

## THE USE OF HYDROCARBONS PROPANE AND ISOBUTANE IN REFRIGERATION SYSTEMS

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**Abstract.** *The object of this work meets the increasing world-wide concern with the environmental problems caused by the use of hydrochlorofluorocarbons refrigerants in refrigeration systems and the viability to substitute them for natural refrigerants. The results of the theoretical study are presented to characterize the hydrocarbons propane (R290) and isobutane (R600a) to be used in refrigeration systems in substitution for the R22. The performances of these refrigerants in refrigeration cycles are compared by using a standart refrigeration cycle, with evaporation temperatures between -20°C to 10°C and condenser temperature of 40°C. This study was carried out with the aid of the Cycle\_D simulation program. The refrigerants thermodynamic properties were obtained from REFPROP (NIST). The results showed that both R290 and R600a can be R22 substitutes in this range of application. The hydrocarbon R600a presented a better thermodynamics behavior than the R22 in the majority of the analyzed performance parameters, mainly for evaporation temperatures higher than -10°C. The hydrocarbon R290, showed similar results to the R134a.*

**Keywords:** *Refrigeration systems, refrigerants, hydrocarbons, R22 drop-in*

## 1. Introduction

Since their introduction in 1930, chlorofluorocarbons (CFC) and hydrochlorofluorocarbons (HCFC) composites have been the preferred refrigerants for the majority of the applications in the refrigeration industry because of their unquestionable advantages (Bhatti, 1999), mainly high efficiency and security. However, nowadays they are being gradually eliminated because of their implication in the destruction of the ozone layer and in the increase of greenhouse effect.

The great refrigeration industry dependence on these composites has delayed the elimination of their production and consumption. To promote and manage a gradual process of elimination and substitution for the CFCs, some countries were congregated in 1985 in the Convention of Vienna and started an agreement that was firmned up in 1987 in Canada, the Protocol of Montreal. This protocol determined the elimination of the CFCs until 1996 and the HCFCs until 2030 in the developed countries, and a lack of 10 years in the developing countries (GTO-Interministerial Ozone Working Group, 1994).

Besides chlorine in their constitution, these composites are characterized by the great stability, what makes them persist in the terrestrial atmosphere for many years. From the commercial point of view, the CFCs R-11 and R-12 and the HCFCs R-22 and R-502 substitution became the most important. Table 1 shows the environmental impacts of refrigerants R12 and R22 through the Global Warming Potential (GWP) and the Ozone Depleting Potential (ODP). These indexes characterize the action level of these chemical composites on the ozone layer and the greenhouse effect, besides the atmosphere lifetime.

Table 1. Environmental impacts of R12 and R22 refrigerants.

Refrigerant	Chemical formula	Time in the atmosphere (years)	Global warming potential (GWP) <sup>†</sup>	Ozone depleting potential (ODP)
CFC-12	CCl <sub>2</sub> F <sub>2</sub>	100	8500	1.0
HCFC-22	CHClF <sub>2</sub>	12	1700	0.05

<sup>†</sup> Global warming potential relative to CO<sub>2</sub>, 100 year basis, accordingly WMO, 1999.

R22 is widely used, both in terms of refrigeration capacity and for commercial application. It is the refrigerant adopted by the great majority of the refrigeration equipment in operation, being used in the most different economic sectors: residential, commercial, industrial and transport. The hydrofluorocarbon (HFC) R134a is being used to substitute for this composite. However, this transition does not happen easily, mainly in function of lubricant compatibility problems. Another refrigerant that has attracted interest to substitute for R22 is R410a, a near-azeotrope mixture of R32 and R125 of 50-50% per mass (Calm and Domanski, 2004).

At the same time, different research lines are being followed, with a renewed interest in natural refrigerants, as the hydrocarbons propane (R290), isobutane (R600a) and their mixtures, mainly for its lower values of GWP and null ODP, that can be observed in the Tab. 2, together with the properties of R134a and R410a.

Table 2. Environmental impacts of R-600a, R-290, R-134a e R-410a refrigerants.

Refrigerant	Chemical formula	Time in the atmosphere (years)	Global warming potential (GWP) <sup>†</sup>	Ozone depleting potential (ODP)
R-600a	C <sub>4</sub> H <sub>10</sub>	<1	<20	0
R-290	C <sub>3</sub> H <sub>8</sub>	<1	<20	0
R-134a	CH <sub>2</sub> FCF <sub>3</sub>	14	1600	0
R-410a	...	a	2340	0

<sup>†</sup> Global warming potential relative to CO<sub>2</sub>, 100 year basis, accordingly WMO, 1999.

<sup>a</sup> The time in the atmosphere for R-410a is not presented because their components (R32 and R125) fractionate in the atmosphere.

Despite the values indicated in Tab. 2, the effect of a refrigerant in the global heating must be analyzed in a broad way: on the one hand there is the direct contribution due to the refrigerant leakages and on the other hand there is the indirect contribution due to the energy consumption to operate the system. The Total Equivalent Warming Impact (TEWI) term combines both direct and indirect equivalent CO<sub>2</sub> contributions and has been used in the environmental effect evaluation of refrigerant systems (Sand et al., 1999). The hydrocarbons have low or no direct effect in the global heating. However when the system is operating they can have a comparable indirect heating to R134a. Higher energy consumption is associated to more fuel burning and, therefore, more CO<sub>2</sub> release. This effect can be reduced with more efficient equipment.

Thus, the evaluation of natural refrigerants must not only include environmental aspects, but the performance criteria, energy consumption besides the security and physical-chemical stability. Associated to a good performance, there is the matter of the conversion of the existing equipment that can include compressors design, heat exchangers, control systems, lubricant and materials compatibility.

Concerning security, the hydrocarbons are flammable, with very low ignition concentration limits (lower and upper limits in the range of 1.5-2.1% and 8.5-11.4% per volume, and ignition temperatures in the range of 365°C to 491°C), what makes their use difficult in some refrigeration systems, and they are only recommended in systems with reduced cooling load (Goetzler and Dieckmann, 2000) or in cooling systems that use secondary refrigerants with efficiency losses.

The R12 substitution in domestic systems for propane (R290), isobutane (R600a) and their mixtures are concrete alternatives and they have already been introduced in Northern European countries (Domanski, 1999). Mobile air-conditioning that use hydrocarbons have also been tested in buses and automobiles in Europe and Japan (Ghodbane, 1999).

Concerning R22, it is difficult to find a substitute that is so versatile. In this sense, this work presents some results of the comparison carried out, from the thermodynamic standing point, with hydrocarbons R290 and R600a and their mixtures in different mass concentrations, for small capacity refrigeration systems application range, such as refrigerators and domestic freezers and window air-conditioning. The refrigerants R134a and R410a are also included, since they are the potential substitutes, mainly in the United States, where the hydrocarbons are not allowed due to their flammability. R134a has been the substitute selected for domestic and commercial systems and chillers and R410a for applications of air-conditioning, heat pumps and chillers of small size.

## 2. Comparative analysis of refrigerant performances

### 2.1 Simulation conditions

In the theoretical analysis of the refrigerants behavior two refrigeration standard cycles were considered. For the refrigerants that behave as pure substances, (with constant temperatures during the phase change both in evaporation and condensation) like R22, R134a, R290 and R600 the reversed Rankine cycle was used. For non-azeotrope refrigerants, those that present a temperature gliding between the liquid and vapor phases for the same pressure, as R290 and R600a mixtures, the Lorenz cycle was used. Although it is a mixture, R410 is considered a near-azeotrope, because of its small glide (0.1 °C), and therefore it is treated as a pure substance.

The performance comparison between different refrigerants was made for the same ranges of temperature. Temperatures from -20°C to 10°C were used in the evaporator, while the temperature in the condenser was kept fixed in 40 °C, with corresponding saturation pressures to these temperatures. These conditions are representative of operational range for domestic refrigeration equipments. For the mixtures these temperatures represent the average between the bubble and dew point temperatures and the corresponding saturation pressure for this temperature. This form of treatment leads to results where the COP variation with the mixture composition is worthless (McLinden and Radermacher, 1997).

The properties of pure refrigerants and mixtures were calculated using the REFPROP 6.0 program (McLinden et al, 1998) and for the cycles analysis the CYCLE\_D program was used (Domanski, Didion and Chi, 2000). For the comparison, the calculations were made for system cooling capacity of 1 kW and the compressor volumetric efficiency, the compressor isentropic efficiency, as well as the electric motor efficiency were considered of 100%. The superheating in the exit of the evaporator and the subcooling in the exit in the condenser were not considered in this analysis.

### 2.2. Results and comparison

The simulation program supplies properties like temperature, pressure, enthalpy, entropy, specific volume and quality in each point of the cycle and the systems data like the performance coefficient, COP, refrigeration capacity, volumetric capacity, compressor superheating, compressor power and refrigerant mass flow rate. Next, these data will be related to analyze the refrigerants behavior using R22 refrigerant as the reference. Table 3 shows the main thermodynamic properties of refrigerants: critical temperature,  $T_c$ , critical pressure,  $P_c$ , molar mass,  $M$ , molar heat capacity,  $\bar{C}_p$ , and latent heat,  $\bar{h}_{fg}$ .

Table 3. Thermodynamics properties of refrigerants.

Refrigerants	M (kg/kmol)	$T_c$ (°C)	$P_c$ (MPa)	$\bar{C}_p^*$ (kJ/kmolK)	$\bar{h}_{fg}^*$ (kJ/kmol)
R22	86,48	96.10	4,97	103.70	17009.7
R134a	102,03	101.10	4,06	139.82	19461.2
R410a	72,58	70.20	4,90	114.58	15132.9
R290	44,10	96.70	4,25	114.26	15873.8
R600a	58,12	134.70	3,64	136.97	20058.4

\* Properties evaluated an average evaporation temperature at 10 °C.

The critical point, characterized by the critical temperature and pressure and the molar heat capacity, showed in Tab. 3, are particularly important in the analysis of the refrigerant performance in the vapor compression cycle. The vapor compression cycle incorporates irreversibility from the real vapor-compression system, specifically refrigerant superheating at the end of compression and the isenthalpic expansion process. The operation of the refrigerant near the critical point affects the relation between the vaporization latent heat and the specific heat of the fluid at constant pressure. Molar heat capacity of the refrigerant affects the sloping of the saturated liquid and vapor lines, that determines the superheating, subcooling and refrigerant expansion behavior.

These effects can be evaluated through the analysis of the following figures and tables. Figure 1 presents the temperature variation versus dimensionless entropy ( $s^*$ ), according to Eq. 1, it shows the saturation curves of different refrigerants and their critical point.

$$s^* = \frac{s - s_l^0}{s_v^0 - s_l^0} \quad (1)$$

where  $s$  is the entropy,  $s_l^0$  is entropy of saturated liquid at 0 °C and  $s_v^0$  is entropy of saturated vapor at 0 °C.

Figure 1 allows a qualitative analysis of the impact of the two phase dome shape on the performance coefficient (COP). The more volatile fluid (lower  $T_c$ ) starts evaporation at a higher vapor quality and has a larger superheated vapor horn, both attributes contribute to a lower COP (Fig. 2a). However, this refrigerant will have a higher volumetric capacity (Fig. 3), since lower critical temperature results in a higher pressure at the compressor inlet (Tab.4). This result can be observed for R410a and the opposite result for R600a.

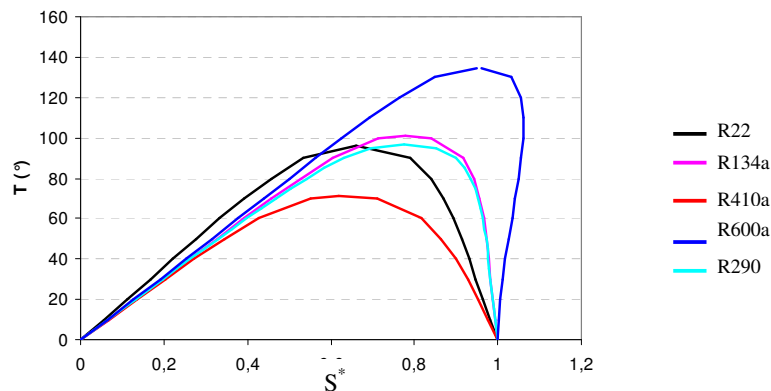


Figure 1. Temperature versus dimensionless entropy,  $s^*$ .

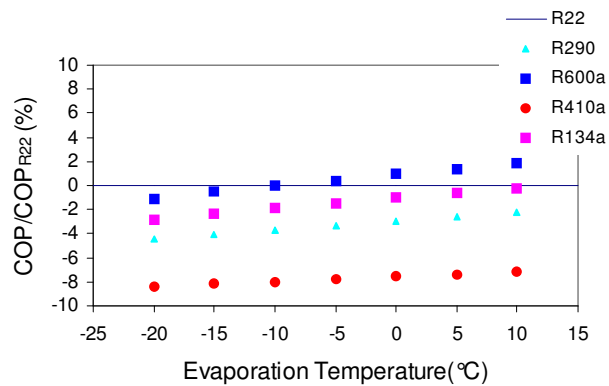
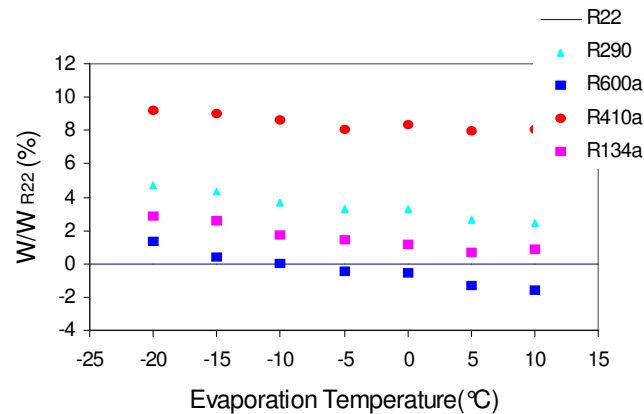


Figure 2.a Performance coefficient (COP) relative to R22 refrigerant ( $\text{COP}_{\text{R22}}$ ).

Figure 2.b. Compressor power (W) relative to R22 refrigerant ( $W_{\text{R22}}$ ).



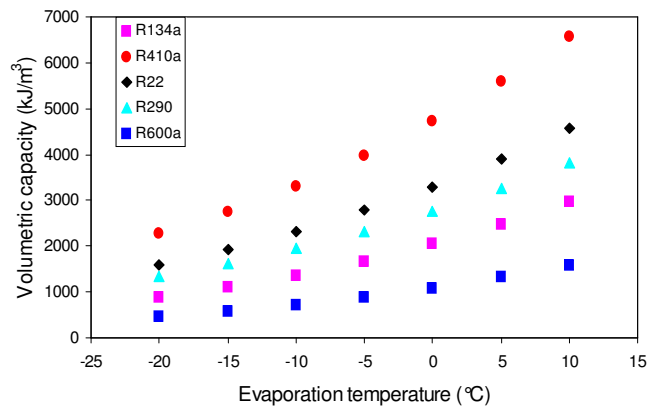


Figure 3. Volumetric capacity and evaporation temperature for different refrigerants.

The molar heat capacity in Tab. 3, affects deeply the performance through its impact on the outline of the two-phase dome. The refrigerant with the high molar heat capacity has its two-phase dome skewed to the right, what may result in significant losses and undesirable wet compression. The refrigerants in this situation are R134a, R290 and R600a. In Tab. 4 it is possible to see this effect in the compression superheating. R600a does not have compression heating, consequently the temperature in the compressor exit is lower, therefore the condenser area is better optimized, since it does not have necessity to lower the temperature until the saturation. R134a, despite the low compression heating value, has influence of the lower critical point. R22 has less molar capacity and therefore the value of the superheating is high.

The isenthalpic (non isentropic) irreversible expansion causes a loss in the refrigeration capacity equivalent to the increase in the cycle work. This loss in the refrigeration capacity, according to Domanski (1995), depends on the latent heat, the molar average specific heat of the liquid and the evaporation temperature.

The Fig. 4 shows the loss of refrigeration capacity ( $Q_{loss}$ ), regarding the refrigeration Carnot capacity (isentropic and reversible processes) as function of the evaporation temperature. It is possible to observe that the refrigerants that present fewer losses are R22 and R600a. These losses increase with the decrease in the evaporation temperature.

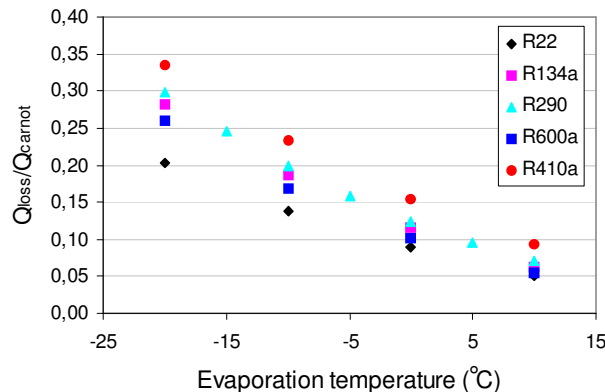


Figure 4. Loss of refrigeration capacity relative to Carnot refrigeration capacity.

Moreover, Fig. 2 shows the COP of refrigerants relative to R22 as reference. R600a presents a higher COP than R22 for temperatures up to -10 °C. R290 loses from 2 to 4% and R410a is in the range of 10% less, in accordance with the explained previously. This has a direct relation with the compressor power. It indicates that the power of R600a would practically be the same as in R22, however the other refrigerants would demand bigger power, mainly R410a.

It is possible to verify in Fig. 2a and 2b the evaporation temperature effect on COP and compressor power. The compressor power reduction affects the motor and equipments selection, and it means minor energy consumption and cost.

From the previous considerations, in Tab. 4, operational conditions are presented, in terms of evaporator and condenser pressure for different refrigerants and hydrocarbons mixtures. Besides the pressures it presents the relation between condensation and evaporation pressure and the superheating in the compressor exit. In Tab. 5 the comparison

results in terms of COP, ideal compression power, refrigeration capacity, efficiency regarding the Carnot cycle, flow rate and volumetric capacity are presented.

Table 4. Operational data of refrigerants and mixtures in the refrigeration cycle at temperatures of -10°C for evaporation and 40°C for condensation.

Refrigerant	Evaporation pressure (kPa)	Condensation pressure (kPa)	Pressure relation	Compressor Superheating (°C)
R-22	354.8	1533.6	4.32	23.7
R-134 <sup>a</sup>	200.6	1016.6	5.07	6.3
R410a	572.4	2417.1	4.22	22.2
R-290	345.1	1369.0	3.97	5.9
R-600 <sup>a</sup>	107.9	530.8	4.92	0
Mixtures: R290/R600a				
40/60%	159.2	891.9	5.60	0.7
50/50%	177.4	976.7	5.51	2.0
60/40%	198.9	1059.2	5.33	3.2
70/30%	224.6	1139.6	5.07	4.3

Table 5. Performance of some refrigerants and mixtures at temperatures of -10°C for evaporation and 40°C for condensation.

Refrigerant	COP	Compressor power (kW/kW)	Refrigeration capacity (kJ/kg)	$\frac{\text{COP}}{\text{COP}_{\text{CARNOT}}}$ (%)	Specific volume (m <sup>3</sup> /kg)	Flow rate (L/s)	Volumetric capacity (kJ/m <sup>3</sup> )
R-22	4.11	0.244	151.55	78.1	0.0653	0.431	2322.1
R-134a	4.03	0.248	136.26	76.7	0.0996	0.731	1368.2
R410a	3.78	0.265	151.76	73.5	0.0457	0.301	3323.9
R-290	3.96	0.253	255.22	75.2	0.131	0.513	1949.4
R-600a	4.11	0.244	245.09	78.1	0.334	1.363	734.7
Mixtures: R290/R600a							
40/60 %	3.47	0.288	251.65	65.9	0.252	1.001	996.7
50/50 %	3.44	0.291	252.91	66.1	0.232	0.917	1089.3
60/40 %	3.44	0.291	253.98	65.4	0.212	0.835	1198.8
70/30%	3.49	0.287	254.82	66.2	0.192	0.192	1330.2

The ideal refrigerant substitute should have similar pressures to R22 refrigerant. The parameters presented in Tab.5 influence directly in the necessity or not of the components substitution, and therefore of re-designing the equipments and accessories. Comparing R290 to R22, it can be verified that the energy consumption of R290 is around 3.7% superior to R22, its condensation pressure is approximately 10.7% less, the refrigeration volumetric capacity is 16% less and the pressure relation is around 8% less.

On the one hand, R600a energy consumption is similar to R22 (Fig.2b), besides the condensation pressure being 65.4% less (it does not present superheating in the exit of the compressor) and the pressure relation is 13.9% less. Its volumetric refrigeration capacity is approximately 68% less (Fig. 3), due to its high specific volume, what demands bigger dimension compressors. On the other hand, as discharge pressure is less, it results in inferior temperatures in the exhaustion, and consequently in less tube and tank walls thicknesses, what decreases the compressor cost.

The heat transfer in the refrigeration occurs mainly in the latent heat exchange between the refrigerant and the fluid to be cooled. In the case of the hydrocarbons the latent heat is higher than in R22, R134a and R410a, as it can be seen in Fig. 5. This property makes possible the use of more compact heat exchangers and, together with the specific volume of the hydrocarbons, it results in a reduction of the refrigerant charge in the system. This fact is particularly important for the hydrocarbons due its high flammability, as previously commented. Studies show that the charge can be reduced between 1/3 to 1/2 in relation to the R-22, R-134a and R-410a (Riffat et al, 1997).

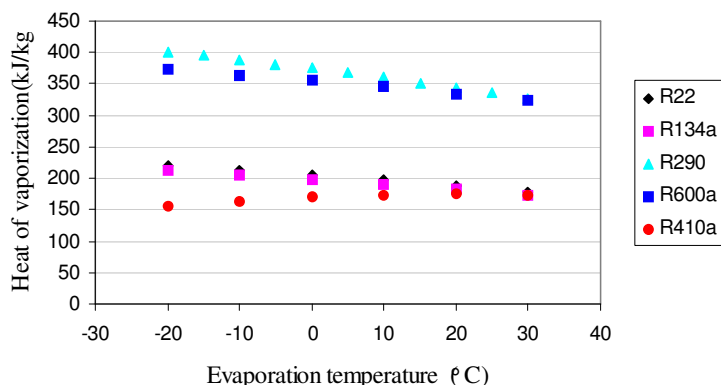


Figure 5. Refrigerants heat vaporization vs. evaporation temperature.

In relation to the hydrocarbon mixtures, R290/R600a, the interesting aspect is the possibility to vary the mass concentration of each component in order to obtain adequate pressure in the evaporator and condenser. The mixtures of R290/R600a with mass concentrations of 40-60%, 50-50%, 60-40% and 70-30% were simulated. For R22 substitution case, as it can be verified in Tab. 4 and 5, the tested mixtures do not present significant advantages.

Another important advantage in the use of the hydrocarbons for R22 substitution is the fact that they work with mineral oil as lubricant. This advantage affects the initial cost of the equipment because of the inferior cost of mineral oil in relation to synthetic oils, besides the reduced cost during the maintenances. The majority of synthetic oils are hygroscopic and its replacement cannot be simple, it should be complete.

Concerning the increase in the manufacturing costs of the equipment when hydrocarbons are used and aiming at the adequacy of security norms, it is important to point out that there is still not a consensus about the appropriated security level for this type of equipment. Serious studies will still have to be carried out to determine the risks involved.

#### 4. Conclusions

The main objective of this work was to compare the thermodynamic performance of the hydrocarbons propane and isobutane as substitutes for R22. R134a and R410a were analyzed too, because nowadays they are used for this purpose.

According to the results, the hydrocarbon that presented better performance for R22 substitution, in the range of temperatures analyzed, was R600a. The propane presents for the same range of temperature a lightly inferior performance, but comparable to R134a. These two hydrocarbons are significantly better than R410a that has been used for its lower flammability index and for its compatibility with mineral oils. In this sense, it presents advantages in relation to R134a.

However, some important advantages presented by the hydrocarbons should be emphasized such as the cost of the refrigerant and the perspectives of price reduction due to the increase in the demand. And the other advantages are the possibility to work with cheaper mineral oils and the possibility to work with more compact heat exchangers in function of its higher latent heat.

Moreover, it is necessary to study the problems concerning system security when these hydrocarbons are used.

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## **5. Responsibility notice**

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