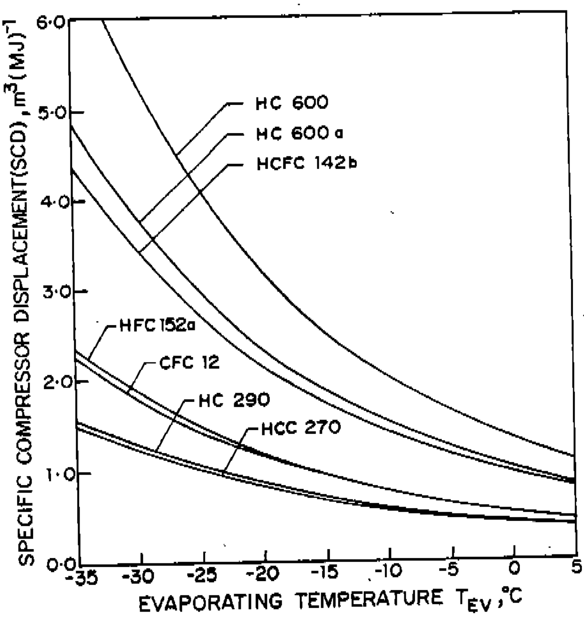

FIG. 2: (SCD) AGAINST T_{EV} FOR T_{CO}= 50°C

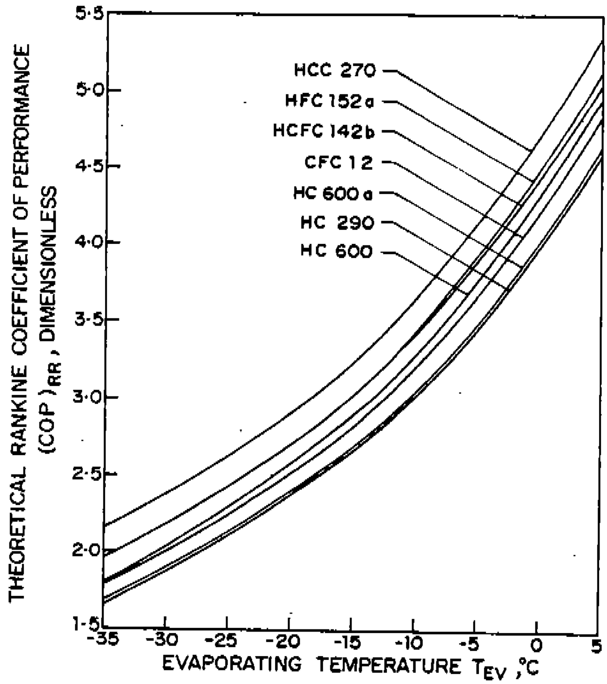

FIG.3: $(COP)_{RR}$ AGAINST T_{EV} FOR T_{CO}=50°C

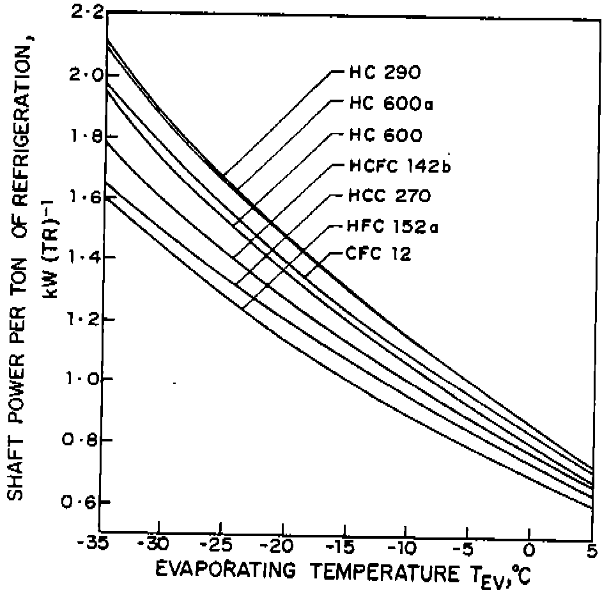

FIG.4 : W AGAINST T_{EV} FOR T_{CO} = 50°C