Refrigerants for light-duty passenger vehicle air conditioning systems

Technical assessment of alternatives to HFC-134a

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Date: July 2011
Paper number: 2011-3
Keywords: HFC-134a, refrigerants, greenhouse gas, global warming potential

Hydrofluorocarbons (HFCs) were widely adopted in the 1990s to replace chlorofluorocarbon (CFC) and hydro-chlorofluorocarbon (HCFC) refrigerants that deplete the stratospheric ozone layer, but today they are among the most potent greenhouse gases. The European Union and the United States recently promulgated rules to control the climate impacts of HFCs used in motor vehicle air conditioning (MVAC) systems. In 2006, the European Commission adopted a rule that restricts the sale of 2011 new model vehicles containing refrigerants with a 100-year global warming potential (GWP100) greater than 150 (EU Parliament, 2006). In 2010 the US Environmental Protection Agency (US EPA) adopted a greenhouse gas standard for model year 2012-2016 vehicles that provides credits to automakers who use refrigerants with a GWP100 lower than 1430 (US EPA, 2010). These performance-based regulations leave the choice of refrigerant to the automobile industry.

The most widely used MVAC refrigerant today is 1,1,1,2-tetrafluoroethane, also known as HFC-134a or R-134a. In 1990 no MVAC systems contained HFC-134a, but by 2003 it was being used in about seventy-four percent of vehicles (Clodic, 2005). By 2004 all vehicles produced or sold in North America, Japan, and Europe were using HFC-134a. This is the culmination of a 20-year shift away from dichlorodifluoromethane, also known as CFC-12 or R-12, which was used ubiquitously in 1990 but banned under the Montreal Protocol to limit depletion of stratospheric ozone.

The phase-out of fluorinated gases that deplete the ozone layer has produced a climate co-benefit that in the year 2010 may be responsible for between 10 and 13 Gt CO2-eq reductions in emissions per year (G. J. M. Velders, Fahey, Daniel, McFarland, & Andersen, 2009).

Table 1. Global Warming Potential of common refrigerants and greenhouse gases

<table>
<thead>
<tr>
<th>Greenhouse gas</th>
<th>20-year GWP</th>
<th>100-year GWP</th>
<th>500-year GWP</th>
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<tbody>
<tr>
<td>CFC-12</td>
<td>11,000</td>
<td>10,900</td>
<td>5,200</td>
</tr>
<tr>
<td>HFC-134a</td>
<td>3,830</td>
<td>1,430</td>
<td>435</td>
</tr>
<tr>
<td>Nitrous Oxide</td>
<td>289</td>
<td>298</td>
<td>153</td>
</tr>
<tr>
<td>Methane</td>
<td>72</td>
<td>25</td>
<td>7.6</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

Source: (Forster et al., 2007)

Ambient measurements of HFC-134a show that emissions have increased and are concentrated in industrialized regions. In 2008, the rate of global emissions was 149 ± 27 Gg/yr (WMO, 2010). This is up from 130-140 Gg/yr from 2005-2006. About thirty percent of these emissions were contributed by North America, thirty-two percent were emitted in Asia, and nineteen percent were emitted in Europe (Stohl et al., 2009).

Motor vehicle air conditioning is increasingly common. In rapidly developing countries like India, ninety-two percent of new vehicles have air conditioning systems...
Air-conditioning systems, motor vehicle air conditioning.

The average vehicle emits 166 kg CO2-eq of refrigerant each year (TEAP, 2005). Emission sources include deterioration of fittings, valves and hoses, slow permeation through hoses and seals, improper releases during servicing and maintenance, and improper disposal (US EPA, 2010). These emissions are equivalent to about 5.1 percent of the total CO2-eq emissions of a light-duty vehicle (on a 100-year GWP basis), or about 13.6 g CO2-eq/mi. Certain high-emitting vehicles may contribute a disproportionate share of fleet-wide emissions, particularly older in-use vehicles (Wyssor, 2008). Emissions during servicing and disposal account for a large share in countries with weak servicing infrastructure (G. J. M. Velders, et al., 2009). Replacing a high GWP refrigerant with a low GWP refrigerant can significantly reduce the climate impact of these emissions.

Several international initiatives over the past ten years have focused on identifying alternatives to the HFC-134a system. SAE International has held at least nine symposia on alternative refrigerants between 1999 and 2010. SAE International has also managed several research projects to compare and evaluate alternative refrigerants on behalf of industry and the regulatory community (SAE, 2011). The German Automobile Industry Association (VDA) has held annual symposia on alternative refrigerants between 2002 and 2009 (VDA, 2011). Between 1998 and 2010 the Mobile Air Conditioning Climate Protection Partnership also operated as a forum between industry and the public sector to identify and evaluate alternative refrigerants, among other goals (US EPA, 2011a), including workshops in India and China and a joint project with India (Chaney et al 2007).

In the pursuit of alternatives, it is important to consider steps to mitigate the toxicity and flammability of refrigerants. Systems in the early 20th century used ammonia, isobutene, sulfur dioxide and methyl chloride, which frequently leaked. These produced toxic and/or flammable concentrations responsible for annoying eye irritation, breathing problems and in some severe cases even death (Tad donio, 2010). Low GWP refrigerants can be equally harmful if not appropriately managed. Leaked refrigerant can enter and collect in the sealed space of the vehicle cabin after a vehicle accident, or from deteriorating valves and hoses. High concentrations can affect driver performance, and an ignition source can ignite certain refrigerants. Under combustion a hydrofluorocarbon can produce hydrogen fluoride, which converts to highly toxic and corrosive hydrofluoric acid.

The American Society of Heating, Refrigerating and Air-Conditioning Engineers (ASHRAE) currently rates refrigerants for their toxicity and flammability (IIR, 2011). Most refrigerants under serious consideration for use in automobiles are either rated A1 for low-flammability or A2 for moderate flammability. Both of these safety groups are considered non-toxic, meaning no toxic exposures will occur at concentrations below 400 ppm.

Some air conditioning systems avoid refrigerants altogether. These include air cycle systems, metal hydride systems, thermo electric cooling and thermo-acoustic systems (TEAP, 2005). However, none of these systems are being seriously explored for broad application to meet the European directive or the US greenhouse gas standard. High costs, low energy efficiency, difficult engineering, and poor compatibility with vehicle applications have impeded their adoption. Instead, current investigations favor the vapor compression system used with HFC-134a and CFC-12. This has narrowed the search to hydrocarbon blends such as propane and isobutene; fluorinated gases such as 1,1-difluoroethane (HFC-152a) and 2,3,3,3-tetrafluoropropene (HFO-1234yf); and carbon dioxide.

Vehicles sold in the United States must contain refrigerants that have been approved by the US EPA Significant New Alternatives Program (SNAP). This program reviews the environmental and health impacts of alternative refrigerants to ensure they pose no additional harm compared to what is already in use. Since global automakers are unlikely to choose refrigerants that are not permitted in the United States, refrigerants that have received SNAP approval and satisfy the EC f-gas Directive are the most likely to be adopted. These include HFC-152a and HFO-1234yf (US EPA, 2008, 2011b). Carbon dioxide has also received SNAP approval, although the US EPA has proposed to modify this in response to toxicity concerns. The following discussion takes a more detailed look at each of these potential alternatives. In 2011, the US EPA agreed to initiate a public rulemaking to remove SNAP approval for HFC-134a as an acceptable refrigerant in motor vehicle air conditioning.

2,3,3,3-Tetrafluoropropene (HFO-1234yf)

HFO-1234yf is a hydrofluoroolefin, an unsaturated hydrofluorocarbon that is susceptible to degradation in the presence of the hydroxyl radical, giving it a short atmospheric lifetime. HFO-1234yf received final SNAP approval from the US EPA in 2011 (US EPA, 2011b). Honeywell and DuPont are jointly commercializing this refrigerant in response to the European MVAC directive. In 2010, they announced a joint venture to construct a manufacturing facility to supply refrigerant by the fourth quarter of 2011 (Honeywell, 2010). No cost estimates have been made public, although early estimates put this at between 20 and 30 US$ per kg. (Sciance, 2010; Weissler, 2008). Prices may climb in response to supply constraints, global demand, and patent filings, with one estimate putting the price at 10 to 15 times that of HFC-134a (Sorg 2009).

Like other fluorinated gases, HFO-1234yf is a volatile organic compound associated with production of ground-level ozone. Exposure to ground-level ozone is associated with acute and chronic respiratory impacts. In addition, tropospheric ozone is a strong climate-forcing agent, so
its production can add to the total climate impact of this refrigerant (WMO, 2010). Luecken et al. (2009) and ICF (2010) found that under a worst-case scenario and ignoring likely increases in AC energy efficiency, HFO-1234yf might lead to an increase in ground-level ozone of 0.1 percent (ICF, 2010), which was not considered a significant impact on local air quality.

HFO-1234yf is also associated with the production of trifluoroacetic acid (TFA). TFA can accumulate in the environment over time and may have an adverse effect on plant and animal ecosystems. Based on a conservative assumption of no more than twice current emissions of HFC-134a, the US EPA found this would not produce adverse effects in plant and aquatic species (US EPA, 2011b; Luecken et al., 2009; Ema et al., 2010a; Ema et al., 2010b).

HFO-1234yf is a class A2 refrigerant suggesting minimal toxicity and moderate flammability (ASHRAE, 2009). The SAE International Cooperative Research Program on the risks of HFO-1234yf identified potential concern with the production of hydrogen fluoride (HF) during a vehicle fire (SAE International, 2009). Researchers with the German Federal Institute for Materials Research and Testing (BAM) produced high concentrations of HF in test vehicles, which has raised health and safety concerns among civil society organizations in Germany (BAM2010; UBA, 2010a, b). The US EPA found that the risk of exposure to HF from ignition and decomposition is no greater than the current risk posed by use of HFC-134a (US EPA, 2011b).

The US EPA requires compliance with SAE International standards to meet safety requirements for HFO-1234yf. Standard SAE J3639 requires unique fittings to connect containers and the air conditioning system, a warning label that communicates the presence of a flammable refrigerant, and devices that minimize leakage from valves. Standard SAE J1739 provides guidelines for designing motor vehicle air conditioning systems to minimize leakage into the passenger space or onto very hot engine exhaust component surfaces that might produce HF. The US EPA has chosen not to place any additional requirements compared to those already in place for HFC-134a.

SAE standards require unique hose fittings for HFC-134a and 1234yf systems to prevent the improper recharge of low GWP systems with high GWP refrigerant. However, a leak in a sealed vehicle cabin is a safety hazard since the gas can displace a significant amount of oxygen. Exposure to concentrations between 4-5% is associated with headache and dizziness, affecting driver performance (Patterson, Heyman, Battery, & Ferguson, 1955; Schneider & Truesdale, 1922; Schulte, 1964). The US EPA has proposed an upper exposure limit of 3% averaged over a 15-minute period and a maximum limit of 4% in the vehicle cabin (US EPA, 2008, 2009). This proposal has not received final approval.

Several methods are available for safeguarding passengers. In direct expansion (primary loop) systems, sensors triggered by high concentrations in the passenger cabin can activate safety valves that direct carbon dioxide outside of the vehicle or direct outside air into the cabin. In secondary loop systems, carbon dioxide is isolated in a closed loop in the engine compartment. Through a heat exchanger it cools a mixture of water and glycol that directly cools the passenger cabin. This avoids direct interaction with the air entering the passenger cabin.

Carbon dioxide systems have faced some engineering challenges. They operate at pressures 5 to 10 times higher than HFC-134a systems, so development of high-pressure hoses, compressors and other components has been necessary. Significant progress has been made to develop and demonstrate the availability of these components, however this alone has not overcome questions about durability from automakers.

Additional challenges stem from lower efficiency of the carbon dioxide system at idle and at high load, which would indirectly increase CO2 emissions (IPCC/TEAP, 2005). In 2009 a demonstration CO2 system showed better fuel efficiency than a HFC-134a system (Graz, 2009). Other systems have also been demonstrated (SAE, 2009). While no automaker has announced plans to commercialize CO2 systems, they have been used in some German public transit buses since 1996 (UBA 2010, Sonnekalb 2002; Försterling, Tegethoff, & Köhler, 2002; Köhler, Sonnekalb, & Kaiser, 1998). Today there are more...
than a dozen public transport buses equipped with such systems (UBA 2010, BVG 2010).

The IPCC in 2005 estimated that the additional cost of a carbon dioxide system over an HFC-134a system is about 48 to 180 US$ (IPCC/TEAP, 2005).

1,1-Difluoroethane (HFC-152a)

HFC-152a or R-152a is a colorless gas produced during a catalytic reaction between vinyl chloride and hydrofluoric acid (OECD SIDS, 2006). At least 5000 metric tons are produced annually of which about eighty percent is consumed as an aerosol propellant, fifteen percent as a foam expansion agent, and the remaining five percent in refrigeration and other uses. DuPont is a major manufacturer in the United States, while smaller scale production also occurs in China and Russia (IPCC/TEAP, 2005).

In the atmosphere, HFC-152a degrades through reactions with the hydroxyl radical into carbon monoxide, carbon dioxide, water and hydrogen fluoride (HF). Like other fluorinated gases, HFC-152a may contribute to ground-level ozone. Its atmospheric degradation may produce trifluoroacetic acid. An analysis directed by the US EPA found that the magnitude of environmental impacts from HFC-152a would not be large enough to warrant additional restrictions beyond those required for safety (ICF, 2010).

HFC-152a is rated a class A2 refrigerant, which indicates minimal toxicity and moderate flammability (US EPA, 2008). Compared to 1234yf, it ignites more readily and requires additional mitigation measures not required for 1234yf (Taddonio, 2010). To protect against flammability, systems can be designed to discharge refrigerant away from the vehicle when sensors detect high concentrations, or when the vehicle airbag is engaged during a traffic accident (TEAP, 2005). This design allows HFC-152a to be used in systems identical to HFC-134a. As an alternative safety measure, the refrigerant can be used in a secondary loop system. A secondary loop system requires additional components that can add to the cost of the air conditioning system. But the amount of refrigerant needed can be as much as 65 percent less than an HFC-134a system (IPCC/TEAP, 2005). And in a closed loop system, opportunities for leakage can be fewer. Additional benefits may come from greater energy efficiency of the system, which would indirectly reduce CO2 emissions.

The IPCC estimates that the additional cost of an HFC-152a system above an HFC-134a system is in the range of 48 US$ (IPCC/TEAP, 2005).

Conclusion

It has proven difficult to engineer a zero leak MVAC system. Hoses, fittings, and valves deteriorate, service technicians fail to follow proper procedures, and improper disposal occurs. These challenges point to a role for lower GWP refrigerants.

The performance-based standards for low GWP refrigerants in Europe and the United States allow automakers to choose a replacement for HFC-134a. However, other concerns including cost, feasibility, and safety can limit these options. HFC-152a, HFO-1234yf, and carbon dioxide are alternatives that may substantially reduce climate impacts and meet safety standards. Table 2 summarizes the GWP values, safety ratings, and refrigerant cost of these alternatives.

A transition to a new refrigerant is not easy. Automakers must change the design of the refrigeration system and the vehicle, expect new training of service technicians, explore changes to design standards, and seek regulatory approval in the United States and Europe. Automakers are also uncertain how or when their competitors will proceed, so voluntary actions before the mandated deadline in Europe and the US introduce some amount of risk that has impeded rapid adoption of alternatives to-date.

Given uncertainties in supply and cost of alternative refrigerants, an industry-wide transition in the United States may not occur until 2017. In Europe, a transition for new model vehicles is required in 2011, but regulators provided automakers with a six-month reprieve from the January 1 deadline. Few automakers had announced their intent by this deadline, so the way forward remains murky.

Future steps will be taken in Europe and the United States to reduce the climate impact of air conditioning. These will likely focus on the energy efficiency of the system, taking into account the indirect production of CO2. The European Commission has launched a process to define a test cycle for efficiency, while in the United States the California Air Resources Board is considering lifecycle emissions in its LEV III rulemaking. Over time, these actions in combination with lower GWP refrigerants can be expected to produce large reductions in the climate impacts of the passenger vehicle fleet.

Table 2. Summary of low GWP alternative refrigerants

<table>
<thead>
<tr>
<th>ASHRAE Designation</th>
<th>IUPAC Name</th>
<th>GWP20</th>
<th>GWP100</th>
<th>ASHRAE Safety Rating</th>
<th>LFL (vol %)</th>
<th>ATEL (ppm)</th>
<th>Refrigerant cost (US$ per kg)</th>
<th>Additional Per-Vehicle Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>R-134a</td>
<td>1,1,2-tetrafluoroethane</td>
<td>3830</td>
<td>1430</td>
<td>A1</td>
<td>Not flammable</td>
<td>50,000</td>
<td>3-4</td>
<td>-</td>
</tr>
<tr>
<td>R-152a</td>
<td>1,1-Difluoroethane</td>
<td>437</td>
<td>124</td>
<td>A2</td>
<td>3.9</td>
<td>50,000</td>
<td>11</td>
<td>+50 US$</td>
</tr>
<tr>
<td>R-1234yf</td>
<td>2,3,3,3-tetrafluoropropene</td>
<td>12</td>
<td>4</td>
<td>A2</td>
<td>6.5</td>
<td>100,000</td>
<td>20-30</td>
<td>+25 US$</td>
</tr>
<tr>
<td>R-1744</td>
<td>Carbon Dioxide</td>
<td>1</td>
<td>1</td>
<td>A1</td>
<td>Not flammable</td>
<td>40,000</td>
<td>&lt;1</td>
<td>+50-200 US$</td>
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