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APPENDIX C.1

Mobile Air Conditioning System Technology Assessment

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CALIFORNIA AIR RESOURCES BOARD, RESEARCH DIVISION

DIRECT EMISSIONS TECHNOLOGY ASSESSMENT

Introduction

This appendix provides a discussion of the technologies available for reducing climate change emissions from mobile air conditioning systems used in light-duty vehicle platforms. The focus in this appendix is on the reduction of "direct" climate change emissions. "Direct" climate change emissions are due to refrigerant releases from mobile air conditioning systems. In contrast, indirect climate change emissions are CO₂ emissions that result largely from the additional load placed on an engine due to operation of the air conditioning system. A discussion of indirect emissions is included in Section II.B of the report and Appendix C.4.

Several competing alternative technologies (each having its own set of advantages and disadvantages) have the potential to substantially reduce climate change emissions from the use of mobile air conditioning systems. In addition, some of these technologies also appear sufficiently mature for near-term fleet penetration. Staff expects that, within the framework of the proposed regulations, market selection forces over time will result in one technology becoming dominant in new cars, just as HFC-134a technology has become dominant today within the requirements to eliminate CFC-12. Additional development work over time is needed to predict which new technology will become the leader. The following sections will discuss the existence and the technical and environmental feasibility of how these approaches may simultaneously meet the needs of the market, industry and the environment.

Background

Mobile Air Conditioning and Direct Climate Change Emissions

The AC industry typically refers to direct emissions as those due to leakage only. In contrast, in a parallel assessment conducted by ARB staff, direct emissions are defined as lifetime vehicle refrigerant emissions, including in addition to leakage or "regular" emissions, those due to sudden releases (i.e., "irregular emissions"), and end-of-life

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releases.)¹ In this appendix, references to direct emissions are primarily concerned with vehicle system leakage.

Mobile Air Conditioning Recent History

The two most widely used refrigerants in mobile air conditioning systems are dichlorodifluoromethane (CCl_2F_2 , known as CFC-12) and 1,1,1,2-tetrafluoroethane (CH_2FCF_3 , known as HFC-134a). CFC-12 is a powerful stratospheric ozone depleting substance whose U.S. production and importation has been banned since the early 1990s. Sale of new automobiles with CFC-12-based systems has been prohibited in California since January 1995. The continued use of CFC-12 in vehicles originally so equipped is permitted², although CFC-12's cost has risen dramatically since U.S. production ceased.

Since the start of the 1995 model year, CFC-12 has been supplanted by HFC-134a in new vehicle mobile air conditioning systems in California, following a gradual phase-out between 1992 and 1995. HFC-134a has been the dominant refrigerant used in vehicles manufactured since that time. Since HFC-134a has no chlorine or bromine, its ozone-depletion potential (ODP) is essentially zero. However, HFC-134a does have a significant global warming potential (GWP) of 1300 times that of CO_2 . Thus, a small HFC-134a leak can have a relatively large climate change impact³.

In light of this issue with HFC-134a, significant resources are being directed towards reducing the climate change impact of mobile air conditioning systems. Some of these efforts look to reduce HFC-134a emissions either by reducing system leakage and improving efficiency (typically referred to as "enhanced HFC-134a" systems)⁴ or by developing mobile air conditioning systems that utilize alternative refrigerants with lower GWPs. The more promising examples of the latter include systems that use 1,1-difluoroethane ($\text{C}_2\text{H}_4\text{F}_2$, known as HFC-152a⁵, GWP of 120⁶), and CO_2 (known as R-744⁷, GWP of 1⁸.) Other refrigerants that have been considered to a lesser degree include various hydrocarbons (for example, propane, known as R-290, and isobutane, known as R-600a)⁹ and hydrocarbon mixtures, and even air (known as R-729). Other measures look to reduce power requirements by improving system efficiency¹⁰, or by reducing cooling load and improving cooling delivery. Data available in the research literature as described in subsequent sections suggests that the leading alternatives are enhanced HFC-134a, HFC-152a and CO_2 systems. To facilitate the discussion of alternative mobile air conditioning system technologies, some definitions and basic descriptions of air conditioning system components and operation are provided in Appendix C.2. At this point, the reader unfamiliar with air conditioning systems may benefit from the material presented in Appendix C.2 before proceeding.

In a significant development that promotes the use of alternative mobile air conditioning systems for reduction of climate change impacts, the European Commission (EC) has proposed regulations to phase out the use of any mobile air conditioning system refrigerant with a GWP greater than 150, beginning in the model year 2008. The

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proposal would allow credits to be generated for HFC-134a vehicles which leak that refrigerant at a rate of 20 g/year or less. However, the regulation in its current form does not specify an actual test protocol for certifying or verifying this leak rate.¹¹ Development of such a protocol is necessary and efforts are emerging to address this need.

It must also be noted that conventional HFC-134a systems have undergone evolutionary improvements over the past several years. Such improvements have generally involved lower-permeability hoses and improved connectors and seals with the intent of improving reliability and reducing manufacturing and purchase costs. Possible changes to current mobile air conditioning systems needed to achieve significant further reductions are discussed in the following sections.

Current and Alternative Technologies

The following sections present the status of the leading alternative technologies that appear to be of principal interest to industry for addressing possible new climate change emission reduction requirements from mobile air conditioning systems. For each of the alternatives presented, the discussions include basic descriptions of the technology, hardware, safety, and corresponding direct emissions for understanding relative benefits and drawbacks. A limited discussion of the indirect emissions is also included to provide a more complete picture and to avoid inadvertently focusing on decreases in one component while ignoring increases in the other.

Current HFC-134a Systems

The system most commonly used in present day automobiles is the vapor-compression cycle utilizing HFC-134a as the refrigerant. Thus, in all subsequent discussions, this system is taken to be the baseline system for comparisons of alternative technologies.

Technical Description

Current HFC-134a vehicular air conditioning systems utilize the vapor compression cycle. HFC-134a's critical temperature of 213.9 deg F (see Appendix C.2 for a discussion of refrigerant critical properties) is high enough to allow subcritical operation under most ambient conditions. Its critical pressure is 588.9 psia¹². Pressures in a non-operating system are in the range of 50 to about 100 psia, depending on temperature. When the system is operating, the compressor discharge pressure can be as high as 200 to 300 psia. The temperature of the cooled air leaving the evaporator is generally in the range of 35 to 40 deg F (the evaporator temperature is limited to levels above freezing to avoid ice formation on the heat transfer surfaces). Figure 1 shows a schematic of a typical system, in particular, the operating environments of the various components, discussed in further detail in the following section.

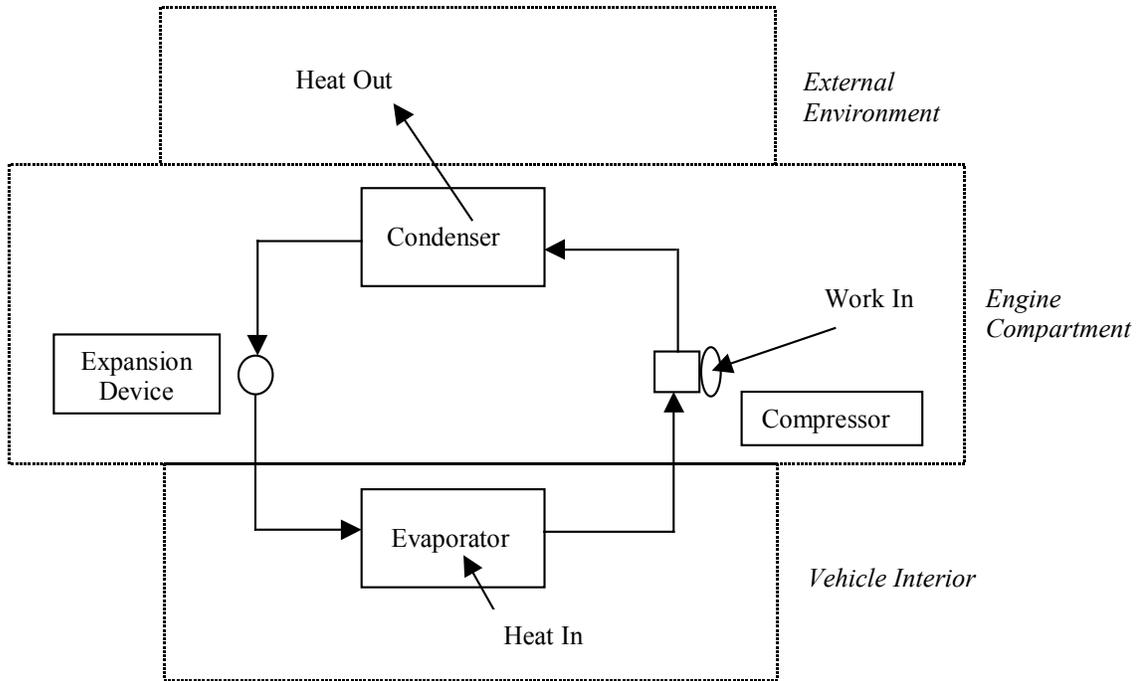


Figure 1 - Mobile Air Conditioning Schematic

Hardware and Operation

Figure 2 is a photograph of the components of a typical expansion valve-type mobile air conditioning system in roughly the same relative locations that they are found in a vehicular installation. In most modern automobiles equipped with air conditioning systems, the compressor is mounted on the engine and driven from the engine's crankshaft by means of a belt and pulley arrangement. The compressor can be a reciprocating piston type, a scroll type, or a sliding vane configuration, usually of constant displacement. The compressor requires an amount of lubricating oil that is usually mixed with the refrigerant. The compressor housing is assembled with seals where its parts interface to control leakage of refrigerant from the compressor interior to the outside atmosphere. The compressor drive shaft has a seal for the same purpose. However, the belt and pulley drive configuration can place significant side loads on the compressor shaft and its bearings, making the system prone to shaft seal leaks, especially when the seal has worn.

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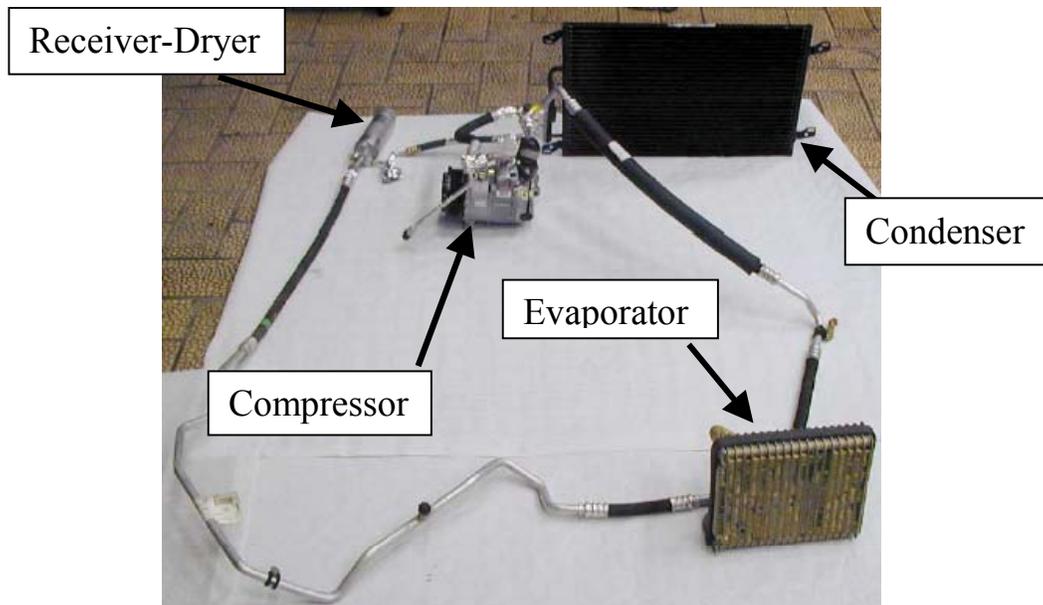


Figure 2 - Typical mobile air conditioning system components¹³

The condenser is usually located just behind the grille and in front of the engine cooling system radiator. This location provides the large quantities of ambient airflow (due to vehicle motion or engine cooling fan action) necessary to remove the transferred passenger compartment heat and the heat of compression from the flowing refrigerant.

The receiver-dryer shown, which does not have a strictly thermodynamic function in the refrigeration cycle, is located in the line carrying refrigerant from the compressor to the expansion valve. Its primary function is to act as a liquid-gas separator to ensure the expansion valve receives only liquid refrigerant. Other functions are to filter out any debris in the refrigerant flow and to remove any moisture from the refrigerant, by way of a desiccant material, that could otherwise form acids and cause corrosion of the components. The expansion valve is located out of sight in this photograph, just behind the evaporator.

The evaporator is placed just inside the passenger compartment near the heater core, in the ductwork that directs outside or recirculated air into the compartment under the influence of the blower fan.

These individual components are connected via flexible hoses, usually made of rubber-like synthetic materials with various component layers to accomplish different structural or sealing functions. Hoses have metal connectors at each end, attached by crimping and gluing. Hose connections are made to components usually with elastomer seals of the o-ring type. Hoses are not perfectly impermeable and elastomer seals also tend to have small but finite leak rates.

Modern home refrigerators use “hermetically” sealed refrigerant systems that all but eliminate refrigerant leakage¹⁴. In such systems, component and flow tubing

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connections are usually of a sealed nature, often epoxied, soldered, brazed or welded, that are not subject to the deterioration of elastomer seals that eventually leak. Indeed, refrigerator compressors and their electric drive motors are located entirely within the same closed housing so that there is no need to seal a mechanical drive shaft to prevent outside leakage. This hermetic design allows for refrigerator systems that commonly last for decades without loss of refrigerant.

Unfortunately, the nature of automobile manufacturing, component placement requirements, and the need for ready reparability do not readily allow for mobile air conditioning systems to be assembled hermetically. For example, the use of belt-driven compressors does not permit a hermetically sealed compressor/motor design. Instead, components are usually installed into the vehicle individually during the manufacture process, and then the flow tubing is connected utilizing o-ring or other elastomer seals. Such seals, while good, are not perfect and will most likely leak refrigerant that will need to be replenished at some point during the vehicle's useful lifetime.

An answer to the shaft seal problem would be to use a sealed electric motor-compressor unit in place of the common belt-driven compressor, though not necessarily using a totally hermetically sealed system. As an example, the 2004 Toyota Prius hybrid car uses an electrically driven compressor in its air conditioning system. This eliminates the need for a shaft seal and the associated refrigerant leakage, while allowing the air conditioner to continue to operate even when the engine is not running. This advance is made possible by the high voltage electrical systems already in use in the Prius's drive train. Unfortunately, compressor power demands exceed the capabilities of the typical non-hybrid car's 12-volt system and so hermetically sealed electrical compressors are not feasible in most vehicles of today.

The location of the condenser subjects it to potentially significant damage in collisions, which almost certainly results in the near-immediate release of most or all of the system's refrigerant charge. The condenser also is subject to rock damage and corrosive road spray that can eventually lead to slow refrigerant leakage. The evaporator is located in a difficult-to-reach area, resulting in little preventive maintenance against leakage. Hoses must be flexible to allow for the relative motion of the engine with respect to the rest of the vehicle, and are therefore made of flexible but permeable materials with imperfect couplings to metal hose ends, as noted above. Finally, the compressor shaft seal is a significant source of refrigerant leaks, aggravated by the strong side loads from the belt drive configuration. Some data indicate that most leaks come from either the hose assemblies or the compressor shaft seal.¹⁵ Industry surveys show that the compressor is the number one system component that requires replacement, either due to an internal failure or leakage¹⁶.

Most current mobile air conditioning systems are of either the fixed orifice tube or the expansion valve type, with constant displacement compressors. Orifice tube systems are generally cheaper to manufacture, but the single orifice tube size is a compromise between operation during cruise and idle conditions. The chief control methodology used in orifice tube systems is to cycle the compressor on and off in response to

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temperature conditions at the evaporator (the evaporator must be kept above freezing to avoid ice buildup on the air flow side that would greatly impact heat transfer effectiveness). Most expansion valve systems can vary the refrigerant flow path cross-sectional area at the valve to control evaporator conditions.

Most compressors in use in current systems are of the constant displacement type, where the refrigerant flow rate is dependent only upon compressor speed and thus on engine speed, because of the typical constant speed-ratio belt drive. System performance is controlled by a simple on-off control to keep the evaporator at the desired temperature (i.e., just above freezing). Since engine speed does not necessarily correlate with air conditioning system demand, a mismatch between necessary flow rate and the actual flow rate can exist, leading to system inefficiencies. Indeed, flow rate demand can be highest under idle (low engine speed) conditions, when little condenser airflow is available, and lowest under cruise (high engine speed) conditions when significant airflow is present.

Since systems are typically sized large to provide rapid cooldown (“pulldown”) of hot, sun-soaked passenger compartments, they typically have excess capacity for cooling under more typical and less extreme ambient conditions or under steady state conditions. Moderation of passenger compartment discharge air temperature, when less-than-maximum capacity is required, is accomplished by mixing heated air from the heater core with cooled air from the evaporator.

Generally, the operator also has the choice to use fresh outside air to be cooled at the evaporator, or to recirculate passenger compartment air to the evaporator. The first choice avoids stuffiness and moisture buildup, while the latter provides for faster cool down, lower passenger compartment temperatures, and reduced greenhouse gas emissions. The greenhouse gas reduction advantage derived from the use of a large fraction of recirculated air is significant, with one reference estimating that full internal air recirculation can reduce the air conditioning load by almost one half under highway conditions, relative to the case of no recirculation.¹⁷

Safety

HFC-134a is considered a highly safe refrigerant. At less than extreme concentrations, it is non-toxic. At ambient pressures and oxygen concentrations it is not flammable. On the other hand, gross overexposure can cause cardiac sensitization and central nervous system depression with dizziness, confusion, loss of coordination, drowsiness or unconsciousness.¹⁸ However, it is felt that a modern car system’s refrigerant charge is too small to develop the necessary concentration levels to trigger adverse effects, even if completely released into a sealed vehicle passenger compartment.¹⁹ Contact of the liquid with the skin can cause serious frostbite injury, and pressures in the system can be injurious if suddenly released, as in a vehicle accident or improper maintenance activity. However, none of these potential hazards have been deemed sufficient to prohibit placement of system components within the passenger compartment and several years of operation seem to support this conclusion.

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Climate Change Emissions

Quantification of climate change emissions from existing mobile air conditioning systems is discussed in the section entitled “HFC-134a Emissions from Light- and Medium-Duty Vehicles”. As stated previously, for comparative purposes, the following discussions of technology, hardware and operation, safety and emission reduction potential for leading alternative technologies are offered relative to the baseline HFC-134a technology.

Enhanced HFC-134a Systems

Technical Description

Some technology developers advocate simple improvements of current HFC-134a systems, rather than replacement of such systems by alternative refrigerant technologies. Such enhanced systems would continue to utilize HFC-134a as the refrigerant, but would make improvements to the hardware to reduce refrigerant leakage and decrease the additional load placed on the engine from air conditioning systems²⁰. This approach would benefit from existing and proven technology while reducing direct and indirect emissions. A rigorous definition of what constitutes an “enhanced HFC-134a” system does not exist at present as different developers will have their own unique approaches of what to include in such a system. Nevertheless, there are some general ideas that can be used to estimate system configuration and performance, as discussed below.

Hardware and Operation

In general, with regards to direct emissions, the literature discusses improved containment through the use of improved hoses of lower permeability, improved hose ends and connectors, and better compressor shaft seals and seal configurations^{21,22}. For example, hose improvement is achieved with the use multi-layer barrier development and low-permeability thermoplastics. One manufacturer is developing a hose with permeability two orders of magnitude below present day hoses²³. Such advances should also carry over to use with other refrigerants.

To reduce indirect emissions, improved systems generally would utilize externally-controlled variable displacement compressors (VDC), improved control systems, and condensers and evaporators with improved heat transfer effectiveness and capacity. These strategies are discussed in Section II.B of the report.

Enhanced HFC-134a systems could be ready for production in 1 to 3 years²⁴, but further development is expected in the near term. However, the continued use of enhanced HFC-134a in mobile air conditioning systems poses the requirement for continued recycling of refrigerant during servicing and reclamation at the end of vehicle life.

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Safety

By virtue of the fact that enhanced HFC-134a systems utilize the same refrigerant as in current systems, no changes in the safety characteristics of these systems as previously described are expected. Furthermore, it is not expected that the improvements in system sealing or component efficiency would change the safety risk to vehicle operators or service personnel due to either flammability or toxicity.

Climate Change Emissions

In an effort to evaluate the characteristics of various alternate mobile air conditioning system technologies, especially the emission performance, the Society of Automotive Engineers (SAE) is sponsoring the "Alternate Refrigerant Cooperative Research Program" (ARCRP). This program was established in 2001 by the SAE Interior Climate Control Standards Committee as part of the industry's response to the listing of HFC-134a as a climate change gas by the Kyoto Protocol. Phase I of the program was supported by a consortium of 25 industry stakeholders, including vehicle manufacturers, system and component suppliers and government agencies, and evaluated several system technologies under consistent laboratory test conditions.²⁵ ARB was not a participant in Phase I of this program, but plans to participate in Phase II. Some of the Phase I findings from the ARCRP have been used by industry experts to generate opinions and support conclusions discussed in the next paragraph.

At the SAE Alternate Refrigerant Systems Symposium held in Phoenix in July 2003, attendees participated in several working groups to discuss different aspects of mobile air conditioning systems including improvements in cost and environmental impacts. The attendees included key stakeholders and experts from all the major original equipment manufacturers (OEMs, the vehicle manufacturers), mobile air conditioning system designers, and system and component suppliers. The consensus of the expert groups was that, despite using the same refrigerant with the same GWP as current systems, enhanced HFC-134a systems could result in significant reductions in direct refrigerant emissions of approximately 50 percent²⁶, relative to the current baseline HFC-134a system. This estimate represents the extent and nature of the best information available to date. Though the estimate may be considered somewhat subjective, it represents at least a reasonable first-order approximation. Significant refinement will require development of a commonly accepted test protocol for measuring, certifying and validating direct emissions from mobile air conditioning systems under a wide variety of operating conditions, regardless of refrigerant type. For purposes of this document, the number presented above is considered by staff to be reasonable for inclusion in the California analysis discussed in this report. However, as part of the regulatory process, the ARB will follow future ARCRP developments closely and consider the needs for a mobile air conditioning system emission certification and verification procedure.

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HFC-152a Systems

Technical Description

A refrigerant that has similar thermodynamic characteristics to HFC-134a, HFC-152a has the potential to minimize the need for system design changes in a changeover of refrigerants. Its thermodynamic properties are sufficiently similar or even slightly superior to those of HFC-134a so that operating temperatures and pressures are reasonably similar (HFC-152a's critical temperature is 235.9 deg F and its critical pressure is 656 psia compared to the values of 214.7 deg F and 589.9 psia for HFC-134a)²⁷ and performance is comparable or somewhat better. However, HFC-152a is considered a flammable substance (see following discussion for details on flammability designations), which introduces additional safety considerations with respect to the system design, operation, and maintenance²⁸. This safety issue is currently being considered by industry and the U.S. EPA as discussed below.

Hardware and Operation

In general, major components, placement, and function are similar between HFC-134a and HFC-152a systems. Possible exceptions include the desiccant since material used with HFC-134a may not be compatible with HFC-152a, and the expansion device, which may be optimized to take advantage of HFC-152a's slightly different thermal properties. Most significantly, because of HFC-152a's flammability, the evaporator may require design and location modifications to avoid placement in the passenger compartment. This could require an evaporator that consists of a refrigerant-to-liquid heat exchanger in the engine compartment, which is then connected to a secondary heat transfer loop containing a liquid-to-air heat exchanger located in the passenger compartment where the actual air cooling takes place. A schematic of such a system is shown in Figure 3. Compared with the more conventional direct or primary-expansion approach (where refrigerant evaporation takes place in the principal air cooling heat exchanger, as shown previously in Figure 1), the secondary heat exchange loop adds safety to the system with a tradeoff of increased complexity, cost and weight, and reduced COP. On the plus side, the liquid coolant in the secondary loop adds thermal inertia to the system, providing cooling under conditions of reduced performance (e.g., low-speed traffic) or for cars that shut off the engine during idle periods. Presently, the issue of the need for a secondary loop is being examined by the industry and by the U.S. EPA²⁹ with no clear indication by the vehicle manufacturers of their preference.

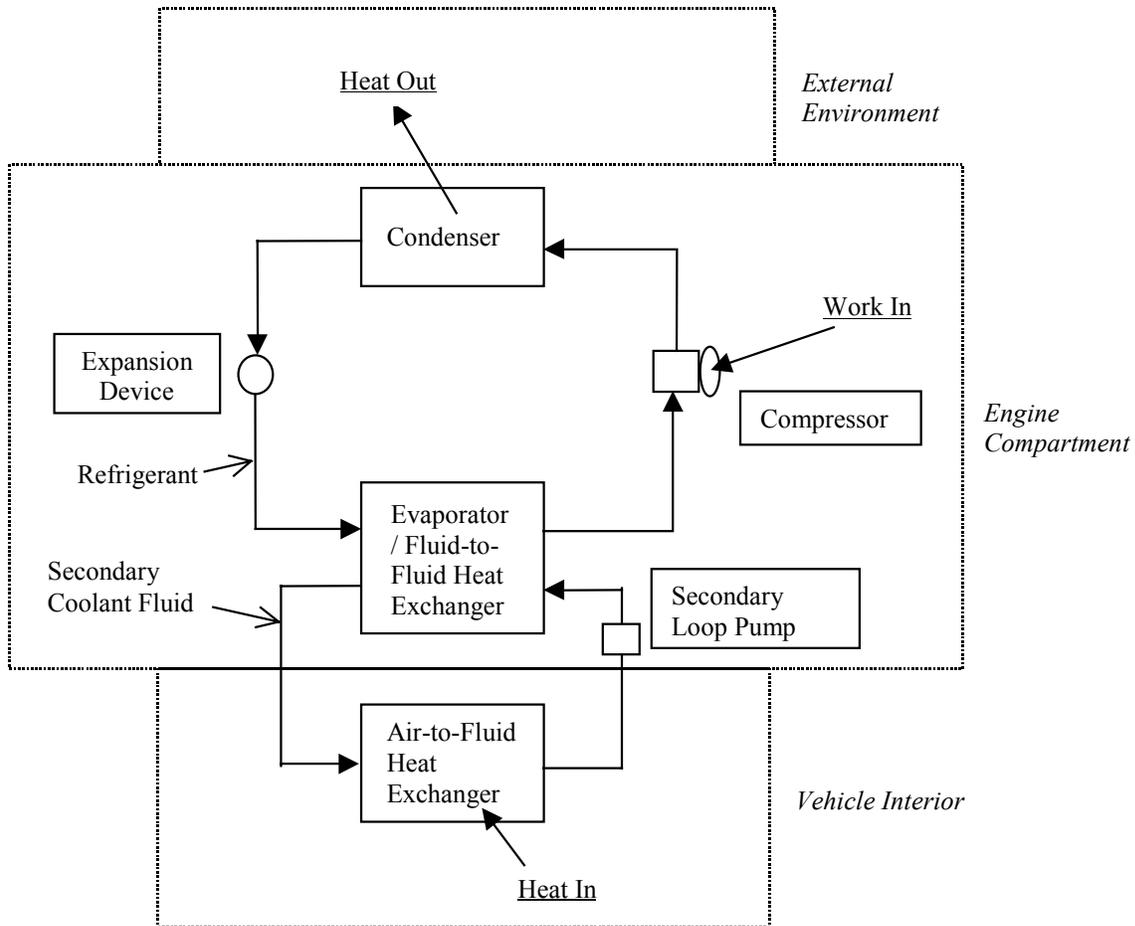


Figure 3 - Schematic of Secondary Loop System

A variation of HFC-152a technology would apply the same types of improvements described above for enhanced HFC-134a systems. These improvements could include reduced leakage hoses, connectors and seals, variable displacement compressors, advanced controls, supercooling condensers, or increased air recirculation, and could result in significant emission reductions over the basic HFC-152a system.

It is anticipated by the SAE Phoenix Symposium expert group that basic primary-expansion HFC-152a systems could be available for use in automobiles within 3 to 5 years, secondary loop HFC-152a systems within 4 to 6 years, and enhanced primary-expansion systems within 4 to 6 years³⁰.

Safety

The safety issues for HFC-152a are similar to those for HFC-134a, with the additional concern associated with its flammability. HFC-152a is considered to be a flammable refrigerant based on a standardized test defined by the American Society of Heating, Refrigerating, and Air Conditioning Engineers (ASHRAE) and ASTM International

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(formerly known as the American Society for Testing and Materials). The test measures flame propagation through a mixture of refrigerant and air after ignition by a kitchen match lit by an electrical spark^{31, 32}.

The ASHRAE classification system assigns one of three classifications of flammability. Classification 1 indicates no flame propagation under the test conditions. Classification 2 signifies a refrigerant with a lower flammability limit (LFL) of more than 0.10 kg/m³ and a heat of combustion less than 19,000 kJ/kg. Category 3 signifies refrigerants that are highly flammable with an LFL less than 0.10 kg/m³ or a heat of combustion greater than or equal to 19,000 kJ/kg. ASHRAE designates HFC-152a as a Classification 2 flammable material or moderately flammable. For comparison, HFC-134a is given a Classification 1 flammability, while a hydrocarbon refrigerant such as propane is placed in Classification 3.³³

However, for use as an aerosol propellant, the U.S. Consumer Product Safety Commission (CPSC) evaluates flammability based on the so-called candle test. As described in Code of Federal Regulations (CFR) 1500.45, this test involves spraying the aerosol towards a lit candle and noting the length of any flame extension past the candle or the presence or absence of flashback towards the spray source. A substance would be considered flammable if it has any flashback, or a flame extension greater than 18 inches.³⁴ Under these criteria, HFC-152a is not listed as flammable by the CPSC. One brand of aerosol compressed gas duster containing HFC-152a, used for removing dust from electronic equipment, is labeled as being “not defined as flammable by 1500.3(c)(6), 16CFR, Fed. Haz. Substance Act, CPSC Regs.”; nevertheless, its label also contains the additional caveat that it “can be ignited under certain circumstances. Do not use near open flame or any incandescent material”³⁵.

The two different tests described attempt to measure flammability under two different conditions of combustion, that of a premixed air-refrigerant mixture, and that of a torch-like diffusion flame. The former could be considered a model for the case of a leak into a passenger compartment where the refrigerant thoroughly mixes with air before any ignition event occurs. The latter example could represent the scenario of a component leak where an ignition event occurs at the leak source, before mixing takes place.

As noted previously, a secondary loop has been proposed as a way of addressing the potential issue of safety in HFC-152a systems. This would allow for the location of all refrigerant-containing components outside of the passenger compartment of the vehicle by utilizing an intermediate heat exchanger and a safe heat transfer fluid to carry heat between the system evaporator in the engine compartment, and a liquid-to-air heat exchanger in the passenger compartment. While such secondary loop systems have advantages in that they readily allow for more than one passenger compartment cooling location in large vehicles and provide thermal mass for better transient cooling under stop-and-go conditions, they do incur weight and COP penalties.³⁶

Another risk mitigation approach involves the use of shut off valves on both the inlet and exit of the evaporator. These valves are triggered to close by a signal such as the

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airbag controller or a passenger compartment HFC-152a sensor, to isolate the evaporator from the rest of the system in the event an evaporator leak is possible or detected³⁷. This isolation would limit the amount of refrigerant leaked into the passenger compartment to that which is already contained in the evaporator. Finally, a variation of this isolation scheme is illustrated by a system demonstrated by Delphi, Inc. This system uses an HFC-152a sensor in the passenger compartment to trigger small explosive squibs that rupture diaphragms and allow the refrigerant to discharge harmlessly through vent tubing into the wheel wells.³⁸ Such a system would require further development, but could allow the safe use of HFC-152a without the disadvantages of a secondary loop system. These and any other mitigation measures remain an important area of development for the industry, though it is uncertain when they will be available or that they will fully address safety concerns.

Evaluation of flammability risk is currently being conducted by the U.S. EPA. This evaluation considers the risk to vehicle occupants from an air conditioning system that leaks HFC-152a into the passenger compartment³⁹. This risk analysis uses a combination of fault-tree analysis and computational fluid dynamics to quantify the probabilities of experiencing a leak into the passenger compartment that reaches flammable levels in the presence of an ignition source, under several scenarios. Preliminary results indicate that HFC-152a can conceivably reach concentration levels of concern in the passenger compartment and, therefore, some risk reduction measures are suggested.⁴⁰ How the industry will view these results and any mitigation actions it may take to address them are not certain at present. However, it is evident that the research on mitigation strategies as described above is driven by the OEM's need to respond to the potential safety concerns raised.

Finally, under Section 612 of the 1990 Clean Air Act Amendments, the U.S. EPA developed the Significant New Alternatives Policy (SNAP) program during the 1990s. In part, SNAP makes determinations of acceptable and unacceptable substitutes for ozone-depleting substances, such as substitutes for CFC-12 in mobile air conditioners⁴¹. Acceptability is based on environmental and safety considerations, including flammability. At present, HFC-152a does not appear on either the list for acceptable nor the list for unacceptable substitute refrigerants^{42,43}. In fact, one of the stated reasons for U.S. EPA's risk analysis effort is to provide input to the SNAP program⁴⁴.

Direct Climate Change Emissions

Coupled with lower GWP and reduced charge mass (due to the lower molecular weight of the refrigerant), HFC-152a systems may offer significant environmental advantages. Specifically, with minimal changes to the system components, and assuming the same volumetric leak rate as the baseline system, the SAE Symposium expert group suggests that the CO₂-equivalent lifetime direct emissions are expected to be over 94 percent lower than the baseline HFC-134a system's.⁴⁵ In addition, because of the low GWP, certification and validation testing would not be as critical as for HFC-134a

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systems, though proper recovery and recycling of the refrigerant are still important to fully ensure environmental benefits.

For enhanced HFC-152a systems not utilizing a secondary loop, the SAE Symposium expert group anticipates that direct emissions would be somewhat lower, with a 96 percent reduction in leakage compared to the baseline system.

Another important environmental concern related to the possible substitution of HFC-152a for HFC-134a should also be considered. An issue results from the failure to restrict retail access of HFC-134a to small containers of the refrigerant, in contrast to the ban that was implemented for small cans of CFC-12. Currently, any consumer can purchase small cans of HFC-134a for use in replenishing a vehicle's air conditioning system, called do-it-yourself (DIY) activity. This leads to leakage and loss of refrigerant through improper servicing, lack of proper reclamation, and the inability to fully empty the cans. (The latter leaves an amount of refrigerant, called the "heel", in the can that likely will eventually escape to the atmosphere.) An industry-wide conversion to HFC-152a technology would reduce and eventually eliminate the demand for and supply of small cans of HFC-134a in favor of small cans of HFC-152a with that refrigerant's lower GWP. One estimate indicates that the difference between R-134a consumed and R-134a use attributed to service industry activity in 1998 was in the tens of millions of pounds⁴⁶, which could be related to DIY activity. While the information necessary to assess the accuracy of this estimate is not readily available, evaluation of the extent of the impact of this activity is underway. In short, the switch to HFC-152a is also attractive for reducing the impact of DIY air conditioning servicing activity.⁴⁷

Carbon Dioxide Systems

Technical Description

CO₂ systems are based on a transcritical refrigeration cycle. The principal advantages of CO₂ refrigerant are its low GWP and inherent abundance. By definition, CO₂ is assigned a GWP of 1 and all other substances are ranked relatively. There are numerous sources of "waste" CO₂ that can be captured for use such that none need be manufactured specifically as a refrigerant. This means that CO₂ refrigerant leakage potentially has no net effect on climate change emissions. In principle, recovery and recycling would not be needed, though regulatory exemptions or changes would be required to allow this.

Hardware and Operation

The major components of a CO₂ air conditioning system are somewhat analogous in form and function to their counterparts in a more conventional HFC-134a system. There is a compressor, an evaporator, an expansion device, and all the connecting tubing. As noted in Appendix C.2, the gas cooler has a similar heat transfer function as the more traditional system's condenser, though due to the transcritical nature of the

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process, condensation in the conventional sense does not take place. The other principal difference of a CO₂ system is the much higher operational pressures required. Compressor discharge pressures can be upwards of 1,500 to 2,000 psia, roughly 5 times those of a baseline HFC-134a system. These higher pressures mean that all components and connecting flow tubing must be built stronger than those of conventional systems, with the subsequent inability to use existing system component designs. These new components could lead to heavier and more expensive systems than existing units, though weight increases could be balanced by the reduction in size afforded by the superior heat transfer characteristics of CO₂. CO₂ systems also require an internal heat exchanger that adds to system cost and complexity. In addition, safety concerns about CO₂ leaks into the passenger compartment (see below) will likely require a CO₂ sensor warning system or perhaps a secondary cooling loop.

Probably the issue of most immediate concern for CO₂ systems involves high refrigerant leakage rates. Such leakage is not so much a concern from an emissions standpoint as from a system reliability and customer acceptance perspective. Though staff do not have detailed data on specific leak rates, there is anecdotal information that it is a significant problem. These high rates apparently are the result of the high system pressures and the need for further development of adequate hoses, connectors and seals. At least one source recognizes the need for nearly leak proof systems, and indicates progress in that direction.⁴⁸

The result is that significant development costs would be incurred to bring these systems to market, and the procurement cost to the new vehicle purchaser could be significantly higher than for other systems. CO₂ systems are in current development by many parties around the world, including such OEMs as BMW, Audi and Toyota. The SAE Phoenix Symposium expert group estimates that CO₂ systems will be widely available for use in passenger cars in 4 to 6 years⁴⁹. However, staff understands that one leading OEM may make available a high-end model vehicle with a CO₂ air conditioning system beginning with the 2005 model year. In part, interest is due to the wide availability of CO₂ supplies, especially in less-industrialized countries. Current efforts focus on improving COP, reducing leakage, reducing component size and weight, and evaluating safety issues (see next section).⁵⁰

Safety

Under ambient atmospheric conditions, CO₂ is an odorless, colorless, and tasteless gas. In sufficient concentrations, it can act as an asphyxiant by displacing breathable air. Additionally, exposure at lower levels has deleterious physiological effects including respiratory depression, dizziness, drowsiness, nervous system damage and even death. CO₂ is approximately 1.5 times as dense as air; hence, it can collect in low and confined spaces. Also, skin or eye contact with the liquid can result in severe frostbite injury.⁵¹

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For these reasons, there is concern about the use of CO₂ in systems with components located within a vehicle's passenger compartment. Preliminary results from the risk analysis currently being conducted by U.S. EPA indicate that risk mitigation will be needed to address passenger exposure risk in small vehicles⁵². This suggests that a monitoring and warning system for the concentration of CO₂ in the passenger compartment air will be necessary. Another possible solution would be to utilize a secondary heat transfer loop, like that suggested for HFC-152a systems, to allow all CO₂-containing components to remain outside the passenger compartment.

Danger of injury due to the release of high pressure gas in an accident or during maintenance must also be addressed. However, it is evident that it would be nearly impossible to build a practical system with the required strength to maintain structural integrity during the worst of accidents. For maintenance, proper training of repair personnel would be needed to reduce chances of injury. System developers continue to investigate these safety issues.⁵³

Climate Change Emissions

By definition, CO₂ with its GWP of 1 (by definition), has the lowest direct climate change emissions per mass of all the leading alternative refrigerants under consideration. However, as noted, the higher operating pressures of CO₂ systems make it more challenging to mitigate leakage. Also, the COP of CO₂ systems is inversely dependent on the ambient operating temperatures. That is, higher ambient temperatures reduce the efficiency of such systems, requiring more work input for a given amount of cooling capacity. Accordingly, the comparison of indirect emissions from a carbon dioxide system with the baseline depends strongly on the operating conditions.⁵⁴

The SAE Symposium expert group anticipates that direct emissions of CO₂ systems relative to the baseline would be reduced nearly 100 percent, and that indirect emissions could also be reduced.⁵⁵

Hydrocarbon Systems

Currently available information suggests that hydrocarbon (HC) refrigerant systems are not considered a leading alternative mobile air conditioning refrigerant technology. At present, systems utilizing HC refrigerants do not seem to be undergoing significant development by the key players in the mobile air conditioning system industry. They appear to be most popular with aftermarket suppliers who sell them primarily for use in non-mobile applications, though there are some who advocate their use in mobile systems. For completeness, a brief discussion of these systems is included in this document.

Various HCs (and CO₂) are sometimes called "natural refrigerants" because they are not synthesized to the extent that the fluorocarbons are synthesized. The principal HC refrigerants that are often identified by the industry stakeholders are listed in the following table.

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Table 1 - Leading Hydrocarbon Refrigerants

Hydrocarbon	Formula	Designation	GWP
Propane	C ₃ H ₈	HC-290	3 ⁵⁶
Isobutane	C ₄ H ₁₀	HC-600a	3 ⁵⁷
Cyclopropane	C ₃ H ₈	HC-270	3 ⁵⁸

Propane has been used in large refrigeration plants for years and isobutane is widely used in Europe in domestic refrigerators. However, especially in the United States, liability concerns due to their high flammability have historically prevented serious consideration of HC use in mobile air conditioning system applications⁵⁹. HC refrigerants are considered to have comparable or somewhat superior thermodynamic properties to HFC-134a. One study has determined that propane and cyclopropane are superior in system performance to HFC-134a, while isobutane is not suitable as an HFC-134a replacement in mobile air conditioning systems due to low efficiency and excessive compressor size requirements⁶⁰.

An Australian study reports the result of tests comparing HFC-134a with a 55 percent/45 percent mixture of propane/isobutane. After discarding test results for a case where the hydrocarbon refrigerant was contaminated with excessive ethane, the hydrocarbon mixture had comparable or only slightly lower efficiency and cooling capacity.⁶¹ Investigating safety issues, another report by the same primary author reports that more than 200,000 car air conditioners, presumably in Australia, use hydrocarbon refrigerants. In over 400,000 accumulated operating years, no accidents with damage or injury due to hydrocarbon refrigerant flammability have been reported. This latter study also claims that suitable ignition sources are not present in cars and that accident repairs to hydrocarbon systems would be less expensive than similar repairs to CFC-12 or HFC-134a systems.⁶²

As noted previously, ASHRAE places HC refrigerants in flammability category 3, described as “highly flammable”. HC refrigerants have roughly 3 times the heat of combustion of HFC-152a. Finally, under U.S. EPA’s SNAP program, hydrocarbon refrigerants have not been approved for use as a substitute for ozone-depleting substances in motor vehicle air conditioning systems, due to safety and flammability issues.^{63,64} Nevertheless, at least one U.S. company has an application pending for SNAP approval of its propane/butane refrigerant blend, and is currently selling it for retrofit of systems presently using non-ozone depleting refrigerants, though primarily aimed at non-automotive applications⁶⁵.

Another aspect of HC refrigerants is that they can be considered to be volatile organic compounds (VOCs) that have potential for forming tropospheric ozone, should they be released to the atmosphere. A substance’s ozone-forming potential is indicated by its maximum incremental reactivity (MIR) value. Table 2 lists the MIRs for four of the most likely HC refrigerants.

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Table 2 - Maximum Incremental Reactivity Values for Select HC Refrigerants⁶⁶

Propane (HC-290)	0.56
Isobutane (HC-600a)	1.35
Cyclopropane (HC-270)	0.10
Butane (HC-600)	1.33

For further comparison, HFC-134a and HFC-152a both have MIR values of 0.0⁶⁷, meaning they have negligible tropospheric ozone-forming potential. Generally, hydrocarbons and other compounds with MIR values less than that of ethane (MIR = 0.31) are considered by U.S. EPA to be “negligibly reactive” as tropospheric ozone precursors and are not defined as VOCs⁶⁸. Only cyclopropane in Table 2 above meets this criterion. Should hydrocarbon refrigerants become popular, an evaluation of total contributions to local ozone formation should be conducted.

Air Systems

Refrigeration systems based on an air (R-729) cycle process have been investigated in the past and limited practical applications to automotive use have evolved. Staff is aware of no significant development work currently underway to develop a viable system based on this concept. However, one reference maintains that air cycle systems have some advantages over CO₂ systems from the standpoints of safety, simplicity, compactness and fuel usage, though they are not as good as HFC-134a systems⁶⁹. The reader is referred to Appendix C.2 for a basic description of the cycle and discussion of aircraft applications.

Comparison of Alternative Systems

Relative Merit of Leading Available Alternatives

In summary, the available information presented above suggests that there are three leading alternatives to conventional HFC-134a systems with potential for significant near-term market penetration. These are being extensively investigated by the mobile air conditioning system industry and include: 1) enhanced HFC-134a, 2) HFC-152a, and 3) CO₂ systems. The anticipated timeline for market penetration for these technologies is consistent with the time frame of this regulation. Presently, the nature of the data available affords only a rough quantitative comparison of how the leading alternative technologies will perform in production systems, based on their principal advantages and disadvantages as discussed in this report. These are summarized in Table 3.

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Table 3 – Comparison of Alternative Technology Merits⁷⁰

<u>Technology</u>	<u>Advantages</u>	<u>Disadvantages</u>
Enhanced HFC-134a	<ul style="list-style-type: none"> 1-Based on known/established technology 2-Non-flammable, non-toxic 3-Potential for reduced direct & indirect emissions 4-Available in 1-3 years 	<ul style="list-style-type: none"> 1-High GWP 2-Additional development costs 3-Cost of recycling/recovery
HFC-152a	<ul style="list-style-type: none"> 1-Similar components/systems/servicing to HFC-134a 2-potential for improved efficiency 3-Reasonably low GWP 4-Moderately improved performance 5-Leakage certification/verification testing less critical 6-Improvements used in Enhanced HFC-134a technology can also be applied to create enhanced HFC-152a 7-Primary-expansion systems available within 3-5 years, enhanced and secondary loop in 4-6 years 	<ul style="list-style-type: none"> 1-Flammable (safety concerns, may need on-board leak detection & mitigation) 2-Requires recycling/recovery 3-Additional servicing safety issues 4-May need secondary loop
Carbon Dioxide	<ul style="list-style-type: none"> 1-Lowest GWP of the leading technologies examined 2-Non-flammable 3-Reduced component size 4-Recycling not needed 5-Available worldwide 6-Leakage certification/verification testing less critical than for HFC technologies 7-Available within 4-6 years 	<ul style="list-style-type: none"> 1-Significantly higher pressures 2-Safety concerns, may need on-board leak detection & mitigation 2-High component costs 3-New service training & equipment needed 4-New refrigerant handling, transportation, storage requirements 4-Internal heat exchanger needed 5-Lower performance at higher ambient temperature conditions

Although the principal characteristics and chief goals of the leading technologies described above are generally understood by mobile air conditioning system stakeholders at large, there may be variants as to how each of the OEMs ultimately deploys the technology. For example, an “enhanced HFC-134a” system has not been rigorously or unanimously defined. One manufacturer’s approach to enhancing the efficiency of HFC-134a systems could include evaporators and condensers with higher heat transfer effectiveness, while another manufacturer may focus primarily on VDCs and controls. Nevertheless, both approaches would likely result in systems with significantly reduced emissions compared to existing HFC-134a systems. In addition, many of the techniques that are anticipated to “enhance” HFC-134a systems could also be used to improve the performance of HFC-152a systems. For brevity, discussions are focused on the basic alternative systems with near-term potential, rather than on the many possible permutations of these systems that some OEMs may choose to develop.

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Relative Benefit in Terms of Climate Change Emissions

The climate change emission improvements presented previously are restated here in Table 4 for comparison. These estimates are based on limited technical data available to date and primarily reflect the consensus of the expert stakeholders of the mobile air conditioning system industry currently active at this stage in the development of the technologies. This information suggests significant reductions in mobile air conditioning system climate change emissions can be obtained through these alternative technologies. Further development will be needed to mature the technologies to the point where more accurate and reliable data for near-production systems are available.

Table 4 – Comparison of Technology Benefits⁷¹

<u>Technology</u>	<u>Direct climate change emission reductions</u>
Existing HFC-134a	Baseline
Enhanced HFC-134a	50%
Primary-Expansion HFC-152a	94%
Secondary Loop HFC-152a	94%
Enhanced Primary- Expansion HFC-152a	96%
Carbon Dioxide	~100%

Presently, the mobile air conditioning system industry is entering a period of intense activity precipitated by the proposed regulatory developments in Europe and the activities in California. Collaborative efforts among industry, academia, and government are in place to address the needed research and development for the alternative technology. The planned activities also include consideration of the need for development of an accepted test protocol for measuring direct and indirect emissions from vehicle air conditioning systems. Such a standard may also be important for regulatory certification and verification of compliance needs.

Relative Safety

The technical data available to date that aids in ranking these technologies in terms of safety suggests that enhanced HFC-134a systems would likely have the same level of safety as existing HFC-134a systems because they both use the same refrigerant. In addition, HFC-152a systems and CO₂ systems with their safety issues will likely require additional mitigation methods to reduce potential risks, as suggested by the preliminary studies by the U.S. EPA. These modifications appear to be able to yield sufficiently safe systems, but at an increased cost and potential associated performance penalties.

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DIRECT EMISSIONS

The current estimate of refrigerant leakage direct emissions from a typical California car equipped with a conventional HFC-134a air conditioning system is 57.6 grams per vehicle per year⁷². The Phoenix Symposium expert group estimated that the enhanced HFC-134a and CO₂ technologies would yield refrigerant leakage rates about 50 percent lower than those of current system leak rates, with enhanced primary-expansion HFC-152a system leakage slightly less than current systems⁷³. When combined with the GWP reductions of some of the alternative refrigerants, the following values of CO₂-equivalent leakage rates and incremental leakage rate reductions result.

Table 5 – Direct (Leakage-Related) CO₂-Equivalent (DEWI) Emissions and Incremental Reductions

Technology	GWP	Equivalent CO₂ Leakage (lb CO₂/year)	Incremental Equivalent CO₂ Leakage Reduction (lb CO₂/year)
HFC-134a (baseline technology)	1300	165	baseline
Enhanced HFC-134a	1300	82	82
Enhanced Primary-Expansion HFC-152a	120	7	158
Carbon Dioxide	1	0.05	165

In new vehicles, the potential for reduction of direct and indirect emissions of HFC-134a is considerable. Industry sources have opined that existing systems can be cost-effectively improved to achieve up to 50 percent reduction in refrigerant leakage. Reduction of direct emissions can be achieved through system improvements such as the use of low-permeability hoses and improved elastomer seals and connections. Work is in progress to define a component-specific blueprint for a baseline (current) air conditioning system and to identify key components for potential improvement (reduced leakage). It is anticipated that upgrades to a few key components (e.g., compressor shaft seal) would result in a low-leak system that can achieve a 50 percent reduction in “regular” emissions. However, improved containment would not reduce accidental releases or releases during scrapping. A 50 percent reduction in “regular” leakage emissions by a low-leak system translates into a reduction of approximately 3 CO₂-equivalent grams/mile for a modest incremental increase in cost to the manufacturer of approximately twelve dollars. Table 6 illustrates the principal components of interest for upgrading to a low-leak system that halves “regular” emissions.

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Table 6 - Preliminary blueprint of a baseline system.

Component	Approximate Contribution to Leakage Emissions
Flexible hose (high and low pressure) construction and dimensions	25%
System component connections (type and number)	25%
Compressor shaft seal	50%
<i>Leakage emissions prior to component improvements</i>	6 CO ₂ -equiv (g/mi)
<i>50% Reduction in Leakage</i>	~3 CO₂-equiv (g/mi)

While low-cost improvements to current HFC-134 systems to reduce leakage appear feasible, the benefits for climate change are modest. Other alternatives can result in greater benefits. Emissions of HFC-134a could be completely avoided in new vehicles by using an alternative refrigerant with a lower GWP. The known candidate alternatives are HFC-152a (GWP = 120) and CO₂ (GWP = 1). HFC-152a could be introduced as a vehicular refrigerant on a schedule that appears to be consistent with the requirements of AB1493.

If new systems would use HFC-152a, the emissions of refrigerant (in terms of CO₂-equivalents) from all sources would be reduced in potency by 91 percent. However, since HFC-152a is flammable under certain conditions, a moderate safety issue must be addressed. Industry representatives report that they are currently evaluating technical solutions for mitigating the potential safety concerns associated with HFC-152a. The schedule on which CO₂ systems could be deployed is uncertain. If the systems would use CO₂, the reduction of potency of the same emissions would be virtually completely eliminated. Safety issues related to high system pressures and in-cabin releases are currently in evaluation.

SUMMARY AND CONCLUSIONS

In summary, information in the relevant available literature suggests that three leading practical alternatives are being developed to replace the current HFC-134a based mobile air conditioning system technology. These technologies are enhanced HFC-134a systems, systems based on HFC-152a, and carbon dioxide based systems. Staff believes that any of these approaches can address the need to reduce both direct and indirect climate change gas emissions from mobile air conditioning systems. With further development and attention to the issues, including the need for risk assessment and mitigation, vehicle manufacturers and consumers will have several sound alternatives for reducing air conditioning system climate change emissions.

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ISSUES

One of the primary issues that deserves final emphasis involves the early stages of development of some of these alternative technologies and, therefore, the uncertainty associated with predicting performance levels, emission levels, safety, costs, and the timeframes for market penetration. Staff emphasizes that predictions discussed in this report are as accurate as the information and data used to make them will allow. Nevertheless, it can be expected that as developers continue to advance the different alternative technologies, both costs and emissions will continue to improve.

Also worthy of reemphasis is the issue of safety. The automotive industry is very aware of its responsibility towards the safety of its customers, both in a legal and in a moral sense. The OEMs will be very reluctant to sell any air conditioning technology that doesn't acceptably address the risks to the driving public, regardless of how low its climate change emissions. But staff expects that, with proper attention to detail, the technology will be available when needed to provide mobile air conditioning systems that are both acceptably safe and environmentally friendly. The people of California expect nothing less.

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