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Stella Papasavva

Stella Papasavva Consulting, greengem09@gmail.com

William Moomaw

Professor of International Environmental Policy at the Fletcher School, Tufts University, william.moomaw@tufts.edu

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Comparison between HFC-134a and Alternative Refrigerants in Mobile Air Conditioners using the GREEN-MAC-LCCP[®] Model

Stella PAPASAVVA^{1*}, William MOOMAW²

¹Stella Papasavva Consulting,
Royal Oak, MI 48073, USA
(248-588-4995, greengem09@gmail.com)

²Professor of International Environmental Policy at the Fletcher School,
Tufts University, 160 Packard Avenue, Medford, MA 02155, USA
(617-627-2732, william.moomaw@tufts.edu)

* Corresponding Author

ABSTRACT

The transition from CFC-12 (GWP=10,900) to HFC-134a (GWP=1,430) in the 1990's in new vehicle air conditioners eliminated the contribution to ozone depletion potential (ODP) from new vehicles and reduced the direct Global Warming Potential (GWP) by over 80%. One proposed alternative is HFC-1234yf (GWP=4). Despite the phase-in success of HFC-134a as a zero ODP automotive refrigerant it is still a potent greenhouse gas and the European Union (EU) issued Directive 2006/40/EC that prohibits the use of automotive refrigerants with GWP greater than 150, starting from January 1st, 2011. Due to such regulations, the automotive Original Equipment Manufacturers (OEMs), chemical manufacturers and Mobile Air Conditioning (MAC) industry have evaluated several alternative refrigerants considering a range of selection criteria that include: refrigerant engineering performance, system design impact, MAC system changes to optimize the use of new refrigerants, cost, flammability, and environmental impacts including global warming, and human toxicity risks.

There has been remarkable success in eliminating refrigerant fluids that deplete the ozone layer, but many of their replacements have high GWP. There is now a major international effort for a third generation refrigerant fluids that are safe both for ozone depletion and climate protection. During 2013, the United States and China proposed phasing out high GWP HFCs that have been introduced to replace ODP substances through the provisions of the Montreal Protocol. Europe is currently debating between two alternative fluids for vehicle air conditioners, and the outcome is being watched closely. This paper will compare the alternatives. New MAC systems that meet the low GWP requirements of the EU Directive refrigerants should also be equally or more efficient than HFC-134a designs. Life Cycle Analysis (LCA) adds a step in the understanding of the dynamics of the industrial activities as a system and not as individual components, with implications for better policy decisions at the technological and environmental levels. The MAC industry and government recognized this need, and Life Cycle Climate Performance (LCCP) was accepted as one of the methods for selecting among alternative refrigerants.

We consider and implement LCA for developing the Global Refrigerants Energy & Environmental-Mobile Air Conditioning-Life Cycle Climate Performance (GREEN-MAC-LCCP)[®] model which is the tool that evaluates the full cycle of Greenhouse Gas emissions (GHG) of alternative refrigerant systems. The goal of this tool is to provide a superior basis for engineers and policy makers to make wise decisions of alternative competing technologies. In this paper, we summarize the evolution of refrigerant fluids and how the world has arrived at the present point. The interplay between the evolution of technology and the regulatory system that governs it, the economic drivers and the environmental health and safety implications will be elucidated. We also provide a short overview of the model and the results obtained by evaluating alternative refrigerant MAC systems and compare them with the HFC-134a production baseline. Using GREEN-MAC-LCCP[®] we estimate the energy consumption and GHG of MACs that operate with HFC-134a and compare these results with new systems that operate with alternative refrigerants.

1. INTRODUCTION

Early mechanical refrigeration in the 1920s, used a wide variety of refrigerants, including carbon dioxide (CO₂), water (H₂O), ammonia (NH₃), hydrocarbons, sulfur dioxide (SO₂), and methyl chloride (CH₃Cl). Carbon dioxide (R-744), water (R-718), ammonia (R-717) and hydrocarbons are also known today as “natural refrigerants”. Refrigerants such as ammonia, carbon dioxide and non-halogenated hydrocarbons do not deplete the ozone layer and have no GWP for ammonia, and only a low GWP for carbon dioxide, and hydrocarbons. Mechanical refrigeration assured safer refrigeration to ice, because of ice contamination and lower safety temperatures for food refrigeration indicated by (Calm, 2007, Elkins, 1999). Nevertheless, mechanical refrigeration using sulfur dioxide and ammonia as refrigerants was associated with dangerous leaks in the 1920s, because these chemicals are toxic to people.

Over the years additional criteria for introducing “ideal” refrigerants have been added to the list of desirable thermodynamic properties that met concerns of both producers and society at large. Engineering concerns include operating efficiency, cost and ease of production and potential profit. Society has imposed additional criteria including fire and explosion safety, toxicity and health, environmental safety in manufacturing, use and disposal, stratospheric ozone depletion potential and global warming potential. There has been remarkable success in eliminating refrigerant fluids that deplete the ozone layer, but many of their replacements have high global warming potential. There is now a major international effort for a third generation of refrigerant fluids that are safe both for ozone depletion and climate protection. Europe is currently debating between two alternative fluids for vehicle air conditioners, and the outcome is being watched closely.

In this paper, we will summarize the evolution of refrigerant fluids and how the world has arrived at the present point. The interplay between the evolution of technology and the regulatory system that governs it, the economic drivers and the environmental health and safety implications will be elucidated with the goal of understanding how a more effective process might be devised that meets both private and public interests.

2. CHLOROFLUOROCARBONS (CFCs)

In 1928, Thomas Midgley, invented the industrial synthesis of chlorofluorocarbons (CFCs). CFCs were considered the “perfect” man-made chemicals for almost any application because they have favorable thermodynamic properties, are non-corrosive to mechanical components, and are safe because they are non-toxic and non-flammable. As a result early mechanical refrigeration systems that employed sulfur dioxide and methyl chloride rapidly disappeared from the market. Until 1996 CFCs were believed to be benign to the environment and harmless to humans and were used widely in residential and transportation air conditioning, industrial and commercial refrigeration, energy-efficient insulation, foam blowing, cleaning solvents for manufacturing processes and electronic components, and fire extinguishing. The most highly used CFCs in the 20th century were CFC-11, CFC-12 and CFC-113. Trichlorofluoromethane (CCl₃F), freon-11 or CFC-11, was the first widely used refrigerant and was once the propellant for about half of all the aerosol cans used in the world. Dichlorodifluoromethane (CCl₂F₂) freon-12 or CFC-12, used mainly as a refrigerant for home and vehicle air conditioners, and Trichlorotrifluoroethane (C₂Cl₃F₃), freon-113 or CFC-113, used mainly as a solvent. DuPont was the major CFC producer in the world and in the mid 1970’s was accounting for more than half of US and about a quarter of world’s capacity production of freons (Maxwell, 1997). The industrial chemical synthesis of CFCs, in particular that of CFC-11 and CFC-12 is a relatively easy and efficient process. For many decades it was also profitable to the industry and the price of CFC-11 and CFC-12 was inexpensive, \$0.5 - \$0.6 per pound (lb) in the 1980’s. Because the transportation costs were high relative to the price of the product, production plants were located close to large markets. DuPont used a CFC synthesis based on the halogen substitution of methane that is chemically reacted with chlorine to produce carbon tetrachloride (CCl₄) which is then reacted with anhydrous hydrogen fluoride (HF) in the presence of antimony chloride (SbCl₅) catalyst to produce Freon (Papasavva & Moomaw, 1998). The production yields of CFCs have been carried out in industrial plants with high yields that exceeded 99% (McKetta, 1985).

Hydrogen Fluoride is a highly corrosive and toxic chemical and is produced by reacting concentrated Sulfuric Acid (H₂SO₄) with Fluorspar (CaF₂). The precipitating Calcium Sulfate (CaSO₄) is the byproduct of the HF production. CaSO₄ commonly known as gypsum tends to concentrate radioactive elements and Arsenic because often Fluorspar contains these toxic substances (Papasavva, 2008a). A typical plant that produces CFCs usually creates a

surrounding hill of CaSO_4 around its property that gets higher with time if no other recycling options take place mainly because these are not profitable options to the plant.

Despite their technological success, in 1974 atmospheric scientists Mario J. Molina and Sherwood F Rowland warned that CFCs could deplete the stratospheric ozone layer that shields and protects the Earth against ultraviolet, UV-B, radiation, indicated by (Molina, 1974). The strong chemical stability of CFCs is the reason of being non-reactive in the lower atmosphere and therefore being able to survive and reach the stratosphere where they are globally distributed. In the stratosphere the ultraviolet radiation causes the strong carbon chlorine chemical bond in CFCs to break and to release chlorine atoms. The chlorine radical Cl^\cdot is long-lived in the stratosphere and it catalyzes the conversion of ozone (O_3) into oxygen (O_2) causing stratospheric ozone depletion. The importance of the stratospheric ozone layer is to absorb UV-B radiation, and protect humans and the environment from adverse impacts. Uncontrollable amounts of UV radiation entering the atmosphere are harmful to humans and the environment because UV causes skin cancer, cataracts, suppresses the human immune system and destroys agricultural and natural ecosystems indicated by (Molina, 1974).

3. HYDROCHLOROFLUOROCARBON (HCFC) & HYDROFLUOROCARBON (HFC)

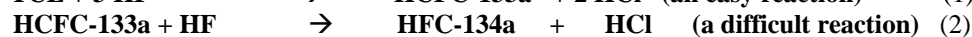
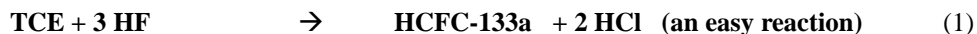
In 1987, in response to the growing evidence that CFCs are causing depletion of the stratospheric ozone layer, 27 nations signed the Montreal Protocol, which called for a complete phase-out of CFCs use in 1996 by industrialized countries and for the rest of the world in 2010. CFCs were replaced by HCFCs and HFCs that have either much lower or zero Ozone Depletion Potentials (ODP). Despite the significantly lower ODPs of HCFCs as compared to the CFCs, HCFCs still cause stratospheric ozone depletion and therefore are controlled under the Montreal Protocol. CFCs were replaced by a variety of HCFC or HFC alternative refrigerants developed by the industry and approved by United States Environmental Protection Agency (U.S EPA) SNAP (Significant New Alternatives Policy) program, as shown in Figure 1.

The increase of environmental concerns, availability of better scientific data that showed worsening of the Antarctic ozone hole, resulted in the abandonment of CFCs as propellants in aerosol spray cans through legislation beginning in North America and a few European countries in the late 1970's. This action played an important role in the successful implementation of the Montreal Protocol and significantly influenced DuPont's decision to decrease the production of CFCs. The banning of CFCs from the spray cans caused DuPont to lose 25% or more of its Freon business (Maxwell, 1997). In addition EPA imposed stringent regulations based upon additional scientific data predicting significant losses in stratospheric ozone, and pressure from Non-Governmental Organizations (NGOs) such as Natural Resources Defense Council (NRDC). This created the basis for major industrial producers to start investing in alternative chemicals with lower ODPs.

Despite the significantly higher initial costs of the CFC alternatives, 10-15 higher than the cost of CFC-11 and CFC-12, the industry resistance to initiate the production of the substitutes was eased with government intervention to impose taxes on CFCs. In addition one of the industry's goals was to introduce CFC alternatives that were close to "drop-in" chemicals which required little or minor modification of existing equipment so that the overall additional expense of the CFC substitutes was very minor to the overall cost of any new refrigerator or air conditioning system. Table 1 presents proposed alternatives to CFC-12 for Refrigerators and Air Conditioners and to CFC-11 for Chillers. These alternatives have been approved for use by EPA's SNAP program.

3.1 Industrial Chemical Synthesis

The industrial chemical synthesis of HFCs and in particular HFC-134a is a more difficult, less efficient and potentially more expensive process than the production of CFC-12 it replaces. Personal communication with a major chemical manufacturer that supplies a third of world's HFC-134a indicates that HFC-134a manufacturing is a multistep process. The raw material ethylene is reacted with chlorine to produce trichloroethylene (TCE) which is then reacted with HF to produce HFC-134a and hydrogen chloride (HCl), as shown in reactions (1) and (2).



Reaction 1 is easy because it favors the formation of 2-chloro-1,1,1-trifluoroethane (HCFC-133a), i.e. its end product. However, reaction 2 favors the reactants, i.e. HCFC-133a and HF.

As a result producing HFC-134a from HCFC-133a takes a lot of energy and chemical engineering skills.

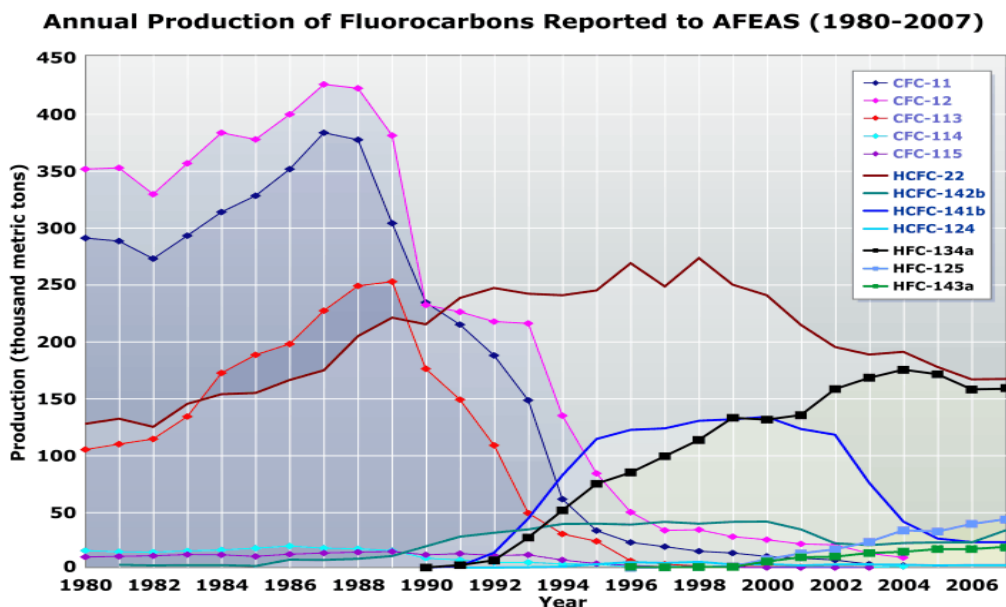


Figure 1: Historic Production of CFCs, HCFCs and HFCs. Source: (AFEAS, 2014)

Table 1: Proposed CFC-12 Substitute Refrigerants for Commercial and Domestic Refrigeration and Motor Vehicle Air Conditioners and CFC-11 Substitute Refrigerants for Chillers. Source: (U.S EPA SNAP, 2014)

Commercial Refrigeration			Domestic Refrigeration			Motor Vehicle Air Conditioners			Chillers		
Refrigerant	GWP	ODP	Refrigerant	GWP	ODP	Refrigerant	GWP	ODP	Refrigerant	GWP	ODP
CFC-12	10,900	1	CFC-12	10,900	1	CFC-12	10,900	1	HCFC-123	77	0.02
R-502 (HCFC-22 & CFC-115)	4,657	0.334	HFC-134a	1,430	0	HCFC-22	1,810	0.055	HCFC-22	1,810	0.055
R-507A (HFC-32 & HFC-125)	3,985	0	HFC-152a	124	0	R-407C	1,774	0	HFC-134a	1,430	0
R-404A (HFC-143a, HFC-125, HFC-134a)	3,922	0	Isobutane (R-600a)	3	0	HFC-134a	1,430	0	HFC-227ea	3,200	0
R-407A (HFC-32, HFC-125, HFC-134a)	2,107	0				HFC-152a	124	0	HFC-245fa	1,030	0
HCFC-22	1,810	0.055				HFO-1234yf	4	0	Ammonia Vapor Compression	0	0
R-407C (HFC-32, HFC-125, HFC-134a)	1,774	0				CO2 (R-744)	1	0	Evaporative Cooling	0	0
HFC-134a	1,430	0						Desiccant Cooling	0	0	
Propane (R-290)	3.3	0						Ammonia / Water Absorption	0	0	
CO2 (R-744)	1	0						Water / Lithium Bromide Absorption		0	
Ammonia (R-717)	0	0						Trans-1-chloro-3,3,3- trifluoroprop-1-ene			
								HFO-1234ze	6	0	

This is accomplished by recycling the reaction by-products, HCFC-133a, HCl and whatever HF amounts are left unreacted back to reactor 2. The output gas stream of reactor 2 is going to the distillation columns in which HFC-134a is separated and purified and directed to the day bank storage tanks. The HCFC-133a, HCl, HF are recycled back to reactor 2, etc.. It is also evident that the stoichiometric amounts of HF needed to manufacture HFC-134a, are much higher than those required for the production of CFC-12 and therefore producing more of CaSO₄ that is piling up around plants contaminated with toxic arsenic or radioactive chemicals.

The higher prices of HFC-134a today, in the range of \$4/lb - \$7/lb as compared to the lower prices of CFCs during their highest use and demand in the 1980's may reflect the additional costs associated for their chemical manufacturing. Often the chemical plants that manufacture HFCs are large scale plants due to the gas-phase reaction type of processes that take place as compared to the liquid phase synthesis of CFCs and they are potentially associated with higher capital costs. This may be one of the economic challenges to transition to the new alternatives with low GWPs that require a new chemical infrastructure.

4. GLOBAL WARMING IMPACTS OF CFC, HCFC & HFC

CFCs, HCFCs and HFCs are also GHGs that contribute to climate forcing, with GWP for HCFCs generally lower than the CFCs they replace. GWP is a measurement of how much heat a gas can trap in the atmosphere. It is expressed as a ratio of a gas's heat-trapping ability relative to that of carbon dioxide (which has a GWP standardized at one), and is often expressed over a 100-year timescale (Forster *et al.*, 2007, Solomon *et al.*, 2007 retrieved 2014). The GWPs of the ODSs range between 5 (methyl bromide) and 10,900 (CFC-12). Thus, on a per mass basis, 1 kg of CFC-12, for example, has the same climate impact as if 10,900kg of CO₂ were emitted. The GWPs of HCFCs are about 2,000 or more times that of carbon dioxide (CO₂). HFCs have GWPs ranging from 4 to 11,700 times that of carbon dioxide (Forster *et al.*, 2007). HFCs are also known to be short-lived climate forcers and they are associated with high potential to contribute to global warming. As compare to the CFCs they replace they have zero ODPs but comparable GWPs. HFC emissions highly contribute to global warming and a significant reduction in their emissions will make a significant impact to moderate global warming. Although the climate change issue was gaining momentum and attracting bigger attention in the 1990's, the systematic implication of the ozone depleting CFCs and their HCFCs and HFCs substitutes to climate change was not considered until over a decade later. In 2007, Parties to the Montreal Protocol accelerated the HCFC phase-out in order to help protect the climate while further protecting the stratospheric ozone layer. A team of scientists quantified the climate change that was avoided by action under the Montreal Protocol to phase-out ozone-depleting greenhouse gases (Velders *et al.*, 2007). ODS phase-out has already reduced CO₂-eq. emissions by about 5.0 GtCO₂-eq per year, which is equivalent to reducing global fossil fuel burning by about 23% (Forster *et al.*, 2007). A global phase-down of HFCs could avoid 100 gigatons of CO₂-eq. emissions by 2050, and prevent a global average temperature increase of 0.5 degrees Celsius by 2100, according to findings announced at the COP meeting of the Montreal Protocol Parties in Bangkok, Thailand, (Kennan, 2013).

5. ENVIRONMENTAL IMPACTS OF HCFC & HFC

HCFCs and HFCs are less stable in the atmosphere, and are more reactive with shorter atmospheric lifetimes than CFCs. Some of the most stable atmospheric products include carbonyl fluoride (COF₂), perfluoroacetyl fluoride (CF₃COF) and trifluoroacetic acid (TFA) (CF₃COOH). Although these chemicals have non-zero GWPs these values are very low in the range between 1 and 20 and therefore their global warming impacts are very small. TFA on the other hand has the potential to accumulate and adversely affect ecosystems by increasing their acidity. Studies show that the decomposition of HFC-134a produce TFA levels below harmful thresholds to ecosystems (AFEAS, 2014).

6. HYDROFLUOROOLEFINS (HFOs)

In response to concern about climate change, policymakers around the world are taking action to reduce GHG pollution from MACs. Although the predominant refrigerant in current MAC systems worldwide is the HFC-134a its high GWP creates a cause of concern for its impact to global warming. MAC is the largest and most emissive sales market for HFC-134a. In 2006, the European Commission issued Directive 2006/40/EC, which requires new types of air-conditioned cars sold in the EU to have a refrigerant with a GWP of 150 or less starting in 2011, and all

new vehicles to have a refrigerant with a GWP of 150 or less by 2017, indicated by (Papasavva *et. al.*, 2009). Several alternatives exist to replace HFC-134a but no one of the proposed alternative refrigerants is perfect. Original Equipment Manufacturers (OEMs) and their suppliers responded to the European F-Gas Directive by examining many alternative refrigerants including carbon dioxide, R-744, (CO₂, GWP=1); hydrocarbons such as propane, R-290, (GWP<10); HFC-152a (1,1-difluoroethane, CH₃CHF₂, GWP=122); HFC-1234yf also known as HFO-1234yf (2,3,3,3-tetrafluoropropene, CH₂=CFCF₃, GWP=4). Some environmental properties of these refrigerants are shown in Table 2.

Table 2: Environmental Properties of Alternative Refrigerants

Refrigerants	HFC-134a	HFC-152a	R744	R290	HFC-1234yf
Chemical Formula	CF ₃ -CFH ₂	CH ₃ -CF ₂ H	CO ₂	CH ₃ -CH ₂ -CH ₃	CH ₂ =CFCF ₃
Molecular Mass	102	66	44	44	114
Atmospheric Life	14 yr.	2 yr.	>100 yr	<1 yr.	11 days
ODP	0	0	0	0	0
GWP	1,430	122	1	20	4

Although DuPont is currently the leader in refrigerants worldwide, Honeywell is the world leader in HFC production. One application of HFC's is the automotive refrigerants. Since the early 1990's DuPont was focused mainly in the HFC-134a production. Honeywell, responded to the HCFC phase out, and replaced HCFC-22 with the patented HFC-410a blend. HFC-410a, mainly for chiller applications, consists of 50% HFC-125 (non-flammable) and 50% HFC-32 (very flammable) and its price is 3-times that of HCFC-22. Some of Honeywell's HFC-134a plants are "swing" production plants i.e. they can produce both HFC-134a and HFC-125 so that when the HFC-134a manufacture shuts down, HFC-125 begins in a relatively short period of time (Papasavva, 2008b).

Honeywell was the first chemical manufacturer to develop a refrigerant blend that consists of 20% CF₃I and 80% Fluid HFC-1234yf (CF₃CF=CH₂). Although the chemical synthesis of HFC-1234yf is proprietary, there are reasons to believe that the existing chemical plant infrastructure that produces HFC-125 is supporting HFC-1234yf synthesis. The original refrigerant fluid blend composition included Trifluoroiodomethane (CF₃I) because HFC-1234yf was originally considered a flammable refrigerant and not safe for replacing HFC-134a in MACs. The significant percent concentration (20%) of CF₃I in the blend assured vehicle OEMs of a non-flammable refrigerant for use in MACs. However, the toxicity of CF₃I mainly as a cardiac sensitization agent for concentrations that were found to be possible inside the vehicle cabin and its small but non-zero ODP made this blend component to be banned. This creates the beginning of the long and often non-trivial flammability testing of HFC-1234yf by all major vehicle OEMs worldwide.

While the moderate atmospheric lifetime of HFC-1234yf leads to a desirably low GWP, this same reactivity means that it has the potential to form ozone and other chemical species of concern in the troposphere. Ground level ozone continues to remain a serious problem in the United States and throughout the world, reaching levels in many places that can pose serious health effects. Concerns have also been raised about the potential effects of other chemical byproducts including TFA and hydrofluoric acid. A recent study (Papasavva *et. al.*, 2009) developed a spatially and temporally resolved inventory of likely future HFC refrigerant emissions from the US vehicle fleet. The study estimated leak rates from regular leaks, irregular leaks, leaks from servicing, and end of life leakages, for a vehicle fleet representative of the year 2017. A different study (Luecken *et. al.*, 2010) estimates the ozone and TFA Impacts in North America from the degradation of HFO-1234yf. It is found that HFO-1234yf produces tropospheric ozone. However, the incremental amount is small, averaging less than 0.01% of total ozone formed during the simulation. It is shown that this production of ozone could be compensated for by a modest improvement in air conditioner efficiency. Atmospheric decomposition of HFO-1234yf produces TFA, which is subject to wet and dry deposition. Deposition and concentrations of TFA are spatially variable due to HFO-1234yf's short atmospheric lifetime, with more localized peaks and less global transport when compared to HFC-134a. Over the 2.5 month simulation, deposition of TFA in the continental U.S. from MACs averages 0.24 kg km⁻², substantially higher than previous estimates from all sources of current HFCs. HFO-1234yf emissions from MACs are predicted to produce concentrations of TFA in Eastern U.S. rainfall at least double the values currently observed from all sources, natural and man-made but lower than the lowest level considered safe for the most sensitive aquatic organisms.

Overall HFO-1234yf is a more environmentally friendly alternative to HFC-134a. Other than requiring different lubricating oil for the compressor, it provides a near 'drop-in' replacement alternative. Some system changes are required if the system cannot tolerate the approximate 5 percent performance loss inherent with HFO-1234yf. For automotive systems, and an increasing number of commercial vehicle systems, this loss in efficiency correlates to a negative impact on fuel economy, which needs to be, accommodated through other system changes.

The ban on HFC-134a does not apply to vehicles in North America, nor are there any regulatory timetables to require low-GWP refrigerants in cars or trucks. The EPA decision means that vehicle manufacturers in the United States can use HFO-1234yf to help comply with rules requiring a 40 percent improvement in overall U.S. fleet average vehicle fuel economy by 2016. The EPA awards regulatory credit for the improved environmental performance of the new refrigerant. For instance, a major US car manufacturer announced it will use HFO-1234yf in some of its models sold in the USA beginning with the 2013 model year. The company said the use of HFO-1234yf will help its vehicles significantly exceed its targets under the new regulations (Lockridge, 2011).

Current production capacity of HFC-1234yf is not capable of supplying a total global demand and therefore costs are extremely high. As no new capacity is being added for HFC-134a, costs are rising as well. Ultimately cost versus benefit will drive the adoption of new refrigerants. While HFO-1234yf will not require major modifications of HVAC systems, it is not intended as a drop-in replacement for HFC-134a. There will be different charge ports for HFO-1234yf to help prevent mixing up the refrigerants. For vehicles that will be using HFO-1234yf, service shops and technicians may need to purchase or use new equipment, according to Society of Automotive Engineers (SAE) (SAE, 2009). These may include recovery/recycle/recharge equipment, refrigerant identifiers and leak detection equipment. The new refrigerant is also mildly flammable, so precautions used with other flammable materials such as gasoline or oil are required. Although it is claimed that HFO-1234yf facilitates the industry transition to new MAC systems, in reality, this transition may do the opposite. Currently, HFC-134a costs approximately \$7/ kg, whereas it is expected that HFO-1234yf will cost \$80/kg, ten times more. Consequently, after the first charge of refrigerant HFO-1234yf has been expended, consumers may be highly likely to refill their MACs with HFC-134a as a cost saving measure. The prohibitively high cost of HFO-1234yf may potentially prove to be an even greater impediment in developing countries where the car market is rapidly growing. Due to the fact that HFO-1234yf has GWP =4 and HFC-134a GWP=1,430, the use of HFC-134a may be unnecessarily prolonged by the introduction of HFO-1234yf into the global market, therefore undermining the ultimate goal of reducing greenhouse gas emissions (Alliance for CO₂ Solutions, 2013).

7. CARBON DIOXIDE (R-744)

The proposed R-744 (CO₂) MAC refrigerants has the benefits of being non-flammable, non-toxic, and readily available. Today CO₂ is released as an industrial waste product directly to the atmosphere. By cleaning and re-using it for cooling and heating a car, i.e. recycling it, R-744 can become environmentally benign. By contrast, competing chemical alternatives have to be manufactured from scratch with all accompanying environmental burdens. However, the drawbacks of CO₂ are amplified in heavy-duty vehicles, including high operating pressures and a need for metal hoses, seals and lines (Hansen, 2009). Virtually every component, from compressors to heat exchangers, would have to be redesigned to handle the higher pressures. A CO₂-based MAC system operates at 8 to 10 times the operating pressure, making it extremely difficult to prevent from leaking in a mobile vehicle environment. A leakage caused drop from 6% to 2% would create a measurable performance loss. There is reportedly R-744 leakage concerns that remain to be solved, particularly at internal system temperatures above 75°C (167°F), as a seven-year life for a MAC refrigerant charge is expected (SAE, 2009). R-744 being a high-pressure system with a very low (31°C/88°F) condensation temperature, has a reduced efficiency at high ambient temperatures. Although estimated cost for an R-744 system has dropped in the past few years, it may still be more expensive than other alternatives, until a mass production of the system is adopted at industrial scale.

8. INDIRECT IMPACT OF REFRIGERATION USE

MAC accounts for 6%-20% of additional fuel consumption running with HFC-134a (Papasavva *et. al.*, 2011, Rugh *et. al.*, 2004). Studies show that current MAC technology based on HFC-134a refrigerant, demands additional fuel during MAC operation in the: USA by 7%, in the EU by 7%, in Japan by 9%, in India by 15% -20% and in China by 7%-10% depending on the humidity. New MAC systems that meet the low GWP requirements of the EU Directive

refrigerants should also be as equally or more efficient than HFC-134a designs. Within the boundaries of global climate change we also suggest that a bigger environmental benefit can be realized only when a systems approach is in place to validate the life cycle GHG emissions of the proposed new alternatives for MAC. A systems approach takes into consideration not only the direct climate impact of alternative refrigerants due to their leaks into the atmosphere but also the additional fuel consumption due to the operation of the systems running with alternative refrigeration options. Understanding the relationship between GHG emissions and product life cycle is paramount to further reducing GHG emissions. Life Cycle Climate Performance (LCCP) adds to the understanding of the dynamics of the industrial activities as a system and not as individual components, with implications to better policy decisions at the technological and environmental levels. This has been recognized by the industry and government and LCCP analysis is one of the criteria for selecting among alternative refrigerants in the Mobile A/C industry.

9. GREEN-MAC-LCCP[®]

In 2005 the first LCCP model was published by (Hill & Papasavva, 2005), and in 2007 based on US EPA and industry consensus the model was further enhanced and disseminated for public use. The Copyrighted **Global Refrigerants Energy & Environmental-Mobile Air Conditioning-Life Cycle Climate Performance (GREEN-MAC-LCCP[®])** Model is documented in peer-reviewed publications and in an SAE Standard document (Papasavva & Andersen 2011, Papasavva *et. al.*, 2008c, Papasavva *et. al.*, 2009, SAE 2009b, Papasavva *et. al.*, 2010).

LCCP = **GWP** [Direct from leaks] + **GWP** [Direct from additional sources: (atmospheric reaction products of refrigerant) + (manufacturing leakage) + (end-of-life refrigerant emissions)]
+
GWP [Indirect from MAC operation] + **GWP** [Direct from additional sources: (chem. prod. refrigerant & transport) + (manufacturing MAC & vehicle assembly) + (end-of-life recycling)] (3)

LCCP is a measure of the total cradle-to-grave climate impact, expressed in terms of energy consumed and GHG emissions, over the life cycle of the product, including manufacturing, transportation, use and End-of-Life (EOL) recycling or disposal. The **DIRECT** emissions result from the leaks of the refrigerant into the atmosphere and are expressed in terms of CO₂-eq. emissions based on the GWP of the refrigerant. The **INDIRECT** emissions result from the energy consumption due to product manufacturing, operation, transportation and EOL disposal, and are reported in terms of CO₂-eq. emissions, considering the carbon content of the fuel utilized in each process and during product operation. A complete LCCP analysis takes into account all the direct and indirect GHG emissions of any refrigeration system.

The latest version (3b) of the model consists of 10 input spreadsheets: MAC-Manufacturing-EOL, Atmospheric Degradation, Leakage, Drive-Cycle, Climate, Capacity, COP, Fan Power, Fuel-Data, and Global Vehicle Registrations. For each MAC system, 67 world cities are analyzed in terms of specific weather and driving conditions. Three vehicle platforms and default engine RPM (Revolution per Minute) data are provided for each drive cycle in each world region. The Drive Cycle input sheet can analyze three different engine vehicle types: Compact, Midsize and SUV with 4-cylinder, V6-cylinder, and V8-cylinder engines respectively. Five different driving schedules with city and highway portions are included: SCO3 and Federal Test Procedure (FTP) for the US, New European Drive Cycle (NEDC) for Europe, China, and Australia, Japanese Cycle (JC08) for Japan, and emissions drive cycle for India. The engine RPM data are based on actual vehicle tests during each second of the driving schedule for each of these drive cycles. All data and assumptions are transparently presented in spreadsheet format so that any differences between system inputs and outputs can be closely examined. The model highlights all cells that are available for user's input, such as refrigerant charge, GWP, leak rates, Coefficient of Performance (COP), evaporator cooling capacity (Q_e), and designates in different color the fixed values agreed. The model takes into consideration key MAC system characteristics such as Coefficient of Performance (COP), and evaporator cooling capacity data obtained from bench tests performed in independent laboratories and integrates them with other vehicle and alternative refrigerant inputs such as: annual driving time, A/C on time, weather data, vehicle lifetime, refrigerant leakage rates, MAC system mass requirements, energy requirements due to manufacturing, and end-of-life impacts of alternative refrigerants and MAC components. All data and assumptions are transparently presented in spreadsheet format so that any differences in climate performance between systems can be closely examined. Typical analysis will use standard input data and assumptions for the energy embodied in production of refrigerants and air conditioning system components, for climate and driving habits of specific locations, and for incremental energy consumption associated with A/C operation. Data that are unique to a competing technology,

such as GWP of refrigerants, refrigerant leak rates, A/C system efficiency, and A/C cooling capacity, are entered on the spreadsheets and automatically integrated into the analysis.

GREEN-MAC-LCCP[®] has been globally peer reviewed by the international experts and approved. Due to its transparency, flexibility, accuracy in predicting the life cycle GHG impact of alternative refrigerants and user friendly interface it has become the global standard methodology for assessing the climate impact of MAC systems. The standard document, SAE J2766, is now also available (Papasavva *et. al.*, 2010). SAE J2766 is likely to be the global standard for measuring climate performance for MAC regulations and possibly for quantifying GHG emissions in carbon trading. The model is hosted on the USEPA Climate Protection Partnership Division website (U.S EPA, 2014).

Figure 2 presents GREEN-MAC-LCCP[®] results that compare proposed alternative refrigerants versus the baseline HFC-134a system for a midsize car. The results assume the use of HFC-134a for Vehicles in the Fleet prior to 2011 and all New Vehicles Produced after 2011 have the New Refrigerant. The results indicate that HFC-1234yf has the potential to lower GHGs in all world regions, whereas, R-744 performs better than R-134a in cooler/mild climates.

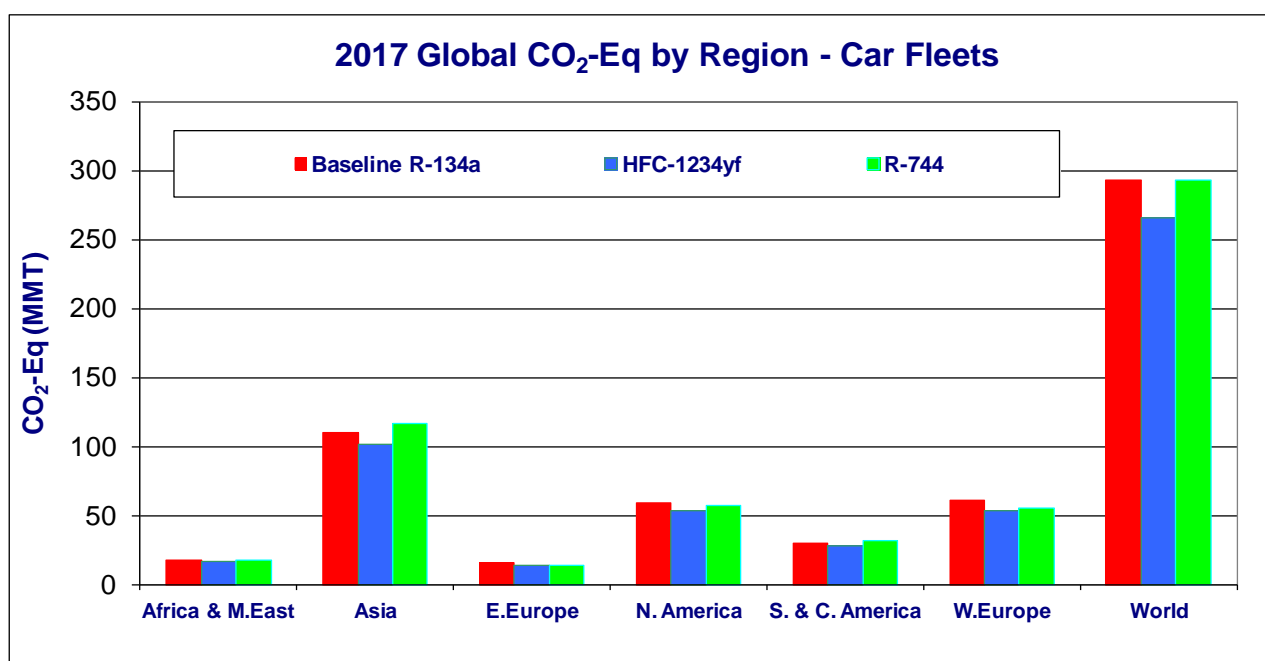


Figure 2: Greenhouse Gas Emissions of New Refrigerants compared to the Baseline using GREEN-MAC-LCCP[®]

10. CONCLUSIONS

The selection of alternative refrigeration systems is a complex scientific and engineering task and several factors, such as system performance, development cost, safety, environmental impacts and business investment, need to be considered and properly addressed during the decision process. The Montreal Protocol success is reflected not only in the protection of the ozone layer but also in the moderation of global warming, reflecting the dynamic intermingles between nature and human actions. Understanding the relationship between GHG emissions and product Life Cycle is paramount to further reducing emissions. LCCP adds a step in the understanding of the dynamics of the industrial activities as a system and not as individual components, with implications to better policy decisions and more cost effective engineering options. GREEN-MAC-LCCP[®] is the first globally harmonized LCCP model that was developed to analyze the holistic global warming impact of alternative refrigerants proposed as replacements to HFC-134a that is subject to the EC regulatory ban beginning in 2011, using a systems approach.

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