Performance and Safety of LPG Refrigerants*

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Abstract

Ozone depletion and global warming require replacement of chlorofluorocarbon refrigerants like R12. The hydrofluorocarbon R134a is nonflammable, difficult to synthesize, has zero ozone depletion and high global warming. LPG refrigerants are highly flammable, occur naturally, have zero ozone depletion and negligible global warming. In Germany, most new refrigerators use R600a and many heat pumps and air conditioners now use R290 with measured energy consumption 10 to 20% lower than R12, R134a or R22. LPG mixtures have successfully replaced R12 and R134a in over 100,000 US car air-conditioners.

Abboud (1994) measured the air-conditioner performance of five popular Australian cars with R12 and then LPG mixtures in our laboratory. He recommended 60% by mass commercial propane from Bass Strait and 40% commercial butane. This gave typically 10% more cooling than R12 with satisfactory superheat and typically 8% higher condenser pressure.

Refrigerant property parameters show that R600a has half the leakage, pressure loss and condenser pressure and double the heat transfer properties of R12 and R134a. This explains the energy consumption savings of R600a refrigerators. Redesign of heat pumps and car air-conditioners for R600a could yield greater benefits.

The insurance risk increment from LPG flammability for domestic refrigerators is zero. The increment for car air-conditioners is negative because of the high cost of R12 and R134a repairs. For large systems, ventilation of plantrooms and other LPG safety precautions can make insurance risk increment zero or negative if required.

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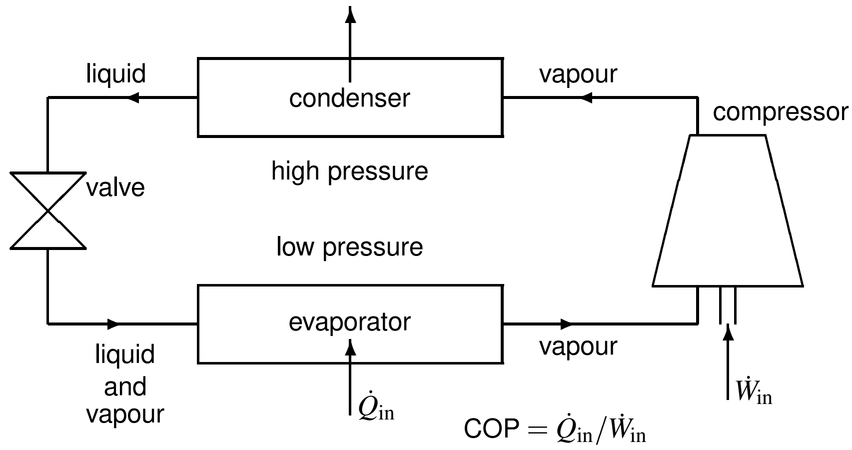

Figure 1: Schematic of vapour compression refrigeration cycle.

1 Refrigerant History

Jacob Perkins patented refrigeration by vapour compression in 1834. Figure 1 shows the four components of a vapour compression cycle schematically. A compressor driven by a motor compresses vapour which a condenser liquefies by removing heat. The liquid passes through a valve or restriction expanding to a mixture of liquid and vapour which an evaporator heats to a vapour which returns to the compressor. The coefficient of performance (COP) is the ratio of the heat absorbed in the evaporator to the work supplied to the compressor. A high COP means low energy consumption and hence lower pollution.

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. He had already achieved fame as a research engineer for General Motors by proposing the addition of lead to petrol in 1921. CFCs have two important advantages as refrigerants, high molecular mass and nonflammability. Centrifugal compressors are cheap, highly efficient and easy to drive with hermetic motors but they require refrigerants with high molecular mass. 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 otherwise superior alternatives existed. Everyone was told that flammable refrigerants (or propellants) caused horrific fires and explosions. Ammonia, LPG and other refrigerants disappeared from domestic 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.

Table 1: Environmental impacts of refrigerants (100 year basis).

Refrigerant	R12	R22	R134a	R600a	RC270
Class	CFC	HCFC	HFC	LPG	HC
Atmospheric lifetime (years)	130	15	16	<1	<1
Ozone depletion potential	1.0	0.07	0	0	0
Global warming potential	7300	1500	1200	8	8

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 and GWPs may be used in future taxes. Table 1 gives some values.

In 1988, Du Pont agreed to phase out CFCs and began promoting hydrofluorocarbons (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.

Translating Table 1 to dollars and cents might help you appreciate the significance of CFC and HFC GWPs. An Australian proposal for a tax on emitted carbon dioxide of 1.25 $/tonne was abandoned in January 1994. Partly because

Table 2: LPG 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				

a tax which adds only 0.2 cents/kWhr to the price of coal-fired electricity would not significantly reduce CO_2 emissions. If the global warming contribution of R134a was taxed at the same rate it would be 1.50 \$/kg R134a which gives R600a a 3.67 \$/kg R600a price advantage. Some governments may do more than tax R134a to meet their treaty commitments (Tickell *et al.* 1995).

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. They are called LPG refrigerants here.

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. Toxicity and flammability are only important in accident and emergency situations.

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 LPG and 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).

4 The LPG refrigerant revival

The revival of LPG refrigerants in domestic and small commercial applications is a happy accident (Vidal 1992). Engineers had known since the 1920's that LPG refrigerants performed well and in the 1980s refrigerator manufacturers again tested them (Kuijpers *et al.* 1988). Fear of a flammability campaign from the chemical industry deterred any manufacture.

In March 1989, the Institute of Hygiene in Dortmund Germany needed a new cold storage room. The young idealistic director, Dr Harry Rosin, could not consider using a CFC refrigerant and so tried propane and isobutane. In 1990, he and his colleague tried mixing the gases and found it worked well. The Institute won a small environmental prize and in January 1991 was visited by a refrigerator manufacturer who told them that R134a was the only acceptable new refrigerant. Suddenly, the Dortmund city council ordered a stop to research on refrigerators.

Greenpeace became interested in the environmental potential of the work and introduced Rosin to DKK Schjarfenstein of Marienbad, the almost bankrupt East German manufacturer of the Foron brand. Greenpeace put up capital for 10 prototypes and persuaded the Treuhand, the government trustee, to allow continued operation. They obtained written orders for over 100,000 Foron LPG refrigerators from all over Europe.

These refrigerators were technical curiosities but the local R134a company did not ignore them. Instead they claimed the refrigerators were 'a potential bomb in the kitchen' and wrote disparagingly to other manufacturers and retailers. It is physically impossible to blowup the smallest possible kitchen with only 50 g of LPG (James and Missenden 1992). The ensuing controversy and lawsuits had Germans demanding Foron refrigerators.

Next R134a companies claimed that LPG refrigerators were inefficient increasing energy consumption and thereby carbon dioxide emissions from power stations. This was dangerous ground because global warming is **the issue** and already Rosin's and Foron's tests had shown 10 to 20% improvement in efficiency (Vidal 1992). Researchers, other manufacturers and electricity suppliers commenced testing and new product development. Greenpeace Australia imported a Foron refrigerator in February 1993 and in December 1993 Email Ltd, Australia's largest appliance manufacturer, displayed prototype LPG refrigerators. In 1994, German manufacturers announced one by one their intention to switch to LPG refrigerants (MacKenzie 1994).

OZ Technology Inc., a startup company in Idaho, introduced OZ-12 a mixture of commercial propane and butane in 1992. They sold over 50,000 170 g cans the first summer. The Mobile Air-Conditioning Society made flammability hazard claims including 'a bomb in the passenger compartment' (Keebler 1993, MACS 1993). The US EPA refused to approve OZ-12 on flammability grounds. OZ then introduced another LPG refrigerant HC-12a, which has already sold over 100,000 cans. The US EPA may not approve this either but OZ's petition (OZ 1994) is convincing, comprehensive and technically sound especially on safety.

The Calor Group is a large European LPG company with a turnover of over 600 million \$/year. LPG as fuel is often less than 0.5\$/L but refrigerant prices have been over 50\$/L. Why should Hüls AG in Germany have this to themselves?

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

Calor released Care 30 in June 1994. Care 30 is a high purity mixture of R290 and R600a and is a drop-in replacement for R12 and R134a. It has been very successful in vehicle refrigeration and air-conditioning. Care 30 and other LPG refrigerants are expected in Australia this year.

5 Performance of LPG refrigerants

Bosch-Siemens, AEG and Liebherr now use LPG refrigerant in all models (Strong 1994) like Foron. Table 3 compares test results on UK R12 and German R600a refrigerators by EA Technology, UK (Strong 1994). Not all the outstanding superiority of the R600a refrigerators is due to the refrigerant. The typical LPG charge of a 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.

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) measured refrigerant charge, suction superheat, condenser pressure and relative cooling capacity on the air-conditioners of five popular Australian cars. R12 was compared with mixtures of commercial propane and butane. The measurements were made on the cars at idle. The relative cooling capacity of the

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

LPG 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 LPG to R12 capacity disagreed sometimes by 20%. A 60% propane/40% butane mixture by mass was measured to increase the cooling capacity by typically 10% over R12. The measurements indicated reduced compressor work but this could not be determined accurately. The superheats measured were satisfactory with typically an 8% increase in condenser pressure.

6 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 LPG 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 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 compressors.

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	LPG	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

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 (Figure 1) 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.

LPG refrigerants are completely soluble in and compatible with hydrocarbon lubricants. LPG liquid absorbs only trace amounts of water, like R12, so LPG refrigerants are completely compatible with R12 driers. LPG 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.

7 Hazards and precautions for refrigerants

All refrigerants are dangerous. The principal hazards are:

Explosion in space Any refrigerant with vapour pressure above ambient can flash to a larger volume. The potential increase in volume is greater if combustion of lubricant or refrigerant occurs. Explosion venting may be necessary to limit pressure rise to what the space can safely withstand. 2 kPa can blow window glass off a building.

Fire Combustible lubricant and refrigerant must be discharged safely outside a building when a fire occurs especially if the heat of combustion exceeds 200 MJ.

Asphyxiation or poisoning All refrigerants except air and oxygen are asphyxiants. Ventilation must prevent serious injury or death on a sudden total release of refrigerant. The quantity of ventilation necessary varies greatly between refrigerants.

Flying metal System must comply with piping and pressure vessel codes.

Corrosion or chemical reaction LPG refrigerants are non-reactive and chemically stable at refrigeration temperatures.

Chemical or cold burns Accidental contact between skin and cold metal must be prevented by insulation. Accidental releases of liquid refrigerant must drain safely.

All refrigerants require safety measures to prevent hazards causing injury to persons or damage to property. The safety measures depend on the mass of the refrigerant, the design of the system and the individual properties of the refrigerants.

Table 6: Fire and explosion data for LPG refrigerants and RC270 (Perry and Chilton 1973 Table 9-20). P50 consists of equal parts of R290 and R600a by mass and is representative of LPG refrigerants which replace R12.

Code	Liquid 25°C sat.	Mol. mass	Flam. limits	Stoch. mixture	Spont. ignit.	Max. flame	Flame temp.	Heat comb.
Units	kg/m^3	g/mol	vol. %	vol. %	°C	m/s	°C	MJ/kg
R290	493	44.1	2.1 to 11.4	4.02	504	0.40	2232	50.3
R600a	551	58.1	1.9 to 10.0	3.12	477	0.37	2241	49.3
R600	573	58.1	1.7 to 10.3	3.12	431	0.37	2238	49.5
P50	523	50.1	2.0 to 10.8	3.58	490	0.38	2236	49.8
RC270	621	42.1	2.6 to 12.3	4.44	498	0.49	2310	49.7

Grouping refrigerants as in AS 1677–1986 results in excessive safety for some refrigerants and inadequate for others. AS 1596–1989 and material safety data sheets from suppliers give more relevant information for LPG refrigerant safety.

A German standard (DIN 7003) allows up to 150 g LPG charge with no special safety precautions, up to 1 kg if the system can resist excess compressor pressures and up to 2.5 kg with specified pressure relief devices. Beyond this the equipment should be outdoors or in a plantroom designed for safety (Krug *et al.* 1993). Table 6 and refrigerant tables (ASHRAE 1993, Gallagher *et al.* 1993) give data for calculating explosion venting and whether a discharge line is necessary on the pressure relief valve. The long term exposure limit for LPG refrigerants is 1000 ppm and for RC270 400 ppm. The ventilation in an unoccupied plantroom should be sufficient to return concentrations below these levels one hour after a complete release of refrigerant. When a plantroom is occupied ventilation must prevent serious injury at floor level on complete discharge of refrigerant. No standards exist. Ventilation which lowers LPG refrigerant concentration below 25% by volume in one minute and RC270 below 10% is a possible precaution.

8 The explosion risk

Some (Vidal 1992, Keebler 1993, MACS 1993) claim the explosion hazard of LPG refrigerants is horrendous even on systems with small charges like domestic refrigerators and car air-conditioners. We will review some experiments to measure the risk.

James and Missenden (1992) tested 142 L refrigerators using R290 for the ‘bomb in cabinet’ accident. They measured the propane charge as less than 40 g on all refrigerators tested. They measured the mass released to atmosphere by a sudden leak as 11.9 g. The rest remained in the oil or in the pipes at atmospheric pressure. On a similar model from another manufacturer they found a sudden leak could release 19 g. They then tried to ignite this and wrote:

> “A connection was made to the evaporator that allowed the refrigerant into the cabinet and an internal ignition device was constructed

to produce a high-energy spark. Tests were made with the ignition being energized immediately after the propane was allowed to leak into the enclosure, and after a settling time of 15 min. The resulting ignition was only partly explosive; a modest report accompanied the door opening and a small short-lived flame was observed inside the cabinet and recorded by video. The intensity of the flame was not sufficient to scorch the plastic liner even after numerous tests. The explosion was rather more robust after a longer mixing time had been allowed, but again part of the gas had stratified at the bottom of the cabinet, to burn off quickly after the ignition. . . . ”

This worst case accident could not injure anyone near the refrigerator at the time. The explosion and fire was unable to even scorch the combustible liner and would be unable to ignite the usual contents of refrigerators. A sudden leak could only occur in normal operation by a very improbable fatigue fracture. The light switch and thermostats on refrigerators are enclosed and could ignite a mixture only if damaged in an unlikely manner. This accident would not cause property damage and is highly improbable. German manufacturers chose R600a partly because its lower vapour pressure makes this accident even more improbable.

Car air-conditioners in Australia have a refrigerant charge of up to 1 L of liquid. The evaporator and frequently the expansion valve are between the dashboard and firewall on the passenger's side. A complete and instantaneous rupture of the liquid line just upstream of the expansion valve could release a white cloud of perhaps 300g of LPG refrigerant into the passenger compartment. Opening a window would create a safe situation in seconds. If all occupants ignored the cloud and one lit a match, the windows would blow off the car in a second. Replacing the glass may cost $1000 and LPG explosion accidents with domestic appliances show occupants' exposed skin would be red and sting for a few days. The glass flies away from the occupants and the resulting in-rush of cool fresh air limits burns and importantly prevents asphyxiation. The authors and their students have made measurements to estimate the probability of this accident.

Razmovski (1994) searched for ignition sources using a propane welding torch attached to a cylinder of hydrocarbon refrigerant. The car was parked in a sheltered outdoor position with fine weather. She started the engine and allowed idling until it reached normal operating temperature *i.e.,* typically for ten minutes. She ignited the welding torch then adjusted it to give a stable yellow flame about 70 mm long. She extinguished the flame with an air blast and tested for easy reignition with lighted matches and cigarette lighter.

The extinguished torch was played over the hot engine, electricals, ignition and exhaust. Then the door, light and brake switches, fan motor, relays and cigarette lighter were tested in the passenger compartment. Each test took over fifteen minutes and 50 to 100 g of flammable refrigerant were used for each test depending on the car. Table 7 lists the model and year of manufacture of the five cars. Razmovski found no ignition sources either inside or outside the passenger compartment on any of the cars tested.

Leakage of fuel into the passenger compartment is not uncommon. A manufacturer would be negligent to use open relays, switches or motors which could

Table 7: Measured LPG refrigerant charge (Abboud 1994) and passenger compartment air flows (Razmovski 1994) give the maximum time a flammable concentration exists in the passenger compartment with fan and vent operating.

Model name Year of manufacture	King. 1970	Comm. 1979	Pulsar 1984	Laser 1988	Berlina 1989
LPG refrigerant charge (g)	298	460	425	315	840
Ambient temperature (°C)	19.5	17.5	18.3	21.0	16.0
Atmospheric pressure (kPa)	100.4	99.9	101.3	100.8	101.2
Compartment volume (m^3)	5.81	3.81	4.16	3.48	4.36
Measured air inflow (L/s)	2.52	85.0	77.4	85.1	173.0
Maximum LPG conc. (vol. %)	2.48	5.83	4.88	4.38	9.14
Maximum flammable time (s)	497	48	48	32	38
Explosion freq. (10^{-9}/year)	29	3	3	2	2
Insurance risk incr. ($/year)	0.0029	0.0003	0.0003	0.0002	0.0002

ignite a fuel/air mixture. Enclosed electrical components are also more reliable saving on warranty claims. The incidental effect is a match or cigarette lighter is the only ignition source for a refrigerant mixture in the passenger compartment as Razmovski found. The consumption of cigarettes over the whole driving population is equivalent to about ten cigarettes a day (Department of Community Services and Health 1990). We will assume that half the cigarettes consumed in cars are lit with the car's cigarette lighter and would not cause ignition. We then have five potential ignitions per driver per day.

Table 7 summarizes Razmovski's results for passenger compartment volume and fresh air flow measured using carbon dioxide gas as a tracer. The measurements were with the engines idling and the vehicles stationary in a sheltered position. The Kingswood had no vent so its air inflow is infiltration only.

Fatigue fractures of pipes which do not leak before the sudden and complete parting of the metal are so rare, that we have never heard of it happening between the firewall and the expansion valve. The unmistakable sign is a sudden white cloud emerging from behind the dashboard on the passenger's side. Tables 6 and 7 show the maximum hydrocarbon concentration for each of the five cars is a flammable mixture. We will assume here that such fractures occur once per million operating years which implies several occur in Australia every year. We also assume a smoker ignores the cloud and does not wind down a window. Figure 2 shows the concentration profile assumed in the passenger compartment to calculate the time which the concentration remains above the 2.0% lower flammability limit for the Pulsar. Table 7 gives this maximum flammable time as 48s. The explosion frequency for the Pulsar in Table 7 is thus $5 \times 48/(86400 \times 1000000) = 3 \times 10^{-9}$. If the vehicle is stationary when the accident occurs the cost could be as little as $1000 but it will be assumed here following Maclaine-cross (1994) that the payout increment is $100,000. The insurance risk increment in Table 7 is trivial.

Table 8 shows a rough estimate (Maclaine-cross 1994) of the annual insurance risk increment from converting an R12 car air-conditioner to LPG refrigerants. The

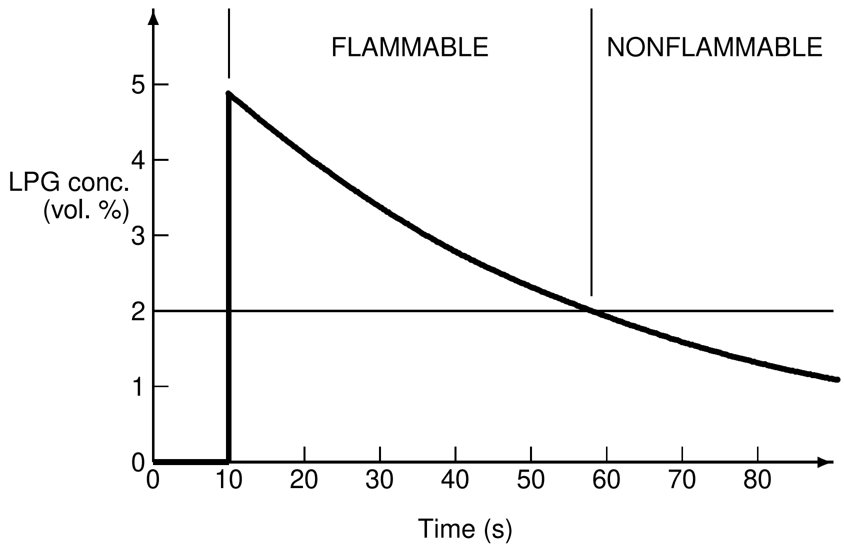

Figure 2: LPG refrigerant concentration assumed in passenger compartment to calculated maximum flammable time for Pulsar in Table 7.

Table 8: Annual insurance risk increment on conversion of R12 car air conditioner to LPG refrigerants (Maclaine-cross 1994).

Scenario	Payout Increment	Frequency year^{-1}	Risk Incr. $/year
Engine bay fatigue fire	$1000	1×10^{-7}	+0.0001
Passenger fatigue fire	$100,000	2×10^{-9}	+0.0002
Slow collision fire	$1000	2×10^{-4}	+0.20
Fast front/rear fire	$100,000	5×10^{-6}	+0.50
Slow collision R12 loss	-$50	2×10^{-2}	-1.00
Slow collision R12 recovery	-$100	2×10^{-2}	-2.00
		Total Risk Increment	-2.30

high cost of crash repairs to R12 air-conditioners results from the price of R12 and the legal requirement to recover it. LPG refrigerants reduce insurance risk over R12 by 2.3$/year.

Dieckman *et al.* (1991) made an earlier, independent and more detailed investigation of LPG in car air-conditioners. They concluded that the risk of injury from LPG refrigerant was 3.5×10^{-7} per year in the US. This is fourteen times lower than the fast front/rear frequency assumed in Table 8 confirming the low insurance risk of LPG refrigerants.

Many car air-conditioners in Australia have the expansion valve in the engine bay. This restricts a leak in the passenger compartment to about one minute to discharge a substantial quantity of refrigerant. If the fresh air flow rate was high like in the Berlina of Table 7 and the refrigerant charge was moderate, a flammable mixture could only be reached close to the leak. The 'bomb in the passenger compartment' accident would be impossible.

Odorized LPG may warn technicians to increase ventilation when invisible leaks occur in handling quantities over 1 kg. The white cloud creating an explosive mixture from small charges warns users so odorization does not significantly reduce the probability of subsequent explosions. Odorant may increase the energy consumption of domestic refrigerators by corroding valves (Preisendanz 1993).

9 Conclusion

The Australian market for nontoxic refrigerants is about 5 million litres of liquid per year and current prices are over 15 $/L in bulk. Customers will demand LPG refrigerants because they occur naturally, cause no ozone depletion and negligible global warming. Initially R290 can replace R22 and LPG mixtures replace R12 and R134a. The market for R600a will grow as new equipment exploits the advantages of its lower vapour pressure.

LPG refrigerants have superior properties often giving 10 to 20% energy savings. They are highly flammable so for charges above 2.5 kg systems should comply with AS 1596–1989.

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