Comparative Performance of Hydrocarbon Refrigerants*

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Summary

Measurements on R600a refrigerators have shown electricity savings over R134a and R12 up to 20%. We propose new parameters which are functions of well known refrigerant properties. These parameters show that R600a has half the leakage, pressure loss and condenser pressure and double the heat transfer coefficient of R12 and R134a explaining the measurements. Use of R600a in small heat pumps and air conditioners is attractive but also requires design changes.

1 Refrigerant History

Early refrigerants were toxic or flammable or both. Early refrigerators leaked refrigerant rapidly, mainly through the seals on the compressor drive shaft, creating a fire and health risk. A hermetic motor is sealed inside the refrigerant circuit so there is no shaft seal to leak. Except for car air-conditioning all small and most large compressors now have hermetic motors minimizing refrigerant risks.

Thomas Midgley Jr proposed the use of chlorofluorocarbons (CFCs) as refrigerants in 1930. CFCs have two important advantages as refrigerants, high molecular mass and nonflammability. Centrifugal compressors are simple, highly efficient and easy to drive with hermetic motors but they require refrigerants with high molecular mass to give useful temperature differentials. Centrifugal chillers for air-conditioning large buildings gave CFCs an initial market which could afford their high development cost.

Enthusiastic marketing of nonflammability allowed rapid expansion of CFC sales in applications where non-toxic but flammable refrigerants were already in use. Everyone was told that flammable refrigerants caused horrific fires and explosions. Ammonia, methyl chloride and hydrocarbons disappeared from domestic

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Table 1: Environmental impacts of refrigerants (100 year basis, WMO 1991, IPCC 1994).

Refrigerant	R12	R22	R134a	R600a	R290
Class	CFC	HCFC	HFC	HC	HC
Atmospheric lifetime (years)	130	15	16	<1	<1
Ozone depletion potential	1.0	0.07	0	0	0
Global warming potential	8500	1700	1300	8	8

systems. In the 1950s, many US states banned flammable refrigerants in car air-conditioners. After the Midgley patents expired, between 1961 and 1971 world CFC production grew by 8.7% per year to over a million tonnes a year.

2 Environmental Impacts

Molina and Rowlands (1974) theory is that: CFCs are principally destroyed by ultraviolet radiation in the stratosphere; the chlorine released in the high stratosphere catalyzes the decomposition of ozone to oxygen; and ultraviolet radiation penetrates to lower altitudes. Credible calculations of the magnitude of this effect (Hoffman 1987) predict 3% global ozone depletion for constant CFC emissions of 700 thousand tonnes/year after a hundred years.

Stratospheric chlorine from CFCs is believed at least partly responsible for peak ozone concentrations occurring lower in the stratosphere and an ozone deficit at the poles (WMO 1991). Manufacture or import of CFCs has now ceased in advanced countries. If these minor effects disappear in fifty years, CFCs were responsible but if they worsen or remain CFCs were not the only causes.

Carbon dioxide concentration in the atmosphere has been steadily rising for over one hundred years and perhaps longer. Early this century the radiation properties of carbon dioxide were known to increase the earth's temperature. The radiation properties of CFCs and their long atmospheric lifetimes make them thousands of times worse than carbon dioxide (Table 1). The consequences of rising global temperatures include inundation of entire cities and countries. Reducing global warming was an overwhelming argument for elimination of CFCs.

The magnitudes of ozone depletion and global warming effects are known only within a factor of ten but the relative effects of different chemicals emitted to the atmosphere are known more accurately. The ozone depletion potential (ODP) for a specified time is the ratio of ozone destroyed by 1 kg of substance emitted instantaneously to the atmosphere to that destroyed by 1 kg dichlorodifluoromethane (R12). The global warming potential (GWP) for a specified time is the ratio of the additional radiant heat at the earth's surface due to 1 kg of substance emitted instantaneously to the atmosphere to that from 1 kg of carbon dioxide. ODPs and GWPs are used in international agreements on controls. Table 1 gives some values.

In 1988, Du Pont agreed to phase out CFCs and began promoting hydrofluo-

Table 2: HC refrigerants used for domestic and light commercial applications.

Code	Chemical name	Triple (°C)	Boil (°C)	Critical (°C)
R290	propane	-189	-42.08	96.70
R600a	isobutane	-145	-11.76	134.70
R600	normal butane	-138	-0.54	152.01
commercial propane				
commercial butane			values vary	
mixtures of the above				

rocarbons (HFCs) as a replacement. An alliance was formed with other chemical companies. Table 1 shows HFCs are better. Unfortunately the radiation properties of HFCs like R134a make them powerful global warming agents.

3 Refrigerant requirements

Acceptable performance and life for refrigerants in domestic and light commercial use requires they be non-corrosive, chemically stable, boil below ambient temperatures and have a critical temperature above ambient. Table 2 shows naturally occurring hydrocarbons and mixtures which satisfy these criteria.

Domestic and light commercial equipment has refrigerant charges less than 5 L of liquid. Most are hermetically sealed giving extremely low leakage and minimal atmospheric impact.

Car air-conditioners have a charge about 1 L. Loss of 0.5 L/year through the seals of the pulley-driven compressors is common. A common practice in the service industry, regassing, was to discharge the residual refrigerant to the atmosphere before weighing in a completely fresh charge. Regassing was equivalent to a leakage rate of 1 L/year. In 1992, Australian CFC refrigerant consumption was estimated as 3204 tonnes with 1530 tonnes going into car air-conditioners (ANZECC 1994) and then into the atmosphere. ODP and GWP of refrigerants in car air-conditioners cannot be ignored. Table 1 shows that only HC refrigerants are acceptable.

R22 is used in many refrigeration and air conditioning applications from small to large and in 1991/92 2252 tonnes were sold (ANZECC 1994). Table 1 shows the ODP and GWP of this HCFC are significantly worse than R134a. R290 however is an excellent drop-in replacement for R22 (Döhlinger 1991, Frehn 1993).

Toxicity and flammability are important considerations in refrigerant applications. The principle safety precaution is to limit the charge depending on the risk. For the controversial car air-conditioner application BS 4434-1995 permits a maximum charge of 1 kg but Australian HC suppliers recommend a charge less than 300 g. Experiment (Section 4) and theory (Section 5) both suggest small HC charges give excellent performance.

Table 3: Energy consumption of domestic refrigerators to ISO 7371 with internal temperature 5°C and ambient 25°C.

Make	Model	Refrigerant	Capacity (L)	Consumption (kWhr/24 hr)
UK	A	R12	129	0.75
UK	B	R12	160	0.71
Liebherr	KT1580	R600a	155	0.38
Siemens	KT15RSO	R600a	144	0.52

4 Performance of HC refrigerants

Foron, Bosch-Siemens, AEG and Liebherr now use HC refrigerant in all models (Strong 1994). Table 3 compares test results on UK R12 and German R600a refrigerators by EA Technology, UK (Strong 1994). The typical HC charge of a small German refrigerator is only 25 g (Döhlinger 1993).

In February 1995, Email released the first of its R600a refrigerators with a 16% energy saving over the previous R134a models. They are the Westinghouse Enviro RA142M and Kelvinator Daintree M142C, both 140 L bar refrigerators. The energy savings obtained by a conversion to hydrocarbons vary considerably with design (Lohbeck 1995).

German refrigeration mechanics had used commercial propane surreptitiously to replace R22 in heat pumps for many years. The Foron furore encouraged heat pump testing. Rheinisch/Westfählische Elektrizitätwerke Essen (RWE) field tested several heat pumps with R22 replaced by R290 for two heating seasons. In 1993, RWE emphatically recommended replacing R12, R22 and R502 with R290 in all domestic and small commercial heat pumps for its power savings (Döhlinger 1993). RWE is Germany's largest electricity supplier.

RWE also tested (Frehn 1993) commercial 20 kW water to water and 15 kW brine to water heat pumps in the laboratory with R22 replaced by R290. Table 4 shows R290 reduced heating capacity but increased COP reducing energy consumption. R22 does not benefit from heat exchange between liquid from the condenser and vapour to the compressor but R290 does significantly at the test conditions. The transport and thermodynamic data (ASHRAE 1993, Gallagher *et al.* 1993) predict that R290 models with the same capacity as R22 will still have a COP advantage.

Abboud (1994) and Parmar (1995) measured the performance of natural HC refrigerants relative to R12 on ten typical Australian cars. The cars were stationary with engines idling and in a shaded and sheltered outdoor position. The superheats measured were smaller for HC as low as 1 K and for some grades the condenser pressure was 8% higher. The relative cooling capacity of the HC mixture to R12 was calculated from the return and supply air states in the passenger compartment and from the compressor speed, pressures and temperatures in the refrigerant circuit. The two measures of the ratio of HC to R12 capacity disagreed sometimes by

Table 4: Capacity and coefficient of performance increase on substituting R290 for R22 in typical German heat pumps (Frehn 1993).

Type	R22 Performance		R290 % Increment	
	Heat kW	COP	Heating	COP
WI 24 10°C to 35°C	22.5	4.2	-10.6	+9.6
WI 24 10°C to 55°C	20.5	3.1	-16.0	+3.2
SI 17 0°C to 35°C	15.5	3.4	-9.0	+5.0
SI 17 0°C to 55°C	13.95	2.49	-15.1	+1.0
With liquid-suction heat exchange for R290				
SI 17 0°C to 35°C	15.5	3.4	-5.8	+16.2
SI 17 0°C to 55°C	13.95	2.49	-10.3	+11.6

20%. The average ratio of HC to R12 cooling capacity was 1.00 with the average energy consumption for HC cooling 13% less than R12. The scatter from differences in charge, ambient and instrumentation was considerable for these results. If air-conditioning adds 10% directly to fuel consumption, Abboud and Parmar's results suggest a 1.2% saving in fuel from converting from R12 to HC. Reduced vehicle mass due to reduced refrigerant mass gives about an 0.1% further saving in fuel. Dieckmann *et al.* (1991) predicted up to 4% reduction in fuel consumption from HC refrigerants but such large savings are likely only in hot humid climates.

5 Comparison of refrigerant performance

The measured performance improvements for heat pumps (Table 4, Frehn 1993) and car air-conditioners (Abboud 1994) are consistent with the transport and thermodynamic property advantages of HC refrigerants (ASHRAE 1993, Gallagher 1993). The large COP improvements in small refrigerators using R600a (Table 3) are also consistent with properties. We explain this in the following in case you suspect it due to German engineering and manufacturing skills applied preferentially to R600a.

Table 5 compares refrigerant properties (Gallagher *et al.* 1993) and parameters affecting COP for domestic refrigerators. Saturated vapour at -15°C is assumed to enter an ideal compressor and saturated liquid at 30°C to enter the expansion valve except for calculating COP with 20 K suction superheat. ASHRAE (1993), Table 7 on page 16.7 also uses these assumptions. Table 5 includes the three refrigerants currently in mass-produced domestic refrigerators and cyclopropane, RC270, which was not in ASHRAE (1993)'s Table 7.

Table 5 shows R600a has one irrelevant disadvantage and many significant advantages for domestic refrigerators discussed in the following: —

1. When R12 was introduced, open-drive compressors were common and R600a's below atmospheric evaporator would cause ingress of air through the shaft seals reducing reliability. Domestic refrigerators no longer use open-drive

Table 5: Comparison of refrigerant properties and parameters affecting the measured energy consumption of domestic refrigerators for an idealized reversed Rankine cycle operating between -15°C and 30°C saturation temperatures. Leading numbers identify comments in the text.

Refrigerant	R12	R134a	R600a	RC270
Chemical classification	CFC	HFC	HC	HC
x_1 Molar mass (g/mol)	120.9	102.0	58.1	42.1
x_2 Refrigerating effect (J/g)	116.9	150.7	262.3	359.1
x_3 30°C sat. liquid volume (L/kg)	0.773	0.844	1.835	1.636
x_4 30°C sat. vapour volume (L/kg)	23.59	27.11	95.26	62.41
x_5 30°C sat. vapour viscosity (μPas)	12.95	12.48	7.81	9.07
x_6 Condenser pressure (kPa)	743.2	770.7	403.6	827.0
1. Evaporator pressure (kPa)	181.9	163.6	89.2	206.0
2. x_7 Condenser gauge $x_6 - 101.3$ (kPa)	641.9	669.4	302.3	725.7
3. COP 0 K suction superheat	4.69	4.62	4.69	4.88
4. COP 20 K suction superheat	4.71	4.71	4.82	4.79
5. Compressor discharge temp. (°C)	39.3	36.6	30.0	52.7
6. Effective displacement (L/kJ)	0.79	0.81	1.52	0.65
7. Cond. loss par. $x_7^2 x_4 x_5/(x_2 x_6)$ (μPas)	1.45	1.31	0.64	1.00
8. 15°C sat. liquid k/μ (kJ/kgK)	0.278	0.293	0.496	0.792
9. Liquid molar volume $x_1 x_3$ (mL/mol)	93.5	86.1	106.7	68.8
10. Leakage speed $x_3 x_7/(x_4 x_5)$ (1/ns)	1.62	1.67	0.75	2.10

compressors.

2. When the refrigerator is in storage, the evaporator must withstand pressures which normally occur only in the condenser. The condenser gauge pressures for R600a are less than half those for the other refrigerants so many metal thicknesses can be half. This reduces capital cost and environmental impacts and increases COP through reduced heat transfer resistance.

3. The COP calculated for a simple reversed Rankine cycle with zero subcooling of liquid and superheat of suction vapour and ideal heat transfer and compression is 1% higher for R600a than R134a. All the refrigerants are close to the reversible COP of 5.74 which is the maximum thermodynamically possible.

4. Domestic refrigerators use a capillary tube in close thermal contact with the compressor suction line instead of an expansion valve. The liquid-suction heat exchange increases COP for some refrigerants and reduces it for others. With 20 K superheat R600a has an idealized COP only 2% higher than R134a. The measured difference of 10% to 20% must contain other effects.

5. The low compressor discharge temperature for R600a allows a cheaper and more efficient design of electric motor.

6. The large effective displacement of R600a implies a larger compressor but because condenser gauge pressures are half compressor wall thickness can be half. An overall reduction in compressor mass and hence capital cost is possible. The compressor will still be much smaller than the driving electric motor. The surface finish of the piston and valves will be the same for R600a and R134a. Because the R600a compressor is bigger the relative roughness will be smaller allowing an R600a compressor to be more efficient.

7. Small refrigerators usually have a serpentine condenser with laminar flow at the beginning of condensation. For condensers of the same length and tube mass but differing diameter and wall thickness, the condenser loss parameter includes all refrigerant properties which contribute to COP loss caused by pressure drop. R600a has about half the COP loss due to pressure drop of the other refrigerants.

8. Heat transfer by forced convection in the condenser and evaporator tubes of small units occurs mainly by conduction through the thin liquid film on the wall. The usual correlations for this heat transfer (ASHRAE 1993) depend mainly on the ratio of the thermal conductivity of the liquid to its dynamic viscosity, k/μ. Hence heat transfer conductance is greater for R600a than for R12 and R134a. A high heat transfer conductance means a smaller COP loss due to heat transfer resistance.

9. For hermetic compressors diffusion through the sealing compounds is a major source of refrigerant loss. Liquid molar volume is related to the size of the molecule. A large molecule means a lower loss rate and a longer period

of operation with high COP. In the absence of measurements, R600a's larger molecule suggests it will have lower diffusion loss.

10. Significant refrigerant leaks occur typically by laminar isothermal flow through pinholes or cracks. The leakage speed is approximately inversely proportional to the time a complete charge of a given refrigerant takes to leak out. R600a systems with large leaks will function with high COP much longer.

These advantages make R600a desirable in other applications where equipment mass and leakage is important and evaporator or condenser temperatures are high *e.g.,* transport air conditioning and domestic water heat pumps. RC270 is a better replacement for R12 and R134a but if the equipment must be redesigned to minimize GWP, R600a will give a better result. Ammonia R717 has higher heat transfer than all these but its vapour pressure, corrosion and toxicity are higher. The toxicity is especially a disadvantage in domestic applications.

HC refrigerants are completely soluble in and compatible with hydrocarbon lubricants. HC liquid absorbs only trace amounts of water, like R12, so HC refrigerants are completely compatible with R12 driers. HC refrigerants with appropriate vapour pressures are 'drop-in' replacements for CFCs on equipment using thermostatic expansion valves. Other expansion devices may require adjustment or replacement.

6 Conclusion

Hydrocarbon refrigerants have environmental advantages and are safe in small quantities. R290 can replace R22 and HC mixtures replace R12 and R134a in applications using positive displacement compressors.

The performance differences between ideal cycles using R600a and popular refrigerants are small but the flow and heat transfer resistance parameters are typically a factor of two better for R600a due to lower molecular mass and vapour pressure. This explains the sometimes over 20% energy savings reported for small refrigerators using R600a. These improvements can be realized in other small applications with equipment redesign.

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LES PERFORMANCES DES HYDROCARBURES COMME FRIGORIGENES

RESUME: Les consommations d'électricité mesurées sur des réfrigérateurs functionnant au R600a sont 20 % plus faibles qu'avec le R12 ou le R134a. On propose de nouveaux paramètres expliquant pourquoi le R600a a moitié moins de fuite, de perte de charge et de pression au condenseur, et double le coefficient de transfert de chaleur par rapport au R12 ou au R134a.