

LOW GWP REFRIGERANT STATUS

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Abstract: HFO-1234yf has been identified as a new low global warming refrigerant which has the potential to be a sustainable solution for automotive air conditioning and potentially for stationary systems. HFO-1234yf is a pure compound which is energy efficient, exhibits low toxicity in testing to date, and can potentially be used in systems currently designed for HFC-134a with minimal modifications. Life Cycle Climate Performance (LCCP) calculations also indicate a significant environmental benefit versus HFC-134a, HFC-152a and carbon dioxide in automotive air conditioning. Although HFO-1234yf is mildly flammable per ASTM E681-2004, 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.

Key Words: *refrigerant, HFO-1234yf, GWP, efficiency, LCCP*

1 INTRODUCTION

Due to increased pressure to address the issue of global warming, the European Commission recently banned the use of HFC-134a refrigerant in mobile air conditioning in EU countries starting January 1, 2011. HFC-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 HFC-134a has been carbon dioxide with a GWP of 1. However, CO₂ has several drawbacks including significantly higher pressure and lower thermodynamic cycle efficiency. These properties necessitate significant design changes to be able to use CO₂ 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 HFC-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 HFC-134a and CO₂ 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 HFC-134a as shown in Table 1 and Figure 1. Boiling point, critical point, and liquid and vapor density are comparable to HFC-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

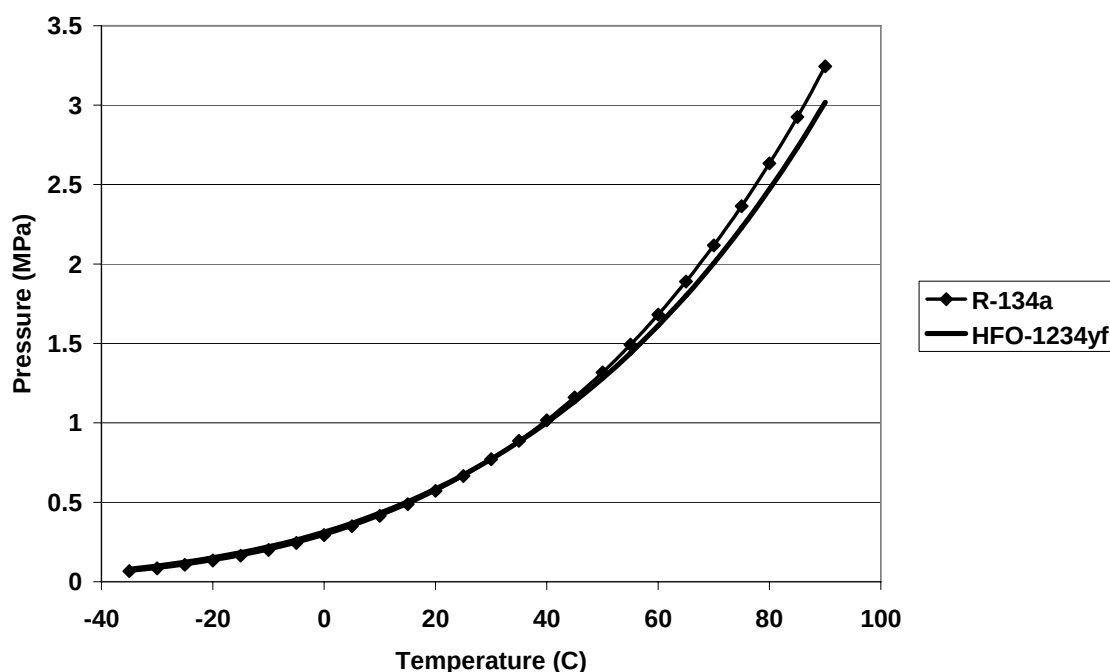


Figure 1; HFO-1234yf and HFC-134a Vapor Pressure

3 TOXICITY

Significant toxicity testing for HFO-1234yf has been completed following Organisation for Economic Cooperation and Development (OECD) guidelines. The toxicity profile to date is comparable to HFC-134a as 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 HFC-134a.

Table 2; HFO-1234yf Toxicity and Environmental Summary

Test	HFO-1234yf	HFC-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 HFC-134a at 14 years. Global warming potential based on a 100 year time horizon was determined to be 4 versus HFC-134a at 1430. Atmospheric breakdown products are also very similar to HFC-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 E681-2004. 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.

Table 3 below shows 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 which employs a 1 liter vessel and metal electrodes to generate a spark up to 1000 mJ. Propane and HFC-152a have very low MIEs, meaning a larger number of ignition sources could potentially ignite these refrigerants. Since HFC-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. HFO-1234yf was tested to the maximum of 1000 mJ and no ignition occurred. This is significantly higher than HFC-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 HFC-152a and less than HFC-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.

Table 3; HFO-1234yf Flammability Summary

Property	Propane	HFC-152a	HFC-32	NH3	HFO-1234yf
Flame Limits (ASTM E681-04) at 21C					
LFL (vol% in air)	2.2	3.9	14.4	15.0	6.5
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	>1000
Burning Velocity (cm/s)	46	23	6.7	7.2	1.5

6 MATERIALS COMPATIBILITY

6.1 Thermal Stability

HFO-1234yf has been evaluated for thermal stability per ASHRAE Standard 97-1999. 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 HFC-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 4 and 5. HFO-1234yf has very similar behavior with plastics and elastomers compared to HFC-134a, indicating that many materials in use in current air conditioning systems may be compatible with HFO-1234yf.

Table 4; HFO-1234yf Plastics Compatibility

Refrigerant	Plastics	Rating	24 h Post Weight Chg. %	Physical Change
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
HFC-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 physical change = 0 (no physical change). Rating = 1 if weight gain is

between 1 and 10% and physical change between 0 and 1 (1 = surface change, dulled or crazed).

Table 5; HFO-1234yf Elastomers Compatibility

Refrigerant	Elastomers	Rating	24 h Post Linear Swell %	24 h Post Weight Gain %	24 h Post Delta Hardness
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
Refrigerant	Elastomers	Rating	24 h Post Linear Swell %	24 h Post Weight Gain %	24 h Post Delta Hardness
HFC-134a	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 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 HFC-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). Test points which are representative of industry conditions are shown in Table 6.

Table 6; Bench Scale Test Conditions

Test Name	Ambient Temp (C)	Compressor Speed (rpm)	Condenser Air Temp (C)	Condenser Face Air Velocity (m/s)	Evap Air Temp (C)	Evap Rel Humidity	Evap Air Mass Flow (kg/min)
I50a	35	900	50	1.5	35	40	9.0
I35a	35	900	35	1.5	35	40	9.0
L35a	35	1800	35	2.0	35	40	9.0
M35a	35	2500	35	3.0	35	40	9.0
H35a	35	4000	35	4.0	35	40	9.0

Results for cooling capacity and energy efficiency relative to HFC-134a are shown in Figure 2. Results show that with no system changes, the cooling capacity and energy efficiency are within 4-8% of HFC-134a. Significant improvements can be expected with minor system optimization, such as TXV adjustment and larger diameter suction line tubing.

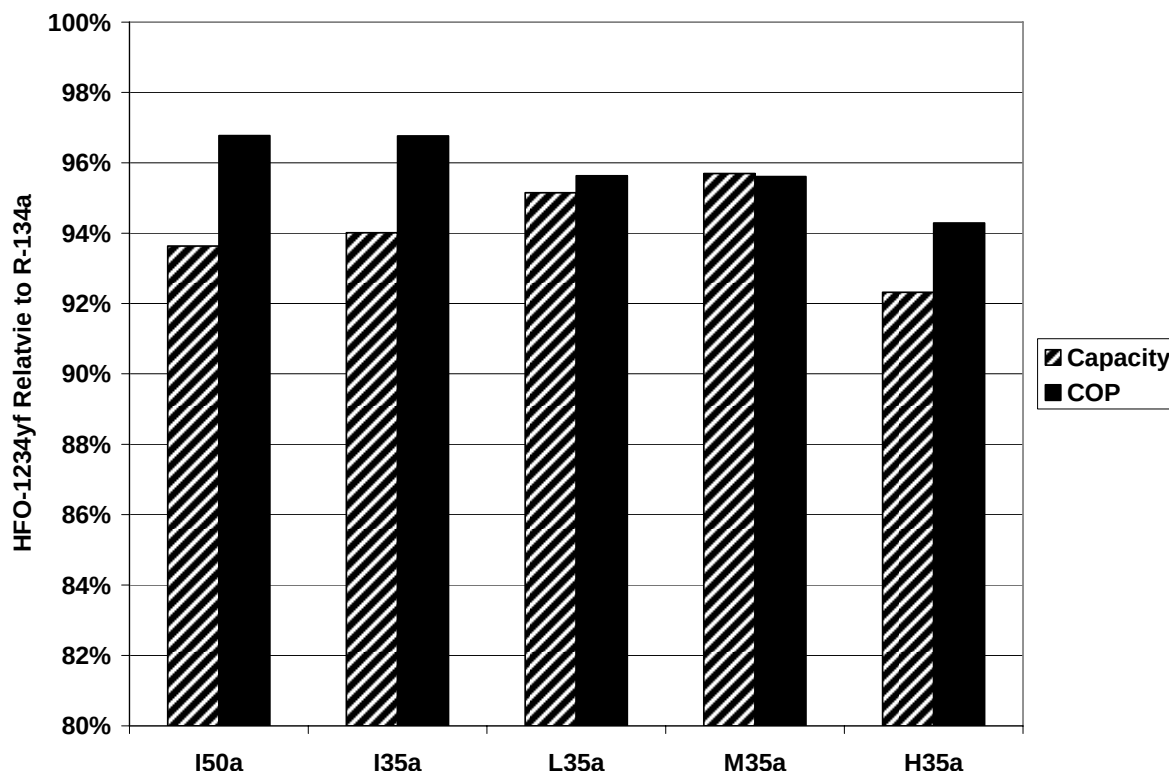


Figure 2; Bench Scale Cooling Capacity and COP for HFO-1234yf Relative to HFC-134a

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 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® model (Papasavva 2005, Hill 2005, GREEN-MAC-LCCP 2007) 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 HFC-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 HFC-134a to HFO-1234yf, and up to 27% reduction in part of Europe. There was an LCCP reduction in every geographic location evaluated.

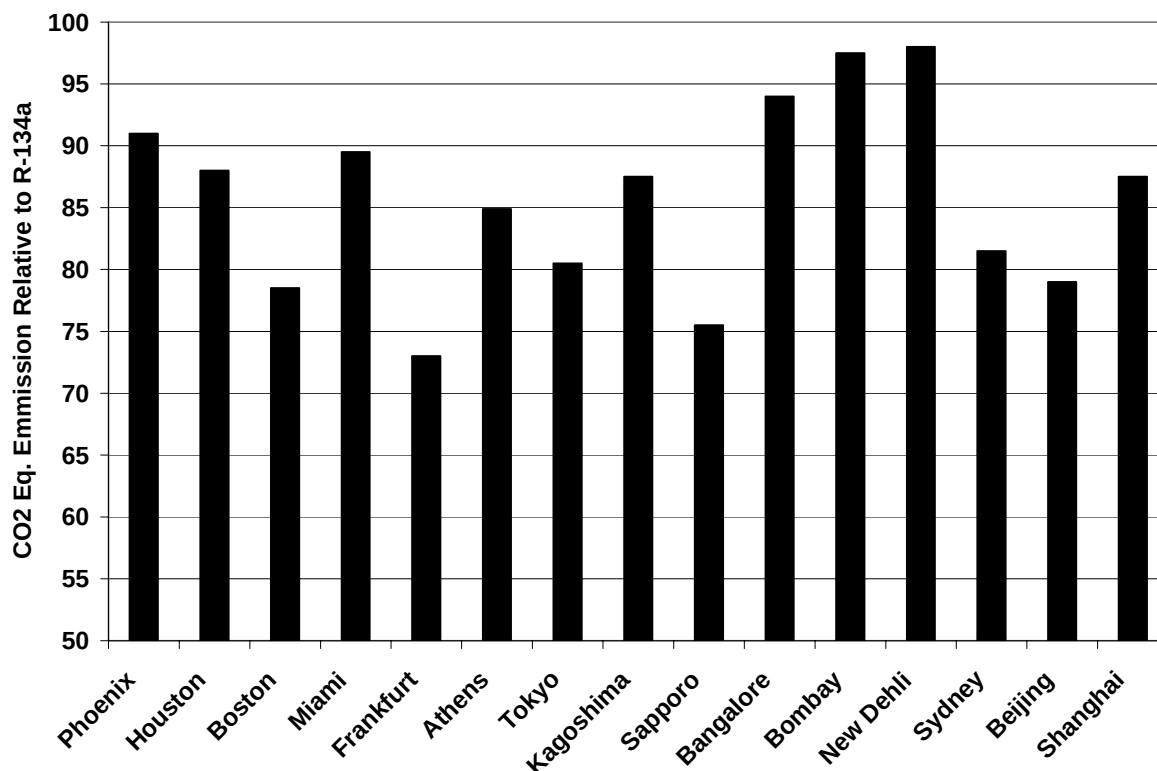


Figure 3; LCCP For HFO-1234yf Relative to HFC-134a

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 HFC-134a technology which can allow for a smooth and cost effective transition. Its mild flammability properties have shown potential for use in direct expansion applications pending completion of risk assessments.

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