Analysis of the behavior of ternary hydrocarbon mixture as substitutes of the CFC-12

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Abstracts: Hydrocarbons are stratospheric ozone friendly and have good heat transfer properties. The use of hydrocarbons (HCs) or their blend as refrigerant is extending in these days. This paper deals with the search of the best ternary hydrocarbons mixture of propane, isobutane and butane as drop-in refrigerant for CFC-12. The results of this study have been reported in the paper.

Keywords: CFC-12, hydrocarbon, refrigerant, LB-12, Cub, ozone, ternary mixture

1 Introduction

After it was discovered the negative effect of CFCs on the ozone layer and global warming, the use of natural refrigerant is saw as the best way. These refrigerants such as air, ammonia, carbon dioxide, hydrocarbons and water are the only refrigerants with no ozone depletion, negligible global warming and low environmental impacts in production.

The Ozone Depletion Potential of hydrocarbon refrigerants is zero and the Global Warming Potential relative to carbon dioxide is three for all integration periods twenty years or over. Hydrocarbons replace fluorocarbons like CFCs, HCFCs and HFCs, which have high environmental impacts [1].

The refrigeration systems that using CFCs or HCFCs may be systems with lower negative effect to the environment using one of the procedures:

- add-in
- drop-in
- retrofit.

The process 'add-in' consists in to complete a system with refrigerant without remove the refrigerant remained in it.

The process 'drop-in' consists in to use a substitute refrigerant to charge the systems. It's not necessary to make modification to the system. The term 'drop-in' is not meaning that one must make the work to repair the trouble that system have. It's including the normal change of the drier –filter.

The refrigerants LB-12, CARE LB-12, HC-12 among others are 'drop-in' refrigerants for CFC-12 technology. It's possible to use any kind of oil.

The retrofit process is when the alternative refrigerant can not operate with mineral oil or other one that the system used and/or it's necessary to make modification to the system [2].

Hydrocarbons or their mixtures are a good solutions for the substitution of CFC-12 in actual or in new household refrigerator technology. There are million of refrigerators using isobutane as refrigerant and cyclopentane as blowing agent. In Cuba there were more than 700 000 refrigerators with CFC-12 technology that used a ternary hydrocarbon blend named LB-12. This ecological refrigerant is produced in the Refinery "Hermanos Díaz" in Santiago de Cuba, Cuba.

2 Properties of hydrocarbons

Hydrocarbons (HCs) have similar properties to CFCs. The HCs with better properties as refrigerant are isobutane (R-600a), propane (R-290), ethane (R-171) and their mixtures [3, 4].

These substances fulfill thermophysics, ecological, physiologic and economic requirements to be located among the best options to substitute CFC or HFCs. The most important characteristics are:

- Low viscosity and high thermal conductivity that guarantee a good performance of the system.
- Miscible with most of oils.
- Their efficiency is slightly better than other leading alternative to CFC-12.
- They are compatible with the materials used with traditional refrigerant: metal components and oils.
- High latent heat in the boiling process
- Density lower than CFCs, it is good for its use, in spite of its flammability, because the refrigerant load is lower too.

- Ecological substances: they have no ozone depletion potential, they are no toxic substances, and their global warming potential is negligible.
- They have good refrigeration capacity.
- <u>They are flammable substances.</u>Other important characteristics that we take in consideration particularly to use HCs as refrigerant in CFC-12 technology are:
- **Dipole Moment**

Hydrocarbon refrigerants have low or zero dipole moment so their liquids are non-polar. This means they are miscible with all organic lubricants including natural and synthetic hydrocarbons, polyol esters (POE) and polyalkylene glycols (PAG).

- **Chemical Stability**

The presence of small amounts of water and air in fluorocarbon refrigerants can form acids, which corrode and damage valves. With hydrocarbons this cannot occur because halogen atoms are not present. The compatibility of hydrocarbon refrigerants with hoses and sealants is similar to that of R12.

At the temperatures occurring in refrigeration circuits, the natural hydrocarbon refrigerants, 170, 290, 600a, 600, and their mixtures are very stable so they do not form gums or tars.

- **Electrical Properties**

The compatibility of hydrocarbon refrigerants with electrical insulating materials is similar to that of R12. The electrical insulating properties of hydrocarbon refrigerants are high and the dielectric constant low.

- **Molecular Mass**

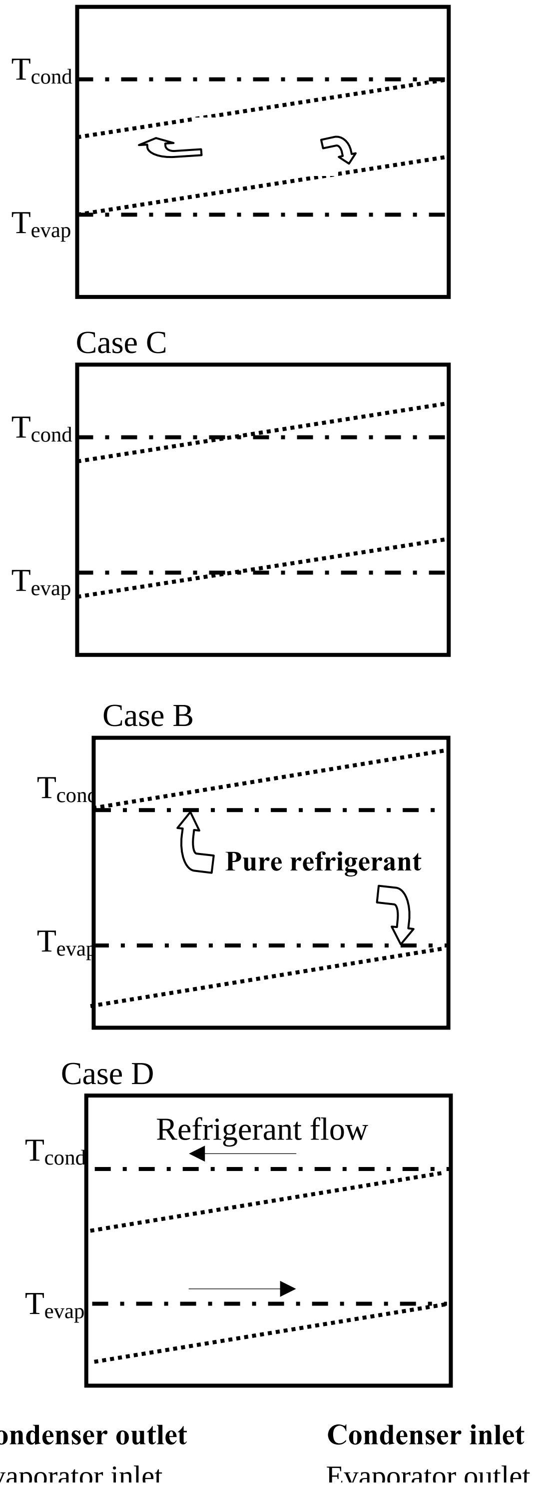
Hydrocarbon refrigerants have a lower molecular mass than fluorocarbons of the same boiling point. This gives them lower density and viscosity and higher thermal conductivity than the fluorocarbons.

These properties result in lower pressure loss and higher heat transfer coefficient. Energy consumption calculated from thermodynamic data and ideal cycles alone differs little for hydrocarbon and fluorocarbon refrigerants [5, 6].

3 Ternary hydrocarbons mixture as refrigerant

If you compare refrigerant taking in consideration the cycle temperatures there are some option:

1. Inlet evaporator temperature in evaporator and saturated vapor temperature in the condenser, *Case A*
2. Outlet temperatures in the condenser and evaporator, Case *B*
3. Average temperature for the phase change processes, *Case C*; and
4. Some combination of the above-mentioned, for instance, *Case D*



It is easy to see that when calculating the COP, this it will depend on the temperatures that are selected. Each one of these cases will have a certain and different value to each other. In our case we made the calculation according to the case C. It is reported, in the bibliography, that this variant is usually used [2, 5, 7].

The software NIST REFPROP Version 7.0 was used to make the thermodynamic cycles for different ternary hydrocarbon mixtures and CFC-12. The mixtures will always have propane, isobutane and butane [5, 8].

The temperature conditions for the thermodynamic cycles:

Condensation temperature 45°C
Evaporation temperature -25°C
Superheat 20°C

The influence in theoretical performance of the cycle according to the variation of the content of each compound in the mixture was analyzed.

The increase of the propane (R-290) content in the mixture causes:

Refrigeration volumetric capacity	++
Compression work	++
Suction and discharge pressures	++
COP.	++

The increase of the isobutane (R600a) content in the mixture causes:

Refrigeration volumetric capacity	+
Compression work	+
Suction and discharge pressures	+
COP (% of isobutane lower than 20)	+
COP (%of isobutane greater than 20)	-

The increase of the butane (R600) content in the mixture causes:

Refrigeration volumetric capacity	-
Compression work	-
Suction and discharge pressures	-
COP (% of isobutane lower than 60)	+
COP (%of isobutane greater than 60)	-

++ Big increment
+ Increment
- Decrease

On the other hand, it is known that for all refrigerants the ratio between refrigeration volumetric capacity (q_v) and the difference of pressure between the condenser and the evaporator (ΔP) it is equal to a constant. Expressed in a mathematical form we have that:

$$\frac{q_v}{\Delta P} = \text{constant} \tag{1}$$

This parameter denominated R was determined for all the mixtures as well as for the CFC-12. The hydrocarbon mixtures with value near to R of the CFC-12 were selected.

Table 1: Hydrocarbon mixtures with value near to R of the CFC-12

Composition %	q_v (kJ/m^3)	W_v (kJ/m^3)	**R=$q_v/\Delta P$**	COP
CFC-12 100	721.3	295.41	**0.73**	2.44
R 290 70 R600 10 R 600a 20	755.5	320.98	**0.7**	2.35
R 290 70 R600 15 R 600a 15	740.6	314.28	**0.69**	2.36
R 290 65 R600 5 R 600a 30	735.1	312.36	**0.69**	2.35
R 290 70 R600 20 R 600a 10	725.8	307.73	**0.69**	2.36
R 290 65 R600 15 R 600a 20	709.9	299.36	**0.69**	2.37
R 290 65 R600 25 R 600a 10	***689.7***	***281.84***	***0.68***	***2.45***
R 290 60 R600 10 R 600a 30	688.4	290.66	**0.68**	2.37
R 290 60 R600 20 R 600a 20	667.8	279.33	**0.68**	2.39
R 290 50 R600 10 R 600a 40	629.14	263.02	**0.68**	2.39

q_v - Refrigeration volumetric capacity
W_v – Volumetric compressor work
COP - Coefficient of performance

The ternary hydrocarbon mixture produced in Cuba named LB-12 is a good refrigerant. It is possible to see in table 2 the most important properties of LB-12 and CFC-12.

Table 2: Properties of CFC-12 and LB-12

Properties	CFC-12	LB-12
Boiling point at 1 atmosphere (ºC)	-29.8	-28.05
Specific heat of liquid at 30ºC (kJ/kg K)	0.99	2.65
Specific heat of vapour at 1 atmosphere, 30ºC (kJ/kg K)	0.62	1.75
Density of liquid at 30ºC (kg/m^3)	1.29	0.53
Density of saturated vapour at boiling point (kg/m^3)	6.30	2.53
Heat latent of vaporization at boiling point (kJ/kg)	165	416.6
Thermal conductivity of liquid at 20ºC (W/mºC)	0.07	0.103
Thermal conductivity of vapour at 1 atmosphere, 30ºC (W/mºC)	0.01	0.018
Superficial tension at 25ºC (mN/m)	8.50	
Viscosity of liquid a 30ºC (centipoises)	0.19	0.120

To evaluate the performance of a refrigerator using LB-12 some tests have been conducted in CFC-12 technology refrigerator; SNAIGE 15E – Russian technology. It is a 220 liters capacity, single evaporator domestic refrigerator-freezer. The results have been reported in next table.

Table 3:Test results

Test	CFC-12	LB-12
Energy consumption (kW-h/day)	1.45	1.59
Pull down after 4 hours (ºC)	-13	-14
Ice Making (min)	110	100

The energy consumption with LB-12 is 9.6% greater than CFC-12. The power demanded is very similar for both refrigerant but the cycle duration is bigger for the LB-12. Besides, the current consumption with LB-12 when the motor starts is also higher because this refrigerant reduced the viscosity of mineral oil [3, 9, 10].

4 Conclusions

1. In our consideration the composition of the ternary hydrocarbon mixture composed by propane, butane and isobutane, with a better theoretical thermodynamic behavior is the following one: Propane 65 percent; isobutane 25 percent and butane 10 percent. The refrigeration volumetric capacity of the mixture (689.7 kJ/m^3) represents 95.6 percent of the value of the CFC-12; it has smaller volumetric compression work by 4.6 percent with regard to the CFC-12, with a value of 281.8 kJ/m^3; and its value of COP is lower in 3.2 percent.
2. The performance of the refrigerator is more or less similar to that CFC-12 refrigerator.
3. The refrigerant LB-12 (ternary hydrocarbon mixture) is a good option to substitute the CFC-12 as drop in solution.
4. It is necessary to increase the viscosity of the mineral oil when you use LB-12 in CFC-12 refrigerator.
5. It is possible to optimize the refrigerator hardware to save energy when using LB-12.

Reference

[1] Didion D., The application of HFCs as refrigerant

[2] Biscali E., CFC substitutes (R 600a and R134a): performance, manufacturing, and costs from the compressor point view, *Eco-refrigeration Conference on Hydrocarbon Fluids in Domestic and commercial refrigeration appliances*, New Delhi, 1996.

[3] Argawal R. S. Et al, *Evaluation of Hydrocarbons refrigerants in single evaporator domestic refrigerator-freezers*, 1994.

[4] Gartshore J., Hydrocarbon refrigerant: properties, purity, and safe handling, *Eco-refrigeration Conference on Hydrocarbon Fluids in Domestic and commercial refrigeration appliances*, New Delhi, 1996.

[5] Document Reference URL: http://ctan.unsw.edu.au/pub/archive/HC/refprop/HCprop.html

[6] Document Reference URL: http://www.esanty.com.au/esanty/tech/FACTS.htm

[7] Bansal P., Krüger R., Test standars for household refrigerators and freezers I: preliminary comparisons, *International Journal Refrigeration*, Vol. 18 No. 1, 1995.

[8] NIST Properties Refrigerants. Software REFPROP Versión 7.1

[9] Domínguez F., Evaluación comparativa del funcionamiento de un refrigerador doméstico empleando los refrigerantes R-12 y LB-12.

[10] Maclaine-cross I. & Leonard. E., Comparative performance of hydrocarbon refrigerant, 1996.