Today mobile air conditioning systems (MACs) in cars, trucks, trains and buses still contain refrigerants which harm the ozone layer and/or increase the greenhouse effect. Currently, mobile air conditioning accounts for about one fifth of total global refrigerant emissions (1). Solutions with halogen-free natural refrigerants for MAC are possible. One of the most promising candidates is the natural refrigerant carbon dioxide (CO₂), which is already used in buses.

**Overview**

Since ozone-depleting refrigerants like the CFC R 12 for MAC have been banned, hydrofluorocarbons (HFCs) are now used for mobile air conditioning. But HFCs also contribute considerably to the greenhouse effect. The global warming potential (GWP) of the widely used HFC R 134a is 1,430 times higher than that of CO₂. That is why the European Union, in addition to requiring better tightness of R 134a systems and their qualified maintenance, prohibits the use of high-GWP refrigerants in new types of car and light-duty-vehicle MACs starting in 2011. Even though the car industry today still prefers fluorinated refrigerants as substitute, in the long term natural refrigerants like CO₂ can reduce the overall environmental impact from mobile air conditioning considerably. CO₂ is already used as a refrigerant for buses and is also suitable for mobile air conditioning systems for cars.

**Relevance**

Worldwide 812 million cars were on the road in 2002, and a strong rise to over 2 billion cars is estimated for 2030 (2).

The number of cars fitted with air conditioning has increased sharply. Today, in industrialized areas like Europe, the U.S. of America or Japan almost every new car is fitted with a MAC. In rapidly developing countries like India, 92% of all new vehicles are equipped with air conditioning (3). In 2050, worldwide estimates foresee a MAC fitting rate of 85% for all vehicles (4). Since the ban on the ozone-depleting CFC refrigerant R 12 (dichlorodifluoromethane) for MACs it has been replaced mainly by the HFC R 134a (tetrafluoroethane) (Fig. 1). Some trains and buses also use the HFC mixture R 407C. Worldwide, approximately 50% of buses and trains still use the ozone-depleting HCFC R 22 (1).

The filling amount per car is about 1 kg, buses and trains contain about 10 – 20 kg refrigerant per MAC unit. Passenger cars contain over 80% of HFCs used in the MAC sector (4).

**Emissions**

Air conditioning systems in vehicles are – unlike household refrigerators – not completely closed systems. Refrigerant is released into the environment not only as a result of accidents or damage from flying stones, but also in normal operation and during filling, servicing, repair as well as disposal. Emission rates are at least 10% of the refrigerant per year and rise depending on age and maintenance of the MAC system.
MACs are responsible for 21% of total global refrigerant emissions. Whereas CFC R12 emissions are decreasing, HFC R134a emissions are rising considerably (6). Looking only at HFC refrigerants, about 60% of global emissions of all HFCs come from MAC (1).

It is expected that global emissions will continue to rise, to over 180,000 tons of R 134a per year in 2020, corresponding to about 240 million tons of CO2 equivalents if no measures are taken (5). In the long term global emissions will more than double to over 500 million tons (Fig. 2).

### Alternative Refrigerants for MAC

#### 1 Carbon dioxide (R 744)

Carbon dioxide (CO2), a component of air, has experienced a renaissance as refrigerant in the last 10 years. Today it has been introduced as refrigerant e.g. in industrial refrigeration, for supermarkets and in hot water heat pumps.

![Picture 1: Image of a CO2 mobile air conditioning system. CO2’s name as a refrigerant is R 744. (© UBA 2009)](image)

Automobile manufacturers and suppliers identified CO2 as a refrigerant suited best also for air conditioning systems for cars even before the EU MAC Directive was issued. Several big automobile companies and suppliers in Europe, USA and Japan have equipped test cars with CO2 mobile air conditioning systems, frequently in joint programmes (7).

In addition to its good refrigeration properties, its small contribution to the anthropogenic greenhouse effect (GWP of 1) compared to other refrigerants and its substance properties “not flammable” and “non toxic” were the reasons for choosing CO2. CO2 is cheap and available worldwide.

The tests with mobile air conditioning systems in passenger cars show the high efficiency of CO2 as refrigerant for this application (7).

### Legal Provisions

In Europe, the refrigerant R 134a with a GWP of 1430 has to be phased out. The EU MAC Directive 2006/40/EC prohibits the use of MAC systems containing HFCs with a global warming potential (GWP) of more than 150, first - from 2011 onwards – in new vehicle types, and from 2017 in the MAC system of every new passenger car and small commercial vehicle.

This has resulted in a worldwide discussion about suitable alternatives with a GWP below 150. The following provides a short overview of alternative refrigerants for MACs.

![Graph: NEDC Fuel Consumption Test R134a versus R744.](graph)

Fig. 3: Difference in fuel consumption between R 134a vs. CO2 for a MAC system in a Volkswagen Touran (8).

Today all components of the CO2 mobile air conditioning system for cars have been developed so that it is ready to go into serial production.

For buses CO2 is already used. Over a dozen city buses in daily operation are equipped with CO2 air conditioning systems in Germany. Instead of 10 kg of R 134a, the system needs only 5 - 6 kg of CO2 as refrigerant. By switching from R 134a to CO2 it is possible to save about 30% of direct and indirect greenhouse gas emissions (7).

Furthermore, in 2011 the German railway company DB AG started to test a diesel trainset with an electrically driven prototype CO2 system (7).

CO2 systems can - in addition to the cooling function in summer - be used in the heat pump mode in winter. Inefficient conventional heating can thus be replaced. Additional heating is particularly important for cars with hybrid or fully electric drives, which do not provide sufficient motor heat; here tighter electrically driven compressors can be used.
For buses, tests with cooling and heat pump mode have already been carried out. A city bus equipped with a CO₂ MAC with a heat pump function saves 50% of the fuel for heating (7).

Pic. 2: Public bus of the Berlin Transportation Company with CO₂ MAC system (@Konvektak 2010)

2 Hydrocarbons

Hydrocarbons such as e. g. propane or butane have proved a success as refrigerants in numerous applications. They do not deplete the ozone layer and their GWP is very low. In projects in Australia and the U.S. conventional MAC systems were filled e. g. with mixtures of the hydrocarbons propane and isobutane (9)(10). It is estimated that about 1 million cars in Australia have been retrofitted with hydrocarbons (11).

The high flammability of hydrocarbons may be a risk for the occupants of a car. That is why their use is prohibited in mobile air conditioning systems in passenger cars, e. g. in the U.S.A. (12). Unlike flammable fluorinated refrigerants, hydrocarbon-based refrigerants form no hydrogen fluoride when burned; e. g. during an accident. Most automobile manufacturers only consider using hydrocarbons if the refrigerant is contained in a hermetically sealed second cycle in the motor compartment as is required for the flammable fluorinated refrigerant R 152a.

3 Fluorinated substitute refrigerants

The chemical industry presented and rejected again in rapid succession a wide range of new halogenated substitute refrigerants with a global warming potential below 150 for MAC systems in cars. Currently, R 1234yf and R 152a are under discussion.

1,1-difluoroethane (R 152a)

The flammable HFC R 152a (1,1-difluoroethane) has a relatively low GWP of 140. Like all fluorinated substances it releases toxic hydrogen fluoride (HF) in case of a fire.

The US EPA approved the flammable R 152 only with safety measures like the installation of a second cycle, which reduces the energy efficiency and increases the costs, size and weight of the system (13). R 152a was excluded as substitute for CFC 12 in the 1990s in Europe. Some experts doubted that it will be possible to resolve all safety problems with R 152a at reasonable cost (7).

2,3,3,3-tetrafluoropropene (R1234yf)

The new refrigerant R 1234yf (2,3,3,3-tetrafluoropropene) also belongs to the group of HFCs. The American chemical companies Honeywell and DuPont hold the major part of the R 1234yf patents for production and use.

R 1234yf has a global warming potential of 4. With 11 days its atmospheric life time is short, but the main decomposition product, trifluoroacetic acid (TFA), is toxic to algae, persistent and accumulates in the environment. R 1234yf contains up to 0.5% of impurities, some of which are toxic such as 1,2,3,3,3-pentafluoropropene (1225ye)(7).

R 1234yf is flammable and has to be labelled as “extremely flammable gas” according to the global UN classification. The autoignition temperature of R 1234yf is 405°C (for comparison: propane 470°C). With a density about 4 times higher than air R 1234yf may accumulate at ground level forming explosive mixtures. As all other fluorine-containing refrigerants R 1234yf may form toxic hydrogen fluoride (HF) during combustion (7).

Investigations carried out by the German Federal Institute for Materials Research and Testing (BAM) showed that there are risks associated with the use of R 1234yf. In practical tests carried out under application-oriented conditions, BAM confirmed the formation of explosive gas mixtures and toxic HF when using R 1234yf. HF formation was found in the case of fire and also without explosion or fire on hot metal surfaces as usually present in engine compartments.

In the event of a fire or an explosion HF concentrations of more than 90 ppm were detected in the passenger compartment, which may result in irreversible damage to human health(7) (14). In the U.S. for example 236,000 vehicle fires are reported for 2008 (15). Thus, should R 1234yf be used, a comprehensive risk analysis will be required and precautionary measures will have to be taken.

Pic. 3: Release of 46 grams of R 1234yf in 70 seconds with formation of hydrogen fluoride (HF) at levels above 90 ppm (© UBA 2010|14)
With R 1234yf a drop-in substance has not been found. It cannot be simply filled into the old R 134a system. The use of 1234yf requires replacing some MAC material like plastics from seals and hoses that would be affected by the new refrigerant, very clean and moisture free interior surfaces of the MAC system, a new refrigerating oil ensuring stability and durability thus preventing acid formation and corrosion, and, finally, reconstruction of the MAC for dealing with the 8 – 15% lower refrigerating capacity compared with R 134a (7).

**Outlook**

Emissions of the refrigerant R 134a from MAC systems will increase if no reduction measures are taken. By using natural refrigerants these emissions may be largely avoided. CO₂ as a cheap, non-flammable refrigerant is already proven for buses and is also suitable for mobile air conditioning systems for cars and excellent for heating and cooling electric vehicles. CO₂ has the highest and most cost-effective global potential for reducing greenhouse gas emissions.

**References**


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