NATURAL REFRIGERANTS FOR MOBILE AIR - CONDITIONING IN PASSENGER CARS

A CONTRIBUTION TO CLIMATE PROTECTION

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1. Introduction

Today mobile air-conditioning systems in passenger cars contain a refrigerant paying a major contribution to increasing the greenhouse effect. For the time being, about 30% of the worldwide emissions of hydrofluorocarbons arise from mobile air-conditioning systems in passenger cars [UNEP 2009]. That is why in Europe this refrigerant – according to Directive 2006/40/EC – has to be substituted by a substance less harmful to the climate beginning in 2011.

2. The present situation

2.1 Vehicle population and fitting rate with mobile air conditioning

41.7 million cars were registered in Germany on January 1, 2011. Already three quarters of all cars registered in Germany are air-conditioned. In the last few years the percentage of new cars with fitted with mobile air-conditioning systems has increased sharply. In 1995 only a quarter of all cars newly registered were air conditioned. In 2008 with 96% nearly all new cars had air-conditioning [KBA 2010; Schwarz 2004; Schwarz 2010].

2.2 The greenhouse gas tetrafluoroethane (R134a)

Today almost exclusively tetrafluorethane is used as refrigerant in mobile air-onditioning systems. Tetrafluoroethane is a hydrofluorocarbon, abbreviated HFC[1] -134a, as refrigerant it is usually designated as R134a, with "R" standing for refrigerant. Its contribution to the greenhouse effect (GWP)[2] is by 1,430 times[3] higher than that of carbon dioxide.

Until 2017 air-conditioning systems in many new passenger cars are allowed to be filled with the refrigerant R 134a (see also Chapter 2.4 Legal provisions). In the last few years the average charge per air-conditioning unit decreased below 0.7 kilograms of refrigerant. Nevertheless the annual consumption of the refrigerant R134a for the initial filling of air-conditioning systems in new passenger cars increased distinctly due to the sharply increasing fitting with air-conditioning systems. In 1995 still 1,400 tons of the refrigerant R134a were filled into mobile air- conditioning systems in passenger cars in Germany, in 2008 already 3,800 tons.

In 2008 altogether about 23,645 tons of the refrigerant R134a were in the mobile air-conditioning systems in passenger cars in Germany which corresponds to about 31 million tons of CO_2 equivalents [Schwarz 2010].

2.3 Contribution to the greenhouse effect: mobile air-conditioning systems in passenger cars and emission of refrigerants

Mobile air-conditioning systems in passenger cars work like a refrigerator with a compression refrigerating system; the passenger compartment of the car corresponds to the interior of a refrigerator. Yet, air-conditioning systems in passenger cars are – contrary to the household refrigerator – no completely closed systems. The compressors are mechanically driven by the automobile motor via a shaft and are exposed to the motor vibration; the refrigerant flows through hoses to the remaining units of the refrigerant cycle. That is why the refrigerant escapes gradually through the seals of the air conditioning system into atmosphere already during the normal operation of the system in the car. Yet, refrigerant is also released into environment during the first filling, service and repair in the garage, when the system is damaged by accidents or flying stones and when the mobile air-conditioning systems are disposed of [Schwarz 2001; Schwarz 2005].

Releasing of refrigerants – the so-called refrigerant emissions – are steadily increasing in Germany. If in 1995 only 133 tons of R 134a were released, in 2008 the amount rose already to 2,700 tons. This corresponds to a contribution to the greenhouse effect of 3.5 million tons of CO_2 equivalents per year. For comparison: If in Germany 2 million economical passenger cars are run for one year they release also about 3.5 million tons of CO_2.[4]

Relating the refrigerants emission to the distance covered by car 7 grams of CO_2 per kilometre are released by the refrigerant in addition to the carbon dioxide coming from fuel.[5]

Today, already more than one third of the overall emissions of hydrofluorocarbon substances group come from mobile air-conditioning systems in passenger cars. If there is a continued use of R134a, a further increase of the emissions to 3,500 tons of this refrigerant is to be expected in 2020 [Schwarz 2003; Schwarz 2010]. In many countries with on average older cars, less developed service and frequently lacking disposal structures the refrigerant emissions are usually clearly higher during a car life. Worldwide it is expected that without taking measures the emissions will rise further to more than 180,000 tons of R134a per year in 2020. This corresponds to about 240 million tons of CO_2 equivalents [UNEP 2009].

2.4 Legal provisions

On July 4, 2006 the EU Directive[6] relating to emissions from air conditioning systems in motor vehicles, also referred to as MAC[7] Directive, entered into force. From January 1, 2011 onwards this EU Directive prohibits the use of mobile air-conditioning systems containing fluorinated greenhouse gases with a global warming potential (GWP) of more than 150 in passenger cars and small commercial vehicles.[8] Opting out will be slowly. First of all, new types of cars with such mobile air-conditioning systems are no longer registered and sold from January 1, 2011 onwards. Also the retrofitting of any vehicles with such systems is prohibited. Beginning with January 1, 2017 all mobile air-conditioning systems of newly built passenger cars and car-like commercial vehicles have to be filled with a refrigerant with a GWP below 150.[9]

In addition, the Directive sets requirements to the tightness of air conditioning systems effective since June 21, 2009 for all newly produced passenger cars and small commercial vehicles with R134a-systems that have to be proved in the type-approval process of the car.

3. Refrigerants for mobile air-conditioning in passenger cars

3.1 Carbon dioxide (R744) – as refrigerant a contribution to climate protection

Since there has been known that synthetic refrigerants damage the ozone layer and intensify the greenhouse effect[10], the ecologically most favourable and sustainable solution is to use natural refrigerants such as CO_2. Carbon dioxide (CO_2), a component of air, has been used for refrigeration already in the middle of the last century. Due to the good refrigeration properties of this refrigerant and its low global warming potential CO_2 experienced a renaissance as a refrigerant in the last 10 years. With the level of knowledge reached in the mean time very energy-efficient refrigeration and heat cycles may be implemented with CO_2. Today CO_2 is introduced as refrigerant e.g. for the supermarket and in hot water heat pumps. As refrigerant CO_2 is designated by the short term R744.

Already in the 90-ies before the EU Directive entered into force German automobile manufacturers and suppliers have identified CO_2 as a refrigerant suited best also for air conditioning systems in passenger cars. In 2007 the German automobile manufacturers announced finally to use the refrigerant CO_2 and started to prepare its series introduction. In addition to its good refrigeration properties, its small s contribution to the anthropogenic greenhouse effect (GWP of 1) compared to other refrigerants and its substance properties “not flammable” and “nontoxic” have been decisive for choosing CO_2. CO_2 is cheap and worldwide available, it is e.g. obtained as a by-product in chemical industry and air fractionation.

Compared with R134a and R152a (1.1-difluoroethane) CO_2 allows a faster cooling and heating of the passenger compartment. This does not only mean a higher comfort for the end customer, but also an increase in the security as misted up car windows are faster freed from moisture. The tests of mobile air-conditioning systems in passenger cars show the high efficiency of CO_2 as refrigerant for this application [Wieschollek, Heckt 2007; Wolf 2007; Neksa etc. 2007; UBA 2008; Graz 2009].

Mobile air-conditioning systems with the refrigerant CO_2 as compared with the refrigerant R134a have to be designed for a higher pressure (up to 135 bar). To this end new components for the refrigeration cycle had to be developed which was successfully solved by the engineering expertise of European engineers. The installation space required, an important factor for the overall car construction, did not have to be extended for the new CO_2 equipment, the system has rather a smaller volume due to the good refrigeration properties of CO_2. Provisions should be made to not allow developing too high CO_2 concentrations in the passenger compartment.

Today all components for the CO_2 mobile air-conditioning system are developed so that the serial production of the equipment may be started. Several big automobile companies and suppliers in Europe, USA and Japan equipped test cars with CO_2- mobile air conditioning systems, frequently in joint programmes [Mager 2003; Wertenbach 2005; Neksa 2007; Parsch 2007; Riegel 2007; Morgenstern 2008; SAE 2009].

A further advantage of the CO_2- mobile air-conditioning system is that in addition to the cooling function in summer it may be used as heat pump in winter for the fast heating of the passenger compartment and, in particular, of the windscreen. This improves the security and allowing renouncing other conventional, less efficient additional heating systems. An additional heating will be required for many cars in future, in particular, for cars with hybrid or fully electric drives as the waste heat of an extremely efficient motor or electromotor is too low to provide sufficient heat [VDA 2004; Heinle a.o. 2003; Heckt 2004; Neksa 2005; TWK 2010].

Analyses of the emission of climate-effective gases of air conditioning systems in passenger cars with various refrigerants (LCCP)[11] with experimentally detected technical data of CO_2 components show advantages of the refrigerant CO_2 as to the greenhouse gas emission over the lifetime against R 134a and R1234yf under nearly all climatic conditions [Hafner 2004; 2007; Neksa 2007; Wolf 2007].

3.2 Hydrocarbons – in the mean time widely used in Australia

Hydrocarbons such as e.g. propane or butane have proved a success as refrigerants in numerous applications. As they do not deplete the ozone layer and their global warming potential is very low their use also in mobile air-conditioning systems is advocated e.g. by nongovernmental organizations. In Australia and the USA demonstration projects were implemented where traditional air conditioning systems were filled e.g. with mixtures of the hydrocarbons propane and isobutane [COM 2003; Maclaine-cross 2004]. Estimates proceed on the facts that hydrocarbons were retrofitted into mobile air-conditioning systems of about 1 million cars in Australia [Hoare 2010].

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. [EPA 2003]. Contrary to the flammable fluorinated greenhouse gases, in the case of the combustion of refrigerants on the basis of hydrocarbons (e.g. during an accident) no hydrogen fluoride is formed. Most of the automobile manufacturers consider, as a rule, only to use hydrocarbons if the refrigerant is in a second cycle hermetically closed in the motor compartment as it is required for R152a (s. Chapter 3.3.1).

3.3 Fluorinated substitute refrigerants – a way of solution?

Parts of the automobile industry aimed at finding a substitute which does not require to change the introduced air conditioning equipment (a so-called drop-in substance). First of all, chemical industry suggested a hydrofluorocarbon HFC -152a (R 152a) and presented and rejected again in rapid succession most various new substitute refrigerants with a global warming potential below 150 for mobile air-conditioning systems in passenger cars since 2006. So far the HFC-1234yf (R1234yf) has been followed up.

3.3.1 1.1-difluoroethane (R152a)

Some, notably US manufacturers considered using another greenhouse gas, the hydrofluorocarbon (HFC) 1.1-difluoroethane (R152a) instead of R134a. With a GWP of 140 as against the present refrigerant R134a with a GWP of 1,430 R152a has a low GWP.

However, R152a is - like hydrocarbons - flammable, its auto-ignition temperature is 455°C. In the case of fire R152a as a fluorinated substance releases a. o. toxic hydrogen fluoride (HF).

In 2008, the American environment authority EPA licensed the refrigerant R152a, yet with conditions to be fulfilled[12] [EPA 2008]. A measure to ensure security is e.g. to install a second heat exchanger in connection with a second cycle reducing energy efficiency and raising costs, size and increasing the weight of the system. The personnel working in the production and service has to be instructed in handling flammable refrigerants.

Already in 1990 security concerns resulted in the fact that R152a was excluded as substitute for the chlorofluorocarbon (CFC) R12[13] by the German automobile manufacturers. Some experts doubted that it will be possible to settle all security problems at an appropriate expenditure [Mager 2005].

3.3.2 2,3,3,3-tetrafluoropropene (R1234yf))

The refrigerant with the short term R1234yf is a comparatively new substance belonging to the group of hydrofluorocarbons (short: HFC). The chemical name of the substance is 2,3,3,3,-tetrafluoropropene.

R1234yf has a global warming potential of 4. With 11 days its atmospheric life time is short, yet the decomposition products correspond to those of the refrigerant R134a [Nielsen at al 2007; Papadimitrou at al 2008; Yau 2008][14]. A very stable decomposition product is the trifluoroacetic acid toxic to algae which may accumulate in the environment [Kajihara 2010; Luecken 2010].

As R152a and hydrocarbons R1234yf is flammable and has to be labelled “extremely flammable gas” according to the CLP Regulation [GHS 2008]. The auto-ignition temperature of R1234yf is 405°C (for comparison: propane 470°C) [Honeywell 2008; Du Pont 2009]. R1234yf has a density about 4 times higher than air. Therefore, it may accumulate at ground level forming there explosive mixtures. As all other fluorine-containing refrigerants R1234yf may form toxic hydrogen fluoride (HF) during combustion.

In practical tests with settings close to application conditions, the Federal Institute for Materials Research and Testing (BAM) confirmed the formation of explosive gas mixtures and toxic hydrogen fluoride (HF) in connection with the use of R 1234yf. In the event of a fire or explosion concentrations of more than 90 ppm HF were detected in the passenger compartment.

Even without an explosion or fire, moreover, hydrogen fluoride forms on hot surfaces such as are commonly found in engine compartments. The concentrations of hydrofluoric acid detected are, as a rule, above the AEGL 2-value[15]. Exceeding of the AEGL 2 - value results in irreversible damages for human health [BAM 2010; UBA 2010a, b].

The investigations carried out by the BAM show that using R1234yf is connected with dangers. They result from hydrogen fluoride developing from the refrigerant R1234yf in the case of fire and high temperatures already without fire. In Germany between 30,000 and 40,000 vehicles are on fire a year. It is to be expected that hydrogen fluoride is formed during such an event. As per order BAM has not quantified the additional risk – this may be only done by the automobile manufacturers for specific vehicles – yet it points to the fact that in the case of R1234yf being used a comprehensive risk analysis will be required and many precautionary measures will have to be taken. Potential measures are e.g. the rigorous shielding of hot surfaces in the motor compartment, installing an automatic fire extinguishing system in the motor compartment, measures preventing hydrogen fluoride from being emitted into the passenger compartment, prevent sparking also in the case of an accident (a. o. switching off power supply) and informing and training of a rescue personnel.

The automobile manufacturers hoped that the new refrigerant would be a substitute which may be directly filled into the traditional air conditioning system instead of the old refrigerant. In refrigeration this is called a drop-in substance. Yet, R1234yf may not be simply filled into the old R134a system. Plastic materials such as seals and hoses have to be replaced and a new suitable refrigerating oil has to be found. Furthermore the compatibility of the refrigerant and its impurities with the refrigerating oil and further materials of the mobile air-conditioning system has to be ensured which may require further changes of the system. Thus, with R1234yf a drop-in substance has not been found.

Although the thermodynamic properties of R1234yf are similar to those of R134a the refrigeration capacity of R1234yf is by 8 to 15 % lower than that of R134a [Petitjean 2010; Eusitice 2010; Wieschollek 2009].

R1234yf is more sensitive to moisture and air than other refrigerants. Oil producers and refrigeration institutes consider the development of suitable refrigeration oils and additives for the refrigerant R1234yf by far more complicated than for R134a. All materials of the refrigeration cycle have to be tested to its compatibility with the refrigerant/oil/additive system still to be developed. R1234yf contains up to 0.5 % of impurities the composition of which differs depending on the production process and which are partly toxic such as 1,2,3,3,3-pentafluoropropene (1225ye). These impurities may reduce essentially the stability of the refrigerant/oil/additive system and of the refrigeration cycle components and seals [Low, Schwennesen 2009; Seeton 2010; Grimm 2010; Dixon 2010].

The American chemical companies Honeywell and DuPont hold the major part of the production patents for R1234yf [Patents 2010]. A European patent for using R1234yf in air conditioning systems was granted [Chemie.DE 2010].

The production technology for R1234yf is not yet adopted in industrial production. DuPont plans first commercial supplies to the automobile industry starting in the 4th quarter 2011. A plant to meet the demand on worldwide level is to be put in operation later [Seeton 2010]. So far specific data relating to the costs of the refrigerant R1234yf as well as to the costs of the equipment of the plants for producing R1234yf are not available. Refrigerant costs by 10 to 20 times higher than those of R134a are mentioned [Sorg 2009; Eustice 2010].

In spite of the disadvantages of the refrigerant and of the open questions the German automobile manufacturers announced in May 2010 that they will use the flammable, fluorinated refrigerant R1234yf for air conditioning systems in the new car types from 2011 onwards.

3.3.3 Other fluorinated refrigerants

In 2009 a chemicals producer presented again a new refrigerant mixture of fluorinated hydrocarbons which, however, will be only available on the market at the earliest in 2014. The global warming potential will be close to 150. This mixture will be also flammable. However, this refrigerant will be in energetic respect better than R134a and R1234yf [Low 2009; Low, Schwennesen 2009; UNEP 2010]. Further information is, for the time being, not available so that it is not possible to assess the refrigerant mixture.

4. Future Perspectives

CO_2 is the new refrigerant suited best for mobile air-conditioning systems in passenger cars. CO_2 is not flammable and has a good refrigeration capacity. CO_2 air conditioning systems are energy efficient: in summer the additional consumption is lower and in winter the air conditioning system may be switched over to function as heat pump. CO_2 is worldwide available at favourable prices.

As refrigerant CO_2 has the highest and most cost-effective reduction potential for greenhouse gas emissions for cars worldwide. The emission of the refrigerant R134a will rise worldwide; without reduction measures the emissions will total to more than 180,000 tons worldwide in 2020. This corresponds to roughly 240 million tons of CO_2-equivalents[16]. If CO_2 was used as refrigerant these emissions might be largely avoided. To reach a comparable saving by taking engine-related measures the automobile manufacturers would have to reduce the fuel consumption by about 10%[17].

Though the fluorinated refrigerant R1234yf fulfils the demands made by the Directive 2006/40/EC relating to emissions from air-conditioning systems in motor vehicles it is not a solution improving sustainably climate protection. The global warming potential of R1234yf is by four times higher than that of CO_2. If the mobile air-conditioning technique so far applied is maintained substances dangerous to climate like R134a or other cheaper refrigerants may be refilled. This will not be possible for systems with the refrigerant CO_2.

Also for mobile air-conditioning for future highly efficient vehicles with internal combustion engines, yet also for hybrid and electric vehicles the refrigerant CO_2 is technologically the best solution to efficiently combine cooling and heating.

On the whole – for technological reasons and from the viewpoint of climate protection – the refrigerant CO_2 will be also in future the best alternative for mobile air-conditioning.

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[1] HFC are hydrocarbons consisting next to carbon only of hydrogen and fluorine.

[2] The global warming potential (GWP) indicates by how many times more a substance contributes to the warming of the earth atmosphere as compared with carbon dioxide. The greenhouse effect is absolutely necessary for life on earth; the gases in the atmosphere retain partly the heat radiation of earth. The principle is similar to that in a greenhouse, therefore the name. The problem is that since industrialization has started ever more greenhouse-effective substances are released into the atmosphere (so-called anthropogenic greenhouse effect) contributing to a rising of the temperatures on earth and resulting in further changes of the climate.

[3] Information: According to latest calculations the global warming potential (GWP) totals about 1430 for R134a: all figures used here are taken from calculations for the World Climate Council (IPCC) where the factor 1300 has still served as basis of calculation. When referring to the GWP, usually the GWP value for a period of 100 years (GWP100) is used.

[4] Average annual driving performance (distance covered) 14,000 km/year [TREMOD 2010], CO2 emission of an economical car approx. 120 g/km

[5] Emission per car and year :10 % at an average total refrigerant charge of 0.69 kg (2008) result to 69 g of refrigerant/year, annual driving performance of 14,000 km/year, Greenhouse effect (GWP 100) of R134a = 1,430

[6] EU Directive 2006/40/EC of the European Parliament and the Council of May 17, 2006 relating to emissions from air-conditioning systems in motor vehicles and the amendment of Directive 70/156/EC of the Council, Official Journal of the European Union no. L 161, June 14, 2006, p. 12-18

[7] MAC – Mobile air-conditioning

[8] The directive refers to smaller motor vehicles for passenger transport (vehicle category M1) and for goods transport (vehicle category N1, class 1). Category M1 includes notably passenger cars and small buses, yet also special vehicles such as motor-caravans, ambulances and hearses and armoured and wheel-chair accessible vehicles. Category N1, class 1 involves smaller commercial vehicles such as small utility vehicles, yet also special vehicles such as caravans.

[9] Vehicles of the categories M1 and N1, class 1, with type-approvals before January 1, 2011.

[10] CFCs (Chlorofluorocarbons) damage the ozone layer and intensify the greenhouse effect, PFC (fully fluorinated hydrocarbons) and HFCs (hydrofluorocarbons) intensify “only” the greenhouse effect. That is why PFCs and HFCs became, first of all, substitutes for CFCs.

[11] LCCP (Life-Cycle Climate Performance) is the analysis of the life cycle calculating the effects of a product on the climate. A US car manufacturer developed this programme allowing to calculate the emission of climate-effective gases of air conditioning systems in passenger cars with various refrigerants (LCCP). Here, the direct and indirect emissions of greenhouse gases are determined over the whole life cycle of the mobile air-conditioning system from its production via its operation up to its disposal. However, different results are obtained for the individual refrigerants depending on the data, measured values and techniques used as basis. A LCCP is not as detailed as a life-cycle analysis including in addition to climate-effective also other substances and other effects e.g. toxicity and acidification and considering apart from the atmosphere other media such as soil, air, plants. Moreover an obligatory standard for making up LCCP does not exist so far.

[12] Foreseeable leakage of the passenger compartment shall not result in R152a concentrations of more than 3.7 % by vol. for more than 15 seconds if the ignition system is switched on.

[13] CFC R12 - a refrigerant damaging the ozone layer and having a high greenhouse effect- is prohibited since 1995 in Germany and was used for mobile air-conditioning of passenger cars before the introduction of R134a.

[14] Decomposition products of R134a are e.g. HC(O)F and CF3-radicals at the earth surface and CF3C(O)F in the tropopause (atmospheric layer, the upper boundary layer of the tropoause is in a height of approx. 10 to 15 km, above which the essentially less moved stratosphere begins) [Tuazon, Atkinson 1993; Hurley a.o. 2008].

[15] AEGL = Acute Exposure Guideline Levels, published by the US National Research Council and National Academy of Science, AEGL 2 value for HF is 95 ppm (duration 10 minutes).
[16] Data from literature [UNEP 2009], with 1.5 billion cars estimated in 2020 this corresponds to 160 kg of CO2-equivalents per passenger car and year [Dargay 2007]

[17] Estimated with 120 g/km CO2 emissions per car and an annual driving performance of 14,000 km/year