Hydrocarbon Refrigerants for Car Air Conditioners

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ABSTRACT

The world needs car air conditioning and the hydrocarbon (HC) refrigerant 290/600a avoids stratospheric ozone depletion and a typical 15% increase in TEWI from R134a leakage and service emissions. Measurements suggest that R290/600a [55/45] matches the performance of R134a best if ethane impurity is below 0.5%. Batches of HC replacement for R12, 134a, 22 and 502 can be manufactured from natural butane and propane by pumping ethane rich vapour off the propane before mixing.

Keywords: motor car, air conditioning, refrigerant, hydrocarbon.

BENEFITS OF CAR AIR CONDITIONING

Passenger cabins of modern motor cars have insulation to reduce road noise, little thermal inertia and about 3 m^2 of glazing exposed to direct and indirect solar radiation. With windows and doors closed cabins are well sealed except for two air vents at the same elevation and with ventilation fan off and low wind conditions infiltration is less than 1 L/s regardless of the position of any fresh air damper (Maclaine-cross 1997). Cabin temperatures may then rise over 20 K above ambient. The ventilation fan and forward motion may limit this to 10 K but additional measures to avoid heat stress and driver errors are necessary in warm climates. The traditional solution is drive with all windows open. The increase in drag coefficient is only about 0.1 but at 72 km/hr this adds 1.4 kW to the crankshaft output required of the engine.

An air conditioner with car windows closed typically loads the crankshaft about 1 kW at 72 km/hr. In hot climates with high speed driving air conditioners usually reduce overall fuel consumption. The heater/demister components of an air conditioner are frequently required by safety regulations. The cooling components of an air conditioner add about 3% to vehicle mass which increases fuel consumption for acceleration and rolling resistance by about 2%. In temperate city driving, air conditioners increase fuel consumption. Car air conditioners are essential safety equipment in warm climates and often reduce fuel consumption.

CAR REFRIGERANT EMISSIONS

Car air-conditioners cool with a simple reversed Rankine cycle. Major components, refrigerant and air flows are shown schematically in Figure 1. A compressor bolted to the engine has an open drive for efficient power transfer and flexible refrigerant hoses to limit vibration stresses. Permanent Schrader valves are provided in both low and high pressure lines, so refrigerant may be added, air released and pressure gauges attached.

A domestic refrigeration appliance leaks less than 0.001 L/year of liquid because the drive motor is sealed inside the circuit. Open drives, hoses and Schrader valves on cars together leak 0.1–1.0 L/year of liquid. Repairs are however usual if leaks exceed 0.4 L/year. A reservoir containing up to 0.5 L of extra refrigerant liquid allows continued operation for several years between recharging. A full charge is 0.4–1.0 L liquid.

Releases of refrigerant to atmosphere must be added to leakage to calculate average emission rate. Releases may occurring during manufacture, handling, shipping or air conditioner servicing. Releases during manufacture, handling and shipping may not be small but depend only slightly on the containers used and hence service procedures. Service releases are frequently
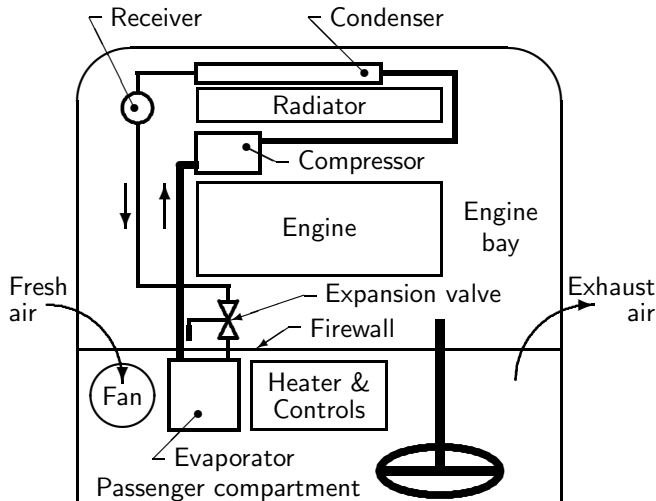
Figure 1: Schematic of car air conditioner with liquid line receiver and expansion valve in engine bay (right hand drive).

many times annual leakage. They depend on charging procedure, skill and effort. The main charging procedures are 'top-up', 'recovery' and 'regas'. Service release from the 'top-up' charging procedure are less than 10 mL liquid per service with low skill and effort. Releases from 'recovery' procedures can be less than 10 mL liquid per service with high skill and effort. Releases from 'regas' procedures may be more than the total refrigerant charge or over 1 L liquid per service if little leakage has occurred since the last regas.

Many small garages and do-it-yourself technicians in North America favour the 'top-up' charging procedure. Even with traditional tools and fittings the procedure is simpler and easier than changing the engine oil and filter. When the low pressure cut-out switch prevents the air conditioner operating about 0.3 L liquid refrigerant is added from a premeasured can. The cans may contain 2% by mass lubricant to make up lubricant lost with leaking refrigerant. Annual total emissions are then just above the leakage rate and are typically half those for regassing. An 0.3 L steel can is readily recycled by modern recycling machinery even if it is accidently full. The container mass is about 80 g less than 50% of HC refrigerant mass compared with about 10 kg or 110% for 20 L reusable cylinders saving substantially on transport energy and pollution. Simplicity and low capital investment make this appropriate to many countries.

For CFCs and HFCs in many developed countries, regulations require 'recovery' procedures. These procedures use a vacuum pump for typically 30 minutes to remove almost all refrigerant from the system and store it in a cylinder before recharging. The procedure removes a large part of the lubricating oil and contaminants from the system with the refrigerant. The commercial value of contaminated refrigerant is negligible. The most profitable legal use of contaminated

Table 1: Carbon dioxide equivalents of car air conditioner emissions.

Refrigerant	12	134a	290/600a
ODP (R11 ODP=1)	0.82	0.00	0.00
GWP (100 year)	8500	1300	3
Liquid density (kg/m^3)	1300	1206	523
Emissions (g/year)	520	482	209
CO_2 equiv. (kg/year)	4420	627	0.6
Ratio to fuel CO_2 (%)	102.8	14.6	0.0

refrigerant is to distill most of it for reuse on site and then return the highly contaminated cylinder to the supplier for cleaning. Such distillation and cleaning are expensive, labour and energy intensive processes. Annual emissions from recovery lie between those for top-up and regas. The capital investment for recovery procedures is inappropriate for many developing countries.

Car air conditioners have no level gauge to indicate the refrigerant remaining before service. The usual 'regas' procedure vents any remaining charge to atmosphere and weighs out a complete new charge. The total emissions are then the slow leakage between regassing and the release of the remaining charge during regas. By conservation of mass these must equal the charge added at the previous regas. Annual total emissions with regassing are thus refrigerant charge divided by the regas interval in years. With regassing the leakage rate has no effected on the average total emission rate. Worldwide this is the most common procedure.

GLOBAL ENVIRONMENTAL IMPACTS

With regassing comparison of refrigerant environmental impacts for any car air conditioner is easy. Table 1 compares refrigerants for a car using 2000 L/year of fuel, having an 0.8 L liquid refrigerant charge and regassed every second year. These assumptions are typical but representative values are not known. One litre of petrol burns to 2.15 kg of carbon dioxide so the fuel consumption emits 4300 kg/year of carbon dioxide. Annual total refrigerant liquid emissions are 0.8/2 = 0.40 L/year for each refrigerant in Table 1.

Aisbett and Pham (1998) have projected the environmental impacts of car air conditioners for thirteen Asian countries with half the world's population. They have considered three scenarios for replacement of CFC-12 from 1985 to 2020. Their scenario two is replacement with HFC-134a and scenario four replacement with the hydrocarbon (HC) mixture R290/600a. By 2020, the HFC scenario gives a total environmental warming impact 286 million Mg/year greater than the HC scenario. More importantly the cost of HFCs is 3.5 billion US $/year greater than HCs mostly in hard currencies.

Measurements at Cape Grim, Tasmania show that global atmospheric concentrations of ozone deplet-

ing refrigerants are still rising and their fluorocarbon replacements are growing exponentially (Fraser 1997, 1998). Major contributors to this are countries exempted from early Montreal Protocol restrictions. A 1998 bulk price for R12 in India was only 1.5 US $/kg and Indian R12 marketed in Indonesia was 3 US $/kg. In 1998 bulk R134a was available in Indonesia for 4 US $/kg.

PHOTOCHEMICAL SMOG AND OZONE

The exhaust from engines using HC fuel contains small amounts of carbon monoxide, HCs and oxides of nitrogen. HCs may also evaporate from the fuel tank and supply system. If sunlight falls on air with high concentrations of nitrogen dioxide and HCs, ozone is formed as a byproduct of HC oxidation and nitration (Carter 1994). These reactions occur with both light and heavy HCs and halons like HFCs and HCFCs (Derwent *et al.* 1996). Ozone concentrations drop after sunset and as HCs become oxides or nitrogen oxides become nitrates.

For heavy halon and HC reactants like liquid fuels, the vapour pressure of the products may be low enough for condensation to a fog, called smog. Refrigerant halons and HCs are light so their product vapour pressure is too high to condense to smog (Avallone and Baumeister 1986).

Johnson and Derwent (1996) found that emissions of refrigerant HCs reduce tropospheric ozone as a whole. When wind is present or sunshine or traffic absent HC refrigerant emissions reduce ozone in cities. For air pollution episodes, emitted refrigerant HCs create less ozone than exhaust HCs (Carter 1994, Derwent *et al.* 1996). For HC refrigerant in car air conditioners to increase ozone during such episodes, their rate of emission would need to be greater than the saving in HC exhaust emissions.

Few HC car air conditioners leak more than 200 g/year or $6.34\mu g/s$. If averaging 20 km/hour in traffic this is 1.14 mg/km. Maclaine-cross and Leonardi (1996) found an average fuel saving on converting from R12 to HC refrigerant was about 1.3%. Exhaust HC emissions of 100 mg/km are well inside current Australian standards for new cars (FORS 1995). We expect the saving in exhaust HC emissions to be proportional to fuel savings or 1.3 mg/km. The net saving in HC emissions is 0.16 mg/km. Typically the reduction in HC emissions from converting to HC refrigerant is much greater.

HC refrigerants in car air conditioners reduce photochemical smog and ozone. These environmental advantages are small compared to reduced global warming and stratospheric ozone depletion.

HYDROCARBONS PROPERTIES

The saturated HCs ethane, propane, isobutane, normal butane, isopentane and normal pentane occur naturally in massive quantities in petroleum gases. The corresponding refrigerant numbers are 170, 290, 600a, 600, 601a and 601 respectively.

The vapour pressure range of HC refrigerants matches that of popular fluorocarbon refrigerants but their significantly lower molecular mass gives them superior transport properties. They are non-hygroscopic and miscible with popular natural and synthetic lubricants. They are good electrical insulators and are compatible with plastic insulation and sealants used in refrigeration systems. They are non-corrosive and chemically stable at temperatures far higher than occur in refrigeration equipment.

HC refrigerants have low toxicity but they are flammable. Among the many necessary precautions in refrigerant safety standards and the literature (Maclaine-cross 1996, 1997) please include:—

- Do not weld, braze or light cigarettes while charging refrigerant or searching for refrigerant leaks.

- Do not use compressed air for leak testing refrigerant circuits. Use dry nitrogen or other inert gas.

- Do not store more than one 20 L cylinder in a closed workshop. Use a lockable wire cage, above ground and outdoors.

The lower liquid density of R290/600a and other property differences make performace best with about one third the charge mass used for R12 or R134a whichever is least. R290/600a can be used with all standard refrigerant tools except halogen leak detectors. Flammable gas detectors can be used for leak detection but soap bubble methods are more effective.

REFRIGERANT PERFORMANCE

The Refrigeration and Air-Conditioning Laboratory at the University of New South Wales has been comparing the performance of refrigerants 12, 134a and 290/600a in car air conditioners since 1993.

From 1994 to 1995, refrigerants 12 and 290/600a were compared on ten typical Australian cars (Maclaine-cross and Leonardi 1996, 1997). 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 mixtures the condenser pressure was 8% higher. The compressor drive shaft torque was not measured. Instead 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 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.

Table 2: Comparison of cooling capacity and COP for three refrigerants at two compressor speeds (Binti Zakaria 1999).

Refrigerant	Charge (g)	Speed (rad/s)	Capacity (kW)	COP
134a	1000	105	3.17	2.78
		209	4.36	1.72
290/600a 1996	303	105	2.14	2.43
		209	3.68	1.70
290/600a 1998	309	105	2.69	2.86
		209	4.06	1.85

From 1996 to 1999, refrigerants 12, 134a and commercial R290/600a mixtures were compared in car air conditioners mounted inside a balanced ambient calorimeter with evaporator and condenser chambers. The chamber and air conditioner was operated at constant temperatures and heat flows for about an hour before a test commenced to eliminate transient effects. The evaporator chamber was at 23.9°C and 50% and the condenser chamber at 35°C for all tests. The most recent tests were on a large car air conditioner designed for R134a. The cooling capacity calculated from an energy balance on the condenser chamber was consistently about 2% less than that from an energy balance on the evaporator chamber for all three refrigerants tested.

Table 2 shows six preliminary results comparing the cooling capacity and coefficient of performance for R134a and commercial R290/600a's manufactured in 1996 and 1998. The 1996 R290/600a has not yet been analysed but the manufacturer believes it contains about 2% ethane. The 1998 R290/600a was analysed as R170/290/600a/600 [0.4/54.7/43.5/1.3]. At 15°C the boiling pressure of the 1996 R290/600a was measured as 590 kPa and the 1998 as 560 kPa. Using Ely and Huber (1992)'s SUPERTRAPP program the temperature glide of the 1996 R290/600a was predicted as 12 K and for the 1998 as only 8.2 K.

Table 3 is the current specification for HC refrigerant used in Australian car air conditioners. Supplies with odorant added are cheaper because of reduced road tanker handling costs. In the workshop, odorant is also a useful safety precaution. The factors effecting performance here are boiling point and glide. The poorly performing 1996 R290/600a in Table 2 is also outside the specification. The test results are consistent with the specification.

REFRIGERANT MANUFACTURE

Total Australian sales of HC refrigerant are small. Combining data from the three main manufacturers and allowing for imports and a number of smaller manufacturers my estimates are:

Calendar year	1995	1996	1997	1998
Domestic sales (Mg)	3	11	18	29

Table 3: HC refrigerant quality specification for car air conditioners (updated from IAHRA 1996).

Component	Unit	Specification Tolerances
Saturated HCs	% mass	> 99.5
Ethane	% mass	< 0.5
Propane	% mass	–
Isobutane	% mass	–
Normal butane	% mass	–
Pentanes	% mass	< 0.5
Normal hexane	mg/kg	< 100
Aromatics	mg/kg	< 10
Unsaturated HCs	% mass	< 0.05
Water	mg/kg	< 10
Ethyl mercaptan	mg/kg	25
Other sulphur compounds	mg/kg	< 5
15°C bubble point pressure	kPa	480–570
Temperature glide	kelvin	< 12
Lubricant additive	% mass	< 2

The 1998 sales represent only 1.5% of the total Australian refrigerant market. Exports sales for Australian suppliers were much smaller than domestic sales. Only batch production was economic for such small volumes. From 1996 to 1998 Australian consumption of hydrocarbon refrigerant grew by over 50% annually. Similar growth rates are occurring in North America and Europe. If this continues for 10 years fluorocarbons will be completely replaced.

The basic cost of mass producing HC refrigerants is less than 1% of fluorocarbons (Aisbett and Pham 1998). Australia produces over three million Mg of commercial propane and butane a year and most of this is naturally occurring. Two thousand Mg of HC refrigerants would displace all competing refrigerants. Naturally occurring sources have a very low content of unsaturated HCs and other impurities. Prices vary but are usually below 0.30 US $/kg delivered by road tanker. Most countries with oil wells are likely to have even cheaper supplies.

ETHANE REMOVAL - R170/290 [6/94] is a good replacement for the CFC R502 used in commercial refrigeration. Commercial propane usually contains more than 2% ethane so it cannot be mixed with commercial butane to make a satisfactory R290/600a and less than 6% ethane so it cannot replace R502. Ethane greatly increases temperature glide and must be removed. The ratio K of ethane mass fraction in equilibrium vapour to that in liquid commercial propane is about three (Ely and Huber 1992). A compressor with 1 L/s displacement can pump over 1 Mg/day of this vapour through a 6 kW condenser coil submerged in the propane liquid. A trap on the coil exit should prevent vapour entering the condensate tank (Figure 2). For

2.0–2.5% ethane in the commercial propane, the condensate may be repumped to get a product with 6% ethane. Commercial propane feed with 3% or less ethane is desirable to avoid producing more R170/290 than can be sold.
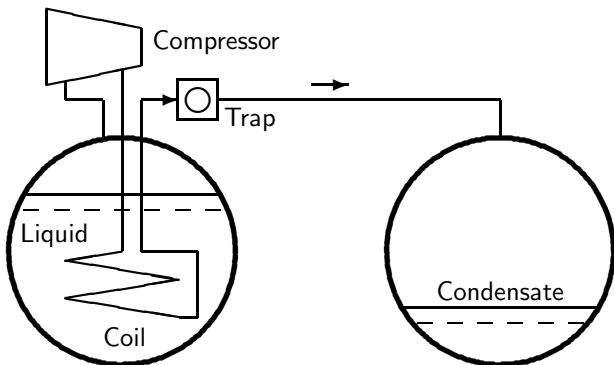

Figure 2: Schematic of batch pumping of ethane rich vapour off propane liquid to lower ethane mass fraction in the liquid.

Conservation of ethane and propane mass in the liquid gives the final mass fraction of ethane in the liquid x_f as a function of the initial mass fraction x_i as

$$x_f = x_i \left(\frac{m_f}{m_i} \right)^{K-1} \quad (1)$$

where m_i is the initial, m_f the final liquid mass and K is assumed constant. Conservation of ethane and propane mass overall gives the average ethane mass fraction in the condensate and vapour phases x_c as

$$x_c = \frac{x_i m_i - x_f m_f}{m_i - m_f} \quad (2)$$

If the volume of the vapour above the liquid is less than half the liquid tank volume when pumping finishes, x_c is close to the ethane mass fraction in the condensate tank. As an example consider $K = 3$, $x_i = 3.00\%$ and $m_f/m_i = 0.6181$ from Equation 1, $x_f = 1.146\%$, and from Equation 2, $x_c = 6.00\%$.

HC replacements for R12, 22 and 502 are manufactured in Australia. The compressor, coil and trap above are the additional major equipment items necessary to use commercial Australian HCs instead of highly refined imported supplies. This method has resulted in manufacturing costs less than half that of landing fluorocarbons even though fluorocarbons have fifty times the sales volume in Australia. These Australian HC refrigerants cost less than 1 US $/kg to produce and are still significantly cheaper than HFCs and even Indian CFCs after shipping to South-East Asia.

In 1998, commercial secondary separation of Australian butane commenced. R600a is energy-efficient in small appliances (Maclaine-cross and Leonardi 1997) and their manufacturers prefer pure isobutane. Commercially pure isobutane has now replaced commercial butane in Australian R290/600a.

Safety precautions in manufacturing Australian HC refrigerants are the same as in the LPG fuel industry (Maclaine-cross 1996). Documentation, sites and equipment are well established and much cheaper than other chemical plant for the same level of safety.

DISTRIBUTION

HCs have no inherent cost advantages in distribution. Freight charges depend on volume not mass.

OZ Technology of Idaho was first to use the 0.3 L can technology for R290/600a with instructions, tags and added lubricant. Contract propellant canners using existing equipment in Australia can ship pallet loads for about 8 US $/kg HC refrigerant.

Australian HC suppliers chose the 20 L cylinder technology for acceptance by the existing market. Their refrigerant distribution improvements include:—

- Distribution with other car parts and supplies through traditional automotive distributors.

- Encouraged new refrigeration distributors specializing in environmentally acceptable technology.

- Encouraged LPG cylinder manufacturers to use their higher volume to make refrigerant cylinders at lower cost.

- A US $120 deposit on each 20 L cylinder instead of rental. The accounting systems of car parts distributors handle deposits but not always rental.

- Cylinders are packed in a cardboard carton which is usually removed and replaced at the cleaning and filling plant. This reduces handling damage to valves, paint and labels.

- Instructions are packed in the crate with each cylinder.

- Double valves to prevent valve leaks in the distribution chain.

- Ethyl mercaptan odorant warns of leaking cylinders.

- Safety improvements and advice and information provided to customers reduce the cost of public liability insurance.

Even with these improvements pallet loads of full cylinders ship for 11 US $/kg HC refrigerant.

Cans are very suitable for top-up charging of car air-conditioners which uses half the refrigerant with half the emissions of the regas method typically used with cylinders. With cans a technician typically uses half the mass of refrigerant servicing the same number of vehicles as with cylinders. Since labour is also less with cans a technician could pay twice as much per kilogram for refrigerant in cans and still profit. The price per

kilogram for pallet loads of HC refrigerant in cans is actually less than for cylinders.

CONCLUSION

The world needs car air conditioning but total refrigerant emissions from leakage and service releases are typically 0.4 L/year of liquid for regas. If the refrigerant is HFC–134a this adds about 15% to the car's total global warming emissions. For Asia the refrigerant is typically CFC–12 adding about 102% to emissions. HC refrigerants can reduce this warming and ozone depletion to zero and slightly reduce tropospheric ozone.

Hydrocarbon refrigerant manufacture can use commercial butane and propane as feedstocks which are naturally abundant with high purity. The only essential secondary processing apart from mixing is to 'pump off' ethane from the commercial propane. This gives HC replacements for R12, 22 and 502 from the same plant which are half the price of competing fluorocarbons.

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