Hydrocarbon Refrigerants and Motor Car Air-Conditioning*

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1 On Refrigerant Environmental Impacts

Jacob Perkins patented refrigeration by vapour compression in 1834. Early refrigerants were toxic or flammable. Early refrigerators leaked refrigerant rapidly, mainly through the drive shaft seals, 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.

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 non-flammability.

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. Replacement refrigerants (Nowak 1990) require screw chillers which are 50% more expensive. After 1995 the cost of premature replacement of centrifugal chillers with imported high-technology chillers will fall mainly on finance and tourism. Low cost non-CFC refrigerants which do not require equipment replacement are available for almost all other applications and will be discussed in the following.

A car air-conditioner may lose 400 g/year of dichlorodifluoromethane (R12) through hoses, pipe joints and shaft seals. Domestic refrigerators lose about 1 g/year in operation and assuming no recovery 10 g/year on a life cy-

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cle basis. Consider the future population of a wealthier world as 10 billion people. This implies 2 billion car air-conditioners and 2 billion refrigerators. If R12 were still used, cars would emit 800 thousand tonnes/year and fridges only 20 thousand tonnes/year. Other environmental impacts are similar. Power consumption averaged over a lifetime for typical fridges and car air-conditioners are both of the order of 50 W.

Hoffman (1987) and his team for the United States Environment Protection Agency predicted 3% global ozone depletion for constant CFC emissions of 700 thousand tonnes/year. The ozone impact of car air-conditioners cannot be ignored. For fridges, a replacement refrigerant must reduce both energy consumption and ozone depletion to reduce environmental impact after manufacture.

Many environmentalists and scientists believe Hoffman's estimates of ozone damage to be a factor of ten too low. If you are one of these, I suggest you should never buy a new fridge. Always buy a secondhand R12 fridge to prevent it being crushed for scrap and the R12 released to the atmosphere. Only after the last functioning R12 fridge in the country has expired should you consider a new ozone friendly fridge. Your slogan should be 'keep that fridge.'

'Polluter pays' policies have been very effective in reducing other pollutants. They would make selecting the refrigerant with the lowest life-cycle cost give the lowest environmental impact. Unfortunately they were not adopt for CFCs and so our progress in eliminating CFCs has been expensive and ineffectual.

Domestic water heaters with lifetime average power consumption of 500 W are a more important problem. Domestic heating and cooling is typically a 1000 W. Application of effort to these areas would reduce pollution more quickly and cheaply than redesigning fridges (Gudgeon 1990).

Refrigerant changes are not even the best option for reducing fridge energy consumption. The U. S. Department of Energy has been funding the development of vacuum (or super) insulation for fridges at the National Renewable Energy Laboratory, Golden CO for over ten years. This insulation design is two thin stainless steel foils with low emissivity coatings held apart by glass beads. The overall thickness is less than 2 mm but it has the same thermal resistance as 200 mm of foam. Prototype fridges have been built and test marketed with half the energy consumption.

The reasons for this workshop are partly the contentious and competing claims of Greenpeace and some executives of a chemical cartel about replacement refrigerants for CFCs (Vidal 1992). My colleagues and students in the Refrigeration and Air-Conditioning laboratory have accumulated much relevant information over the years. In addition, Vidal's article motivated us to perform some inexpensive experiments to test the claims. Our results and information to help you duplicate them are also here.

2 Refrigerant Characteristics

Vapour compression refrigerants are chemical compounds or mixtures with small molecules and high vapour pressure. At refrigerator temperatures they should be stable and nonreactive. Thermal design and performance depend on the mass of the molecules and the forces between them.

The van der Waals forces exist between all molecules. They are believed due to oscilations in the relative positions of the positively charged nuclei and surrounding electron clouds. If only van der Waals forces act between the molecules, pure compounds with similar boiling points have similar energy consumption and require similar compressor displacement and motor sizes. There may be differences but neither basic thermodynamic data nor performance measuring technique have been sufficiently accurate to tell what these are.

Some molecules *e.g.*, water, ammonia, have the centres of positive and negative charge permanently displaced from one another. The dipole electric moment is the product of the electric charge times its displacement. Polar molecules have a large dipole electric moment. These dipole forces are much larger than the van der Waals forces and follow a different law. Ammonia (R717) a polar molecule and R12 only slightly polar have similar boiling points. Their thermal performance has frequently been compared for simple ideal refrigeration cycles and ammonia is usually found to be 1 or 2% better (ASHRAE 1993, Threlkeld 1970).

This slight advantage of polar molecules is frequently outweighed by the practical difficulties created by their insolubility in hydrocarbon oils and their miscibility with water. The insolubility may require either special circuitry or special oils. The miscibility usually requires more expensive driers which must be replaced more frequently. These disadvantages are both a consequence of their polarity. Ammonia has the additional difficulty of being corrosive to copper.

The capacity of both fridges and car air-conditioners is so small that only positive displacement compressors can be considered. For both applications the size of these must be kept small. The compressor size depend principally on the boiling point. A boiling point over -20°C will result in an unacceptably large compressor in either application.

Noncondensible gases such as air even is small quantities greatly increase energy consumption and reduce capacity. The simplest way of ensuring that air does not enter a refrigerant circuit is to select a refrigerant that will be above atmospheric pressure for every conceivable operating condition. The design temperature of freezers is -18°C (ASHRAE 1988). A refrigerant boiling point below -20°C is essential to maintain a pressure in the circuit above atmospheric.

Low boiling points imply increased friction losses in the compressor but may allow gains in piping losses. It is unlikely that boiling points below -45°C would ever be considered for fridges. The increased refrigerant leakage for car air-conditioners are unlikely to be balanced by the reduced compressor size.

New computer codes called REFPROP 4.0 have been released by the National Institute of Standards and Technology, Gaithersburg MD (Gallagher *et al.* 1993). They calculate thermodynamic and transport properties of a broad range of refrigerants and refrigerant mixtures. These codes summarize the latest knowledge of refrigerant properties and allow accurate prediction of performance without building numerous prototypes.

3 'Drop-In' Replacement Refrigerants for R12

Fridges are charged at the factory and the charge is intended to last over twenty years. Their replacement refrigerant for R12 need not be a 'drop-in'. If design modifications are necessary, the manufacturer can include them at the factory. Consumers should not worry about what the replacement refrigerant is. Any of the chemicals in Table 1 would be satisfactory and many others besides. They should be concerned about the overall energy consumption, reliability and utility.

Many existing car air-conditioners use R12 and refrigerant must be added annually. A 'drop-in' replacement would save the cost of a conversion and may be a substantially cheaper refrigerant. The boiling point of R12 is -29.8°C and its dipole moment is low. The closest match to R12 in Table 1 is RC270. A literature search showed that the data available on RC270 was considerable but also Gallagher *et al.* (1989) have made computer codes available.

Kuijpers *et al.* (1988) have reported results on an R12 fridge using RC270. The increased energy consumption over R12 they reported was consistent with the higher motor loadings resulting from its high refrigerating effect compared with R12. With car air-conditioners this higher refrigerating effect is an advantage not a disadvantage. You get a bigger air-conditioner for the price of a change in refrigerant.

Evaporator superheat is not a refrigerant property but an operating parameter of the air conditioning system. It is the difference between the refrigerant temperature leaving the evaporator and the vapour pressure or dew point near the evaporator outlet. This must be several kelvin or liquid may enter the compressor and damage the valves. Cyclopropane's higher vapour pressure will result in a higher superheat with most control valves. ASHRAE (1991) discusses such design details of car air-conditioners.

Cyclopropane was first prepared by August Freund in 1881. Commercial preparation is by catalytic reaction of acetylene with methane ensuring a bulk price under 10$/kg. Its major applications are as an anesthetic and a feed stock for synthesis of fine chemicals and insec-

Table 1: Some chemical compounds with boiling points at 101325 Pa between -45 and -20°C which do not contain chlorine.

ANSI 34-1992 Designation	Chemical Formula	Boiling at 101325 Pa	Chemical Name	Dipole Moment
R290	C_3H_8	-42.1°C	propane	low
R717	NH_3	-33.3°C	ammonia	high
RC270	C_3H_6	-32.8°C	cyclopropane	none
R134a	CF_3CH_2F	-26.2°C	1,1,1,2–tetrafluoroethane	moderate
R152a	CH_3CHF_2	-25.0°C	difluoroethane	moderate

ticides. Unfortunately stocks are not held in Australia and it must be imported from North America or Europe.

4 Hydrocarbons Mixtures as Refrigerants

Kuijpers *et al.* (1988) recommended a mixture of propane and isobutane as a refrigerant. Vidal (1992) reported claims that Greenfreeze a mixture of commercial propane and butane could achieve between 10 and 20% greater energy efficiency than conventional fridges.

Non-azeotropic mixtures of refrigerants can reduce energy consumption when cooling is required over a broad range of temperatures and heat is discharged over a range of temperatures. This effect is however small for propane/butane even with two compartment refrigerators. If the reported figures are correct the improvement must have been contributed to by better engineering and improved lubrication conditions in the compressor using hydrocarbons.

Australia is both a major producer and a major consumer of commercial propane (barbecue gas) and butane. So shipping would not delay our experiments.

5 Hydrocarbon Hazards

The liquid density of R12 is 1460 kg/m^3 and of R134a 1350 kg/m^3. The liquid densities in Table 2 show that even for cyclopropane a 1 kg charge of R12 is equivalent to only a 460 g charge. This low density and the matching high latent heat reduce both the cost and fire and explosion hazard of hydrocarbon refrigerants.

Even a large fridge releasing its 100 g charge suddenly in a small 12 m^3 kitchen creates a mixture only 0.6% by volume so the data in Table 2 show explosion is impossible. Many aerosol cans have a larger charge but very few fires or explosions have caused injury.

Fire is a hazard for cars. The 300 g charge in a car air-conditioner is only 1% of the 30 kg petrol mass in a fuel tank. For a fire to occur not only must the refrigerant be released but the autoignition temperatures in Table 2 show a spark or flame must be present.

6 Car Air-Conditioning Experiments

The composition of a commercial propane/butane mixture suitable as 'drop-in' replacement for R12 was calculated crudely as 64% propane and 36% butane by mass.

In March 1993, students and staff of the Refrigeration and Air-Conditioning Laboratory at the University of New South Wales charged an R12 air-conditioner on a Ford Laser with a mixture of 64% propane and 36% butane by mass. They encountered no difficulties in charging and measured superheats between 5 and 10 K depending on the operating condition. A month later comparative capacity measurements were made on propane/butane, R12 and cyclopropane. They detected no difficulties or differences in operation except the cooling capacity was 10% higher for propane/butane and 20% higher for cyclopropane than for R12. The cyclopropane was a small quantity imported from Germany so this month I added readily available propane/butane mixture.

Table 2: Data on the fire and explosion hazard of hydrocarbon refrigerants.

Code	Name	Density liquid	Flammability limits by vol.	Autoignition temperature
R290	propane	560 kg/m^3	2.4% to 9.6%	494–549°C
RC270	cyclopropane	677 kg/m 3	2.4% to 10.4%	
R600	n-butane	624 kg/m^3	1.8% to 8.6%	482–538°C

7 From R12 to Greenfreeze

The Refrigeration and Air Conditioning Laboratory has a full range of refrigerant recovery and charging tools. You may wish to repeat our experiments with or without the high technology. This is reasonable provided you are familiar with the operation and maintenance of motor vehicle air-conditioners and the hazards and precautions in handling propane and butane. If you do not have copies of the suppliers material safety data sheets you should ask for them. You should read these data sheets.

The following information applies only to motor vehicle air-conditioners designed for use with R12. New cars are now fitted for R134a or other ozone friendly refrigerants. Do not use this procedure with any refrigerant other than R12. No warranty or representation of any kind is made about the results to be expected. Personal injury and damage to the motor vehicle is possible. There may be errors and there are omissions in the following description and you must use your engineering knowledge to rectify them. The R12 air-conditioner should be operating normally except for gas bubbles in the sight glass indicating low charge.

7.1 Tools, equipment and supplies

The hand tools required are a screwdriver, a sharp knife and a multigrip wrench.

The equipment and supplies which we purchased from K-Mart were:

No	Item	Price $
1	Taymar LG870 Butane Gas Blowlamp with gas can	42.00
2	Taymar RF80 gas cans	8.80
2	Jackeroo gas hoses	27.70
1	1.25 kg Jackeroo L.P. gas cylinder	22.95
1	Packet of two small hose clamps	3.95
	Total	105.40

The equipment purchased from CIG Gas & Gear Centre was:

No	Item	Price $
1	36in long 0.25in SAE refrigerant charging hose	14.88
1	0.25 in Schrader access valve solder union type	2.66
	Total	17.54

The supplies purchased from Mitre 10 were:

No	Item	Price $
1	partial gas cylinder fill with propane	1.95

7.2 Mixing procedure

1. Attach hose to gas cylinder (This is a left-hand thread so turn it in the opposite direction to normal.) then cut the end furthest from cylinder off with the knife.
2. Unpack Taymar blowlamp, use screwdriver to remove flame holder and them multigrips to remove nozzle.
3. Place one hose clamp over hose, insert blowlamp tube 25 mm into hose and fasten hose to blowlamp with clamp.
4. Tighten hose to cylinder finger tight, close cylinder and blowlamp valve.
5. The remainder of this procedure should be performed outside or in a garage with the main door and several windows open. All flames and cigarettes should be extinguished.

6. Take first can and shake to check contents then fasten to blowlamp.
7. With butane can upside down above cylinder, open blowlamp valve and cylinder valve to allow butane liquid to flow into cylinder.
8. Hold butane can upside down in both hands for 30 seconds to warm and encourage liquid flow.
9. Take screwdriver and turn air release screw at side of cylinder valve to release some air then tighten after two seconds.
10. Shake can to check liquid flow.
11. Warm can again for 30 seconds to encourage liquid flow.
12. Repeat the can warming and air release until the liquid in the can is transferred then close the blowlamp valve and remove the can.
13. In similar fashion empty the other two cans of butane into the cylinder.
14. Close the cylinder valve, remove the hose with blowlamp valve and store.
15. Take cylinder to propane filling station (our's was Mitre 10) and ask assistant to add the propane on top of the butane.
16. Thoroughly mix the propane and butane by rotating the cylinder for at least 60 seconds.
17. In open air, hold the cylinder upside down for 30 seconds.
18. With the valve pointing to the ground and away from any person, open it slightly for 1 second to expel any water from the cylinder. Keep your hands clear of the valve outlet.

7.3 Charging procedure

1. Attach the other gas hose to the gas cylinder and cut off the end furthest from the cylinder.
2. Take the Schrader valve, slip it 25 mm into the hose and fasten with hose clip.
3. Unscrew the knurled cap from the Schrader valve and with needle nosed pliers unscrew and remove the valve stem from inside the body.
4. Screw the charging hose to the Schrader valve body.
5. Open and raise the engine hood and support it on its stand.
6. Locate the compressor of your air-conditioner and its inlet and outlet Schrader valves. The outlet Schrader valve will be closest to the hose connected to the condenser which is in front of the radiator.
7. Locate the sight glass on your system.
8. Start your engine and air conditioner. If the air conditioner is working and the sight glass is showing bubbles it is time to add refrigerant.
9. Stop the engine, support the cylinder upside down from hood and attach charging hose loosely to the Schrader valve on the compressor inlet.
10. Open the gas cylinder valve for two seconds to expel air from the charging line.
11. Tighten the charging hose on the compressor inlet until it opens the Schrader valve.
12. Start the engine and air-conditioner again.
13. Observe the sight glass, if bubbles are still present open the cylinder valve slowly until you can hear the hiss of refrigerant flowing slowly.
14. Close the cylinder valve as soon as the bubbles have all disappeared from the sight glass.
15. Turn the engine off and depress the compressor outlet Schrader valve for two seconds with a screwdriver to release any air.
16. Turn the engine and air conditioner on again and check the sight glass for bubbles. If bubble are present add more refrigerant as previously.

17. If no bubbles are present, make sure the gas cylinder valve is closed finger tight and turn the engine off.

18. Remove the charging hose from the compressor quickly to avoid loosing refrigerant.

19. Remove the cylinder from the hood and all tools and equipment from beneath the hood.

20. Close the hood and check that the air-conditioner is functioning normally.

7.4 Further tests

If you have a pressure gauge set and thermometer and have replaced all or part of the refrigerant, you may check the pressures and superheat. The pressures should be similar to R12. The superheat should be over 6 K if all the R12 has been replaced.

8 Conclusion

The total cost of the supplies purchased as described above was $15.15. The quantity of refrigerant mixed was 1.2 kg so the cost was 12.5 $/kg. This a quarter the cost of competing ozone friendly refrigerants. There were no conversion costs. If sufficient interest is shown in Greenfreeze replacement refrigerant for car air-conditioners there are a number of suppliers who would be prepared to premix the refrigerant and reduce the cost towards 2 $/kg.

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