HFO-1234yf Low GWP Refrigerant Update

Barbara Minor
DuPont Fluoroproducts

Mark Spatz
Honeywell International

HFO-1234yf Low GWP Refrigerant Update

Barbara MINOR[1]*, Mark SPATZ[2]

[1]DuPont Fluoroproducts,
Wilmington, DE, USA
Phone: 302-999-2802, E-mail: barbara.h.minor@USA.DuPont.com

[2]Honeywell International,
Buffalo, NY, USA
Phone: 716-827-6238, E-mail: mark.spatz@Honeywell.com

ABSTRACT

HFC-134a has been scheduled for phase-out in automobiles in the European Union beginning January 1, 2011. HFO-1234yf has been identified as a new low global warming refrigerant which has the potential to be a global sustainable solution for automotive air conditioning. HFO-1234yf is a pure compound which is highly energy efficient, exhibits low toxicity in testing to date, and can potentially be used in systems currently designed for R134a with minimal modifications. Life Cycle Climate Performance (LCCP) calculations also indicate a significant environmental benefit versus R134a, R152a and CO_2 (R-744) in all major regions of the world. Though HFO-1234yf is mildly flammable per ASTM E-681-04 (ASTM, 2004), it is significantly less so than HFC-152a and HFC-32 and has the potential to be used in direct expansion systems without a secondary loop. In this paper, an update will be provided on recent status of HFO-1234yf evaluations.

1. INTRODUCTION

Due to increased pressure to address the issue of global warming, the European Commission has effectively banned the use of R-134a refrigerant in air conditioning in new car platforms in EU countries starting January 1, 2011. R-134a has a 100 year global warming potential value (GWP) of 1430 according to the Intergovernmental Panel on Climate Change 4th Assessment Report (AR4). Replacement refrigerants must have a GWP less than 150. Until recently, the leading candidate to replace R-134a has been carbon dioxide with a GWP of 1. However, CO_2 has several drawbacks including significantly higher pressure and lower thermodynamic cycle efficiency. These properties necessitate significant design changes to be able to use CO_2 with associated higher cost equipment, reliability questions, and other transition costs such as system maintenance, tools, and training.

HFO-1234yf was recently identified as a potential alternative that has vapor pressure and other properties similar to R-134a, but a 100 year GWP of 4 which meets the EU regulation requirements. It also has zero ozone depletion potential and excellent Life Cycle Climate Performance (LCCP) compared to R-134a and CO_2 which indicates it has the least overall impact on global warming in automotive air conditioning applications. Following is a review of properties and performance of HFO-1234yf.

2. THERMODYNAMIC PROPERTIES

HFO-1234yf thermodynamic properties are very similar to R-134a as shown in Table 1 and Figure 1. Boiling point, critical point, and liquid and vapor density are comparable to R-134a. Vapor pressure is slightly higher at temperatures below 25°C and slightly lower at temperatures above 60°C which can yield a lower compression ratio and better compressor efficiency.

Table 1: HFO-1234yf Thermodynamic Properties

Properties	HFO-1234yf	HFC-134a
Boiling Point, T_b	-29°C	-26°C
Critical Point, T_c	95°C	102°C
P_{vap}, MPa (25°C)	0.677	0.665
P_{vap}, MPa (80°C)	2.44	2.63
Liquid Density, kg/m^3 (25°C)	1094	1207
Vapor Density, kg/m^3 (25°C)	37.6	32.4

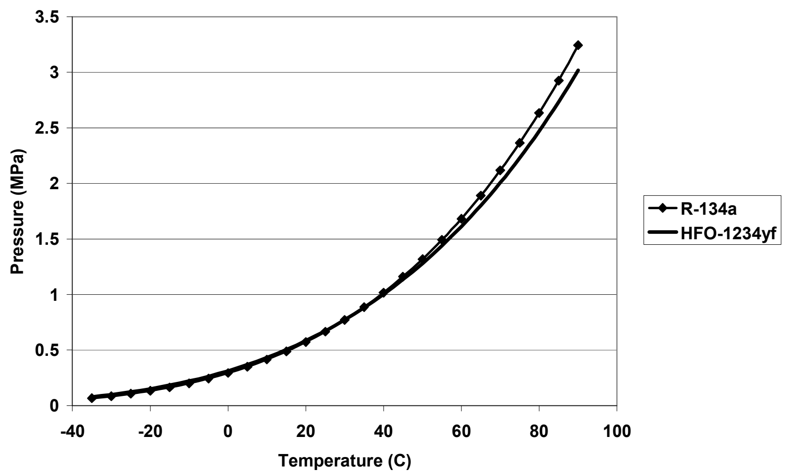


Figure 1. HFO-1234yf and R-134a Vapor Pressure

3. TOXICITY

Significant toxicity testing for HFO-1234yf has been completed following Organization for Economic Cooperation and Development (OECD) guidelines. The toxicity profile to date is shown in Table 2 below. All acute toxicity testing has been completed, as well as a 13 week inhalation study and rat developmental testing with very promising results. Although an Ames test showed slight activity, subsequent in vitro testing, including mouse and rat micronucleus and unscheduled DNA synthesis showed no activity indicating HFO-1234yf is not mutagenic. Environmental tests on daphnia, fish and algae results are also similar to R-134a.

Table 2: HFO-1234yf Toxicity and Environmental Summary

Test	HFO-1234yf	R-134a
LC50	No deaths 400,000 ppm	No deaths 359,700 ppm
Cardiac Sensitization	NOEL > 120,000 ppm	NOEL 50,000 ppm LOEL 75,000 ppm
Ames	Slight activity	Not active
Chrom AB	Not active	Not active
Micronucleus (mouse and rat)	Not active	Not active
Unscheduled DNA Synthesis	Not active	Not tested
13 Week Inhalation	NOEL 50,000 ppm	NOEL 50,000 ppm
Developmental (Rat)	NOAEL 50,000 ppm	NOAEL 50,000 ppm
Environmental Tox (acute daphnia, fish, algae)	NOEL > 100 mg/L	NOEL > 100 mg/L

4. ENVIRONMENTAL

HFO-1234yf atmospheric chemistry has been evaluated experimentally (Nielsen et al. 2007). HFO-1234yf has no ozone depletion potential. Atmospheric lifetime was determined to be 11 days versus R-134a at 14 years. Global warming potential based on a 100 year time horizon was determined to be 4 versus R-134a at 1430. Atmospheric breakdown products are also very similar to R-134a with no high GWP breakdown products formed.

5. FLAMMABILITY

HFO-1234yf was determined to be flammable by exhibiting lower and upper flammability limits when tested using ASTM-E681-04. However, results indicate mild flammability when comparing the lower flammability limit versus other refrigerant candidates as shown in Table 3. Also, flammability limits are only one factor in determining whether HFO-1234yf can be safely used in a given application. Another important consideration is the amount of energy that is required to ignite the refrigerant, represented by the minimum ignition energy, and the damage potential if an ignition were to occur, represented by the burning velocity.

5.1 Laboratory Flammability Measurements

Of the relevant comparisons shown in Table 3 below, HFO-1234yf has the smallest gap between lower and upper flammability limits, indicating a smaller flammable envelope which reduces the likelihood an ignition will occur. Minimum ignition energy (MIE) was determined using ASTM E-582 (ASTM, 2007) which employs a 1 liter vessel and metal electrodes to generate a spark up to 1000 mJ. Propane and R-152a have very low MIEs, meaning a larger number of ignition sources could potentially ignite these refrigerants. Since R-32, ammonia, and HFO-1234yf are slower burning materials, a 1 liter vessel was determined to be too small to test these refrigerants because interference of the vessel wall can quench the flame. Therefore these refrigerants were retested in a 12 liter vessel. At 5,000 mJ there was no ignition of HFO-1234yf, and at 10,000 mJ an ignition occurred. This is significantly higher than R-32 which ignites between 30 and 100 mJ and ammonia between 100 and 300 mJ, although these are considered mildly flammable refrigerants. These results indicate there will be fewer potential ignition sources for HFO-1234yf.

Finally, burning velocity gives an indication of the potential damage which could be caused if an ignition were to occur. HFO-1234yf was recently tested in a spherical vessel (Takizawa 2007) and the burning velocity at room temperature was determined to be 1.5 cm/s. This is a very low value compared to propane and R-152a and less than R-32 and ammonia indicating that HFO-1234yf has low potential for damage should an ignition occur. These flammability results are being used as input to risk assessments to confirm HFO-1234yf is safe to use in direct expansion systems without a secondary loop. Also, a spark ignition test also was conducted using a 12-volt car battery hooked up to electrodes in a 12 liter vessel containing HFO-1234yf /air mixtures between 8-9% (most ignition sensitive range). Sparks were generated from a the 12-V battery short at 20, 60, or 80°C. There was no ignition of HFO-1234yf. However, for comparison, a 20 vol % ammonia/air mixture was tested and ignited at both 20 and 60°C.

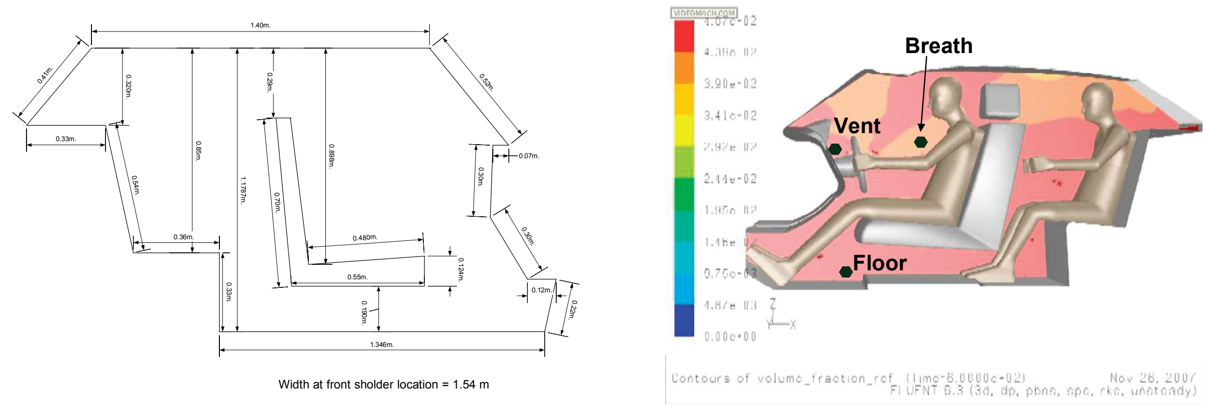
Table 3: HFO-1234yf Flammability Summary

Property	**Propane**	**R-152a**	**R-32**	**NH3**	**HFO-1234yf**
Flame Limits (ASTM E681-04) at 21°C					
LFL (vol% in air)	2.2	3.9	14.4	15.0	6.2
UFL (vol% in air)	10.0	16.9	29.3	28.0	12.3
Delta UFL-LFL	7.8	13.0	14.9	13.0	5.8
Minimum Ignition Energy (mJ)	0.25	0.38	30-100	100-300	5,000-10,000
Burning Velocity (cm/s)	46	23	6.7	7.2	1.5

5.2 Automotive Mockup Flammability Testing

A mockup has been constructed to measure the time varying local refrigerant concentration for the 0.5 mm corrosion hole (worst case corrosion type) and ruptured line scenarios. The mockup was constructed to simulate these scenarios for the case of a 2.5 m^3 passenger compartment representative of a typical European size automobile.

Figure 2(a) shows the interior dimensions of the mockup, while Figure 2(b) indicated the position of the different ignition locations used in the study: vent, floor and breath.



(a) (b)

Figure 2. Dimensions and locations of ignition sources

The flammability testing used two ignition types: a butane torch representing a high power cigar lighter and a MIG arc welder with approx. electrical discharge of 1.5 kW used without shielding gas. The settings for the flammability tests are:

Blower setting – low, blower inlet damper adjusted for 60 CFM output
Air velocity exiting vents: 1.7 m/sec
HVAC Mode: 100% recirculation of air inside mock-up.
Temperature – approximately 22 ºC
Rupture Line leak rate – 12 g/s (deviations: 11 to 14 g/sec)
0.5 mm corrosion leak – 1.4 g/s (deviations: 1.4 to 1.7 g/sec)

A series of tests were conducted that depicted an ever <u>decreasing</u> likelihood that this event will occur. As shown in Table 1, the most likely type of evaporator leak is one from a small diameter hole. Even with a large corrosion leak emanating from a 0.5mm diameter hole that would represent only 1% of evaporator leaks, both CFD modeling and experimental results show that concentrations inside the passenger compartment never reach the LFL. It was decided to run tests with this leak as well as the much less likely tube rupture leak with various ignition sources, sequences, and locations. The results of the series of flammability tests that were conducted in the mock-up are shown in Table 4.

Table 4. Results of Mockup Flammability Tests.

	Test No.	Test Description	Ignition Source	Time of Ignition	Result
Deceasing Probability of Occurance		**Large Corrosion Leak (0.5 mm diameter)**			
	1	Cigarette lighting at breath level	Butane lighter	After leak starts	No Ignition - only flame color change noted
	2	Pooling Test- no blower operation	Arc welder on floor	Four minutes after end of leak	No Ignition
	3	Cigarette Lighting at Vent Outlet	Butane lighter	After leak starts	No Ignition - only flame color change noted
		Ruptured Tube Leaks (6.4 mm diameter)			
	4	Cigarette lighting at breath level	Butane lighter	After leak starts	Butane lighter failed to light.
	5	Simulation of battery short	Arc welder on floor	After leak starts	No ignition
	6	Simulation of PTC heater short	Arc welder at vent outlet	After leak starts	No ignition
	7	Cigarette Lighting at Vent Outlet	Butane lighter	After leak starts	Butane lighter failed to light.
	8	Cigarette lighting at breath level	Butane lighter	At start of leak for entire leak event	Minor flame extension
	9	Cigarette Lighting at Vent Outlet Lighter held on for typ lighting time	Butane lighter	At start of leak for 5 secs	No flame extension

1) **Large Corrosion Leak** (0.5 mm diameter) – flammability tests 1 and 3 were conducted at the vent outlet and breath locations with the butane lighter. **No flame extension or any other propagating flame was seen in any of the tests for this scenario.** One observation made was that the flame color changed from orange to a blue, Figure 3. This phenomenon is the same as the older halide torch leak detectors used by the industry. Test 2 was conducted to simulate a leak into the passenger compartment with the blower shut-off allowing the refrigerant to pool. To simulate a short of a battery that was installed under the front seat, an arc welder positioned on the floor was activated. Again no ignition took place.

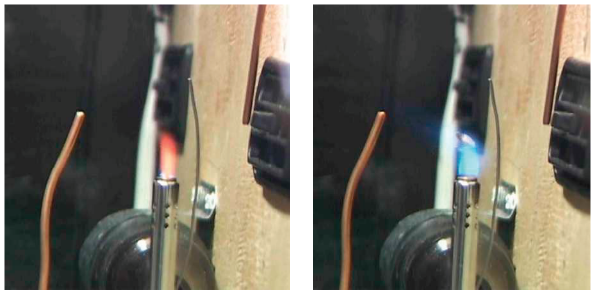


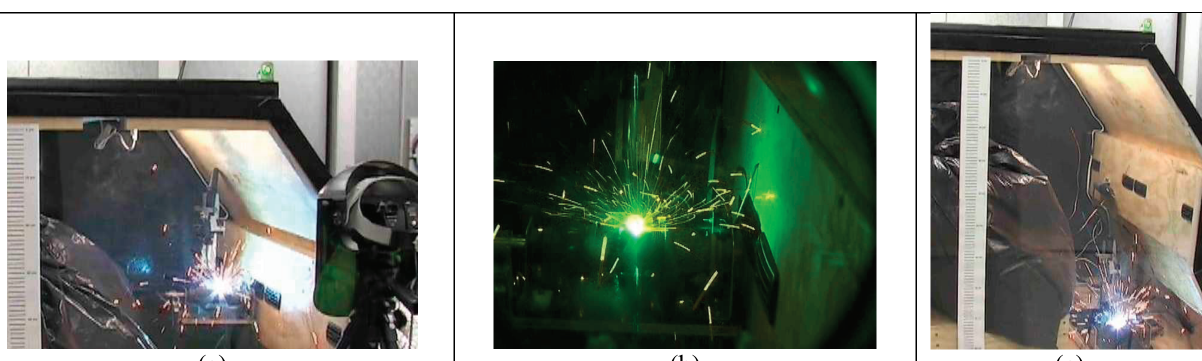
Figure 3. Butane lighter in 0.5 mm Corrosion Leak Test

2) Ruptured Line Leak – flammability tests 4 thru 9 were conducted to simulate the ruptured tube event.

Tests 4 and 7 were conducted at both the breath level to simulate a cigarette lighting location and for a worst case location (area of highest concentration) at the vent outlet with the butane lighter**.** Results – as the HFO-1234yf concentration increased the butane lighter became inoperable; operation of the butane lighter was not again possible until the local refrigerant diffused to lower concentrations. It is currently postulated that the inclusion of HFO1234yf raised the butane/HFO1234yf minimum ignition energy above the energy release for the lighter's sparker. When the local concentration dropped, lighter operation was again possible. The flame behaved as in the corrosion leak test.

Elevated Temperature (45 ºC) – tests with the butane lighter were also conducted at an elevated cabin temperature of 45 ºC. The operation of the lighter and the flame are the same as the room temperature tests.

Tests 5 and 6 utilize an arc welder without shielding gas which was placed on the floor of the mockup (test 5) to simulate a shorting battery connection, or shorts in the electrical seat motor or heater. The welder was also placed at the vent outlet location (test 6) to simulate an HVAC module short (the concentration at the vent outlet is assumed to be the same as the interior of the HVAC module interior). The videos from the arc welder are very dramatic with sparks flying about the cabin, however, **No detectable flame was evident.** Figure 4 show stills from the video capture.



(a) (b) (c)

Figure 4. Electrical Arc Welder located at the vent outlet and floor location

Extraordinary measures had to be taken to achieve ignition of HFO-1234yf even with the worst possible leak scenario of the ruptured tube. Tests 8 and 9 were conducted to overcome the issue of the failure of the lighter to light in areas of higher HFO-1234yf concentrations. The extraordinary steps taken to carry out these tests show that the likelihood of ignition of HFO-1234yf is quite remote.

6. MATERIALS COMPATIBILITY

6.1 Thermal Stability

HFO-1234yf has been evaluated for thermal stability per ASHRAE Standard 1997-99 (ASHRAE, 1999). Tests were conducted with refrigerant and either polyalkylene glycol (PAG) or polyolester (POE) lubricant and water concentrations varying from less than 100 ppm to 10,000 ppm. Refrigerant and lubricant were placed in sealed glass tubes containing aluminum, copper and carbon steel coupons and held at 175°C or 200°C for two weeks. Results indicate HFO-1234yf is thermally stable with no significant corrosion to the metals observed.

6.2 Plastics and Elastomers Compatibility

HFO-1234yf and R-134a have been evaluated for compatibility with typical plastics and elastomers used in automotive air conditioning systems. Some commonly used plastics and elastomers were immersed in sealed tubes containing HFO-1234yf and PAG lubricant and held at 100°C for two weeks. Plastics were then inspected for weight change after 24 hours and physical appearance. Elastomers were evaluated for linear swell, weight gain and hardness using a durometer. The results of specific plastics and elastomers that were tested are shown in Tables 5 and 6. HFO-1234yf has very similar behavior with plastics and elastomers compared to R134a, indicating that many materials in use in current air conditioning systems may be compatible with HFO-1234yf.

Table 5: HFO-1234yf Plastics Compatibility

Refrigerant	Plastics	Rating	24 h Post Weight Chg. %	Physical Change
HFO-1234yf	Polyester	1	4.4	0
"	Nylon	1	-1.5	1
"	Epoxy	1	0.3	1
"	Polyethylene Terephthalate	1	2.0	0
"	Polyimide	0	0.2	0
Refrigerant	**Plastics**	**Rating**	**24 h Post Weight Chg. %**	**Physical Change**
R-134a	Polyester	1	5.6	0
"	Nylon	1	-1.4	1
"	Epoxy	1	0.3	1
"	Polyethylene Terephthalate	1	2.8	0
"	Polyimide	0	0.7	0

The following ratings were used to assess changes to plastics: Rating = 0 if weight gain is less than 1% and there is no physical change. Rating = 1 if weight gain is between 1 and 10% and physical change = 2.

Table 6: HFO-1234yf Elastomers Compatibility

Refrigerant	Elastomers	Rating	24 h Post Linear Swell %	24 h Post Weight Gain %	24 h Post Delta Hardness
HFO-1234yf	Neoprene WRT	0	0.0	-0.3	1.0
"	HNBR	0	1.6	5.5	-7.0
"	NBR	0	-1.2	-0.7	4.0
"	EPDM	0	-0.5	-0.6	4.0
"	Silicone	1	-0.5	2.5	-14.5
"	Butyl rubber	0	-1.6	-1.9	0.5

Table 6 (cont): HFO-1234yf Elastomers Compatibility

Refrigerant	Elastomers	Rating	24 h Post Linear Swell %	24 h Post Weight Gain %	24 h Post Delta Hardness
R134a	Neoprene WRT	0	-0.6	-1.3	2
"	HNBR	0	2.1	8.6	-5.5
"	NBR	0	0.0	3.0	-3.5
"	EPDM	0	-1.1	-0.4	-2
"	Silicone	0	-1.4	1.4	-2.5
"	Butyl rubber	0	-1.1	-1.6	-3.5

For elastomers, Rating = 0 if for < 10% weight gain, < 10% linear swell and < 10% hardness change. Rating = 1 for > 10% weight gain or > 10% linear swell or >10% hardness change.

7. SYSTEM PERFORMANCE

System performance was measured in a bench scale apparatus using mobile air conditioning components from a small car. The fully instrumented bench system was constructed in an environmental chamber to allow control of temperature and humidity. Baseline tests for R-134a were conducted and the refrigerant was replaced with HFO-1234yf. No other system changes were made, including no adjustment to the thermostatic expansion valve (TXV). The test matrix covered the range of automotive vehicle operation and are defined in currently proposed SAE standard (SAE J2765).

Results for cooling capacity and energy efficiency relative to R-134a are shown in Figure 5. Results show that with no system changes, the cooling capacity and energy efficiency is within 4-8% of R-134a. Significant improvements can be expected with minor system optimization, such as TXV adjustment and larger diameter suction line tubing.

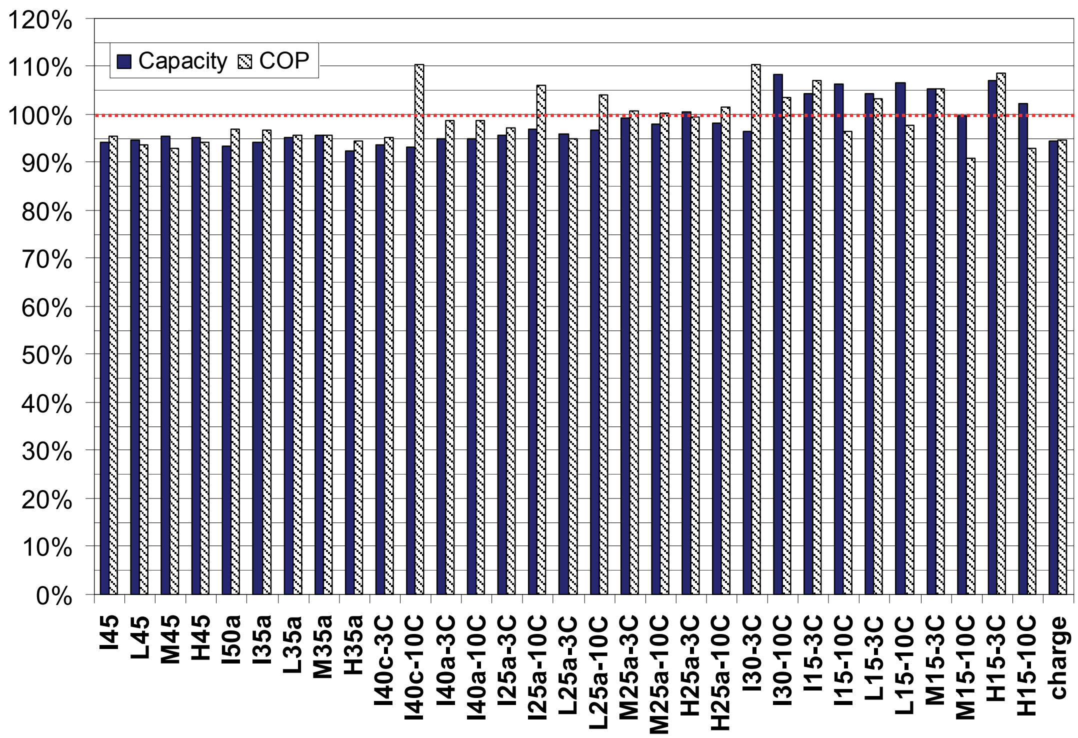


Figure 5. Bench Cooling Capacity and COP for HFO-1234yf Relative to R-134a

8. LIFE CYCLE CLIMATE PERFORMANCE

Life cycle climate performance, (LCCP) has been used quite extensively in the mobile air conditioning industry and has become a useful tool to understand total product environmental impact beyond the direct global warming potential (GWP) of the refrigerant. This is a cradle-to-grave analysis of the environmental impact at all points in the life cycle chain, including manufacture of components, system operation and end-of-life disposal. The GREEN-MAC- LCCP® 2007 model was used as the basic foundation for this analysis. Although there are several other models available for automotive LCCP calculations, this model was chosen for its robustness and volume of data available. Data from the bench scale tests described in Section 7 were used as inputs to the model to calculate LCCP values for HFO-1234yf versus R-134a in several locations including cooler and warmer climates. Results in Figure 3 show an LCCP reduction of 15% on average for the transition from R-134a to HFO-1234yf, and up to 27% reduction in part of Europe. There was an LCCP reduction in every geographic location evaluated.

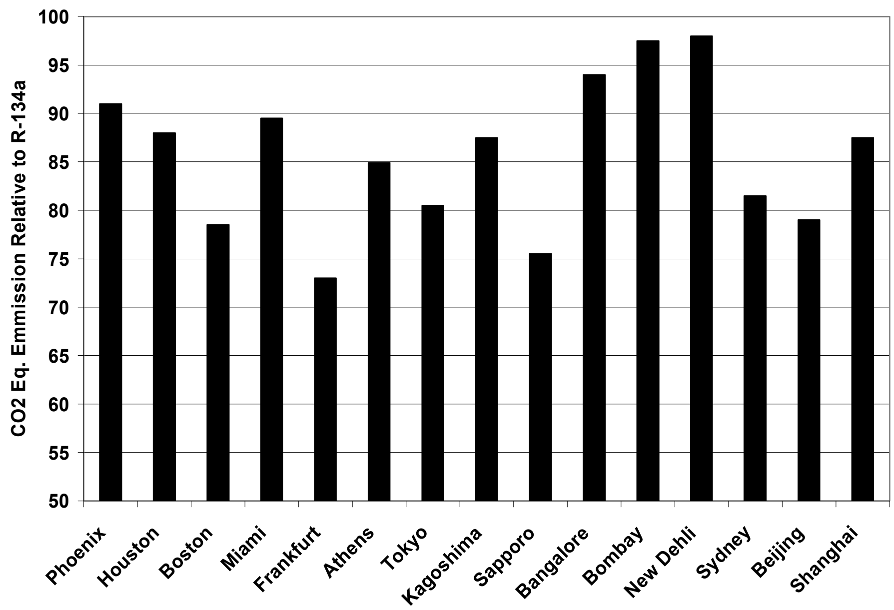


Figure 3: LCCP For HFO-1234yf Relative to R-134a

9. CONCLUSIONS

HFO-1234yf has excellent potential as a new low global warming refrigerant for automotive air conditioning and potentially for stationary applications. It has excellent environmental properties which can have a long term favorable impact on climate change and meet current and future climate regulations. Significant toxicity tests have been completed with encouraging results. It is compatible with existing R-134a technology which can allow for a smooth and cost effective transition. The mild flammability properties of HFO-1234y have shown its high potential for use in direct expansion applications, pending completion of risk assessments.

10. REFERENCES

ASHRAE Standard 97-99, 1999, “Sealed Tube Thermal Stability Test”. *American Society of Heating, Refrigerating, and Air-Conditioning Engineers, Inc*., Atlanta, GA.

ASTM E582-07, 2007 "Standard Test Method for Minimum Ignition Energy and Quenching Distance in Gaseous Mixtures*” American Society for Testing and Materials (ASTM*), West Conshohocken, PA.

ASTM E681-04, 2004 "Standard Test Method for Concentration Limits of Flammability of Chemicals (Vapors and Gases*)," American Society for Testing and Materials (ASTM),* West Conshohocken, PA.

GREEN-MAC-LCCP© model 2007. www.epa.gov/cppd/mac/.

Nielsen, O.J. et al., 2007 “Atmospheric Chemistry of CF_3CF=CH2”, *Chemical Physics Letters*, vol. 439, p. 18-22.