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Evaluation of HFC-245fa as a Potential Alternative for CFC-11 in Low Pressure Chillers

by

N. Dean Smith
Air and Energy Engineering Research Laboratory
U. S. Environmental Protection Agency
and
Angelita S. Ng, Michael W. Tufts, Ann M. Drago, and Krich Ratanaphruks
Acurex Environmental Corporation

It has been reported previously that HFC-245ca (1,1,2,2,3-pentafluoropropane) has numerous attributes which make it an attractive candidate alternative for CFC-11 and HCFC-123.[1] In the present paper, results of an initial evaluation of HFC-245fa (1,1,1,3,3-pentafluoropropane) are described together with updated results of HFC-245ca testing.

HCFC-123 (1,1-dichloro-2,2,2-trifluoroethane) is currently the only alternative refrigerant for low-pressure CFC-11 chillers. This chlorine-containing alternative is scheduled for a production cap beginning in 1996 followed by a production phase-down through the year 2030 at the end of which production must cease. This phaseout timeframe is expected to allow new equipment designed for use with HCFC-123 and placed into service in the next few years to be utilized over the useful lifetime of the equipment. Meanwhile, the search for a long-term alternative continues.

Thermophysical Properties

HFC-245fa was first prepared in laboratory quantities by researchers at Clemson University in a project sponsored by the EPA's Air and Energy Engineering Research Laboratory (AEERL). The laboratory method involved hydrogenation of 1,1,1,3,3-pentafluoropropene in the presence of a palladium/carbon catalyst:

$$CF_3CH{=}CF_2 + H_2 \xrightarrow{Pd/C} CF_3CH_2CF_2H$$

This synthesis route resulted in production of 99.8 percent pure HFC-245fa with a 98 percent yield. Thermophysical properties were initially determined with this material. Under the sponsorship of AEERL, work is in progress by the National Institute of Standards and Technology (NIST) to refine and expand the thermophysical property database for HFC-245fa. Table 1 compares some of the pertinent properties of HFC-245fa with those of HFC-245ca, CFC-11, and HCFC-123. A rather complete compilation of the thermophysical properties of HFC-245ca is already available in the NIST REFPROP database.[2]

Chiller Performance Modeling

HFC-245fa's performance as a refrigerant in low-pressure centrifugal chillers was assessed using a computer model based on the Carnahan-Starling-DeSantis-Morrison (CSDM) equation of state.[3] This model allowed analysis of a simple theoretical vapor compression cycle consisting of constant pressure evaporation, isentropic compression, constant pressure condensation, and adiabatic expansion. Table 2 compares the results of chiller performance modeling for HFC-245fa, HFC-245ca, CFC-11, and HCFC-123 at an evaporating temperature of 4.4°C (40°F), a condensing temperature of 40°C (104°F), and an assumed compressor efficiency of 1.0. Modeling results are accurate to ± 2 percent.

Table 1. Comparison of Thermophysical Properties for HFC-245fa, HFC-245ca, CFC-11, and HCFC-123

	HFC-245fa	HFC-245ca	CFC-11	HCFC-123
Molecular weight	134.1	134.1	137.4	152.9
Normal boiling point, T_b (°C)	15.2	25.0	23.8	28.0
Heat of vaporization @ T_b (kJ/mol)	28.0	29.2	24.8	25.7
Critical temperature (°C)	157.5	174.4	198.0	183.9
Critical pressure (kPa)	3623	3860	4409	3674
Critical density (kg/m^3)	529	529	554	550
Sat'd liquid density @ 25°C (kg/m^3)	1323	1386	1476	1465
Sat'd vapor density @ 25°C (kg/m^3)	8.45	5.67	5.86	5.9
Vapor pressure @ 25°C (kPa)	147	102	106	91

Table 2. Comparison of Modeled Refrigeration Performance for HFC-245fa, HFC-245ca, CFC-11, and HCFC-123. Simulation Condition: 4.4°C - evaporating; 40°C-condensing; minimum superheat; 0.0°C subcooling

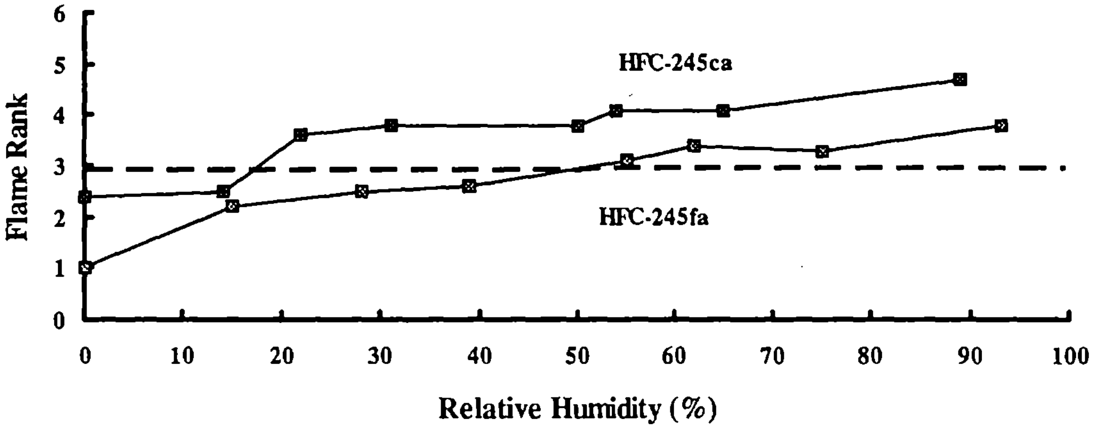
Refrigerant	Coeff. of Perform.	Volumetric Capacity (kJ/m^3)	Suction Pressure (kPa)	Discharge Pressure (kPa)	Minimum Superheat (°C)
HFC-245fa	6.7	594	62.7	246	1.4
HFC-245ca	6.6	403	42.0	173	3.8
CFC-11	7.0	463	48.7	175	0.0
HCFC-123	6.9	386	39.9	155	1.0

This analysis indicates a 4 to 5 percent lower efficiency for HFC-245fa compared to CFC-11 in a centrifugal chiller operating at these conditions. By comparison, HFC-245ca shows an efficiency loss of 5 to 6 percent and HCFC-123 an energy penalty of 1 to 2 percent relative to CFC-11. For all alternatives, the thermodynamic analysis indicates the possibility of wet compression; that is, refrigerant leaving the compressor would be in both vapor and liquid states. HFC-245fa is predicted to require 2.4 degrees less superheat than HFC-245ca to avoid wet compression. In actual practice, inefficiencies in compressor operation are likely to result in sufficient superheating to avoid wet compression. Another advantage of HFC-245fa is its volumetric capacity which is the highest of the four refrigerants compared. However, the slightly higher discharge pressure of HFC-245fa compared to the other refrigerants suggests the need for pressure-coded vessels when using this refrigerant.

Flammability

HFC-245fa can exhibit weakly flammable behavior in ASTM E681-85 or ASHRAE Standard 34-1992 flammability tests. As indicated in Figure 1, HFC-245fa is less flammable at room temperature than even HFC-245ca, but like HFC-245ca, the flammability of the "fa" isomer is markedly dependent on humidity. The dashed line in Figure 1 indicates the point at which the refrigerant/air mixture just achieves the flammable limit with a spark ignition source as defined by the ASTM standard method.

Figure 1. Effect of Moisture on Flammability of HFC-245ca and HFC-245fa



A plausible explanation of the observed humidity effect for these and other weakly flammable HFC refrigerants having a hydrogen-to-fluorine atom ratio less than unity is that such refrigerants require an additional source of hydrogen atoms in order to combust completely to carbon dioxide and hydrogen fluoride. The most likely source of additional hydrogen atoms in a combustion scenario is water vapor. In the absence of water vapor or at low humidities, an alternate but less thermodynamically favored combustion reaction is possible yielding carbonyl fluoride as one of the products. Balanced chemical equations and associated free energies of combustion for the alternative combustion reactions of both HFC-245fa and HFC-245ca are shown below. Free energies of combustion were calculated using free energies of formation of HFC-245fa and HFC-245ca estimated by the method of Domalski and Hearing.[4] As the moisture level increases in the refrigerant/air mixture, the more thermodynamically favored combustion reaction (i.e., the reaction with the more negative free energy change, Δ G) can occur and the HFC exhibits greater flammability.

HFC-245fa

$CF_3\text{-}CH_2\text{-}CF_2H + 5/2O_2 + H_2O \text{ ---> } 3CO_2 + 5HF$ $\quad \Delta G = -1{,}297 \text{ kJ mol}^{-1}$
$CF_3\text{-}CH_2\text{-}CF_2H + 5/2O_2 \text{ ---> } 2CO_2 + 3HF + COF_2$ $\quad \Delta G = -1{,}148 \text{ kJ mol}^{-1}$

HFC-245ca

$CF_2H\text{-}CF_2\text{-}CFH_2 + 5/2O_2 + H_2O \text{ ---> } 3CO_2 + 5HF$ $\quad \Delta G = -1{,}355 \text{ kJ mol}^{-1}$
$CF_2H\text{-}CF_2\text{-}CFH_2 + 5/2O_2 \text{ ---> } 2CO_2 + 3HF + COF_2$ $\quad \Delta G = -1{,}207 \text{ kJ mol}^{-1}$

Smaller combustion free energies for HFC-245fa compared to HFC-245ca are indicative of a lesser tendency for HFC-245fa to burn, a fact which is borne out by the results of the ASTM or ASHRAE flammability tests. At a relative humidity of approximately 50 percent at room temperature (25 to 30 °C), HFC-245fa was found to exhibit a flammable range of 8.9 to 11.2 volume percent in air.

Miscibility, Stability, and Materials Compatibility

Sealed tube samples were prepared containing 10, 20, and 30 weight percent HFC-245fa in a fully formulated, commercially available, polyolester lubricant of nominal 68 centistokes viscosity and containing 50 ppm water. These samples were subjected to a gradual temperature change over the range of -40 to + 100°C to test for refrigerant/lubricant miscibility. HFC-245fa and HFC-245ca were found to be completely miscible in the polyolester lubricant over this temperature range.

To test its temperature and hydrolytic stability, HFC-245fa was sealed in glass tubes alone, with added polyolester lubricant, and with added water (0.001 ppm) in the absence and in the presence of aluminum, steel, and copper. These samples were then subjected to sustained heating at 175°C for 14 days. Following the heating period, the samples were analyzed for possible degradation of the HFC-245fa using a combination of gas chromatography, Fourier-transform infrared spectrometry, and mass spectrometry. Chromatograms and spectra of the aged refrigerant and lubricant were identical to those of the unaged materials indicating no degradation of the HFC-245fa or polyolester.

A large matrix of elastomeric and plastic materials were tested for compatibility with HFC-245fa with and without the polyolester lubricant. Materials tested for compatibility included 13 elastomers, 4 desiccants, and 5 metals. A complete list of these materials is presented in Table 3.

Table 3. Materials tested for Compatibility with HFC-245fa at 125°C

Brass
Bronze
Stainless steel
HNBR (hydrogenated nitrile butyl rubber)
Hypalon™ (chlorosulfonated polyethylene)
Natural rubber (isoprene polymer)
Thiokol™ (dicholorodiethylformal + alkali polysulfide)
Geolast™ (nitrile/polypropylene 701-70)
NBRS (butadiene styrene copolymer)
E-70 (ethylene propylene diene methylene rubber)
S-70 (silicone rubber)
Neoprene™ (chloroprene)
Buna-N™ (nitrile)
Kalrez C™ (perfluoroelastomer)
Viton™ (fluoroelastomer)
Teflon™
Desiccant 4AXH-5
Desiccant 4AXH-6
Desiccant XH-7
Desiccant XH-9

Again, no evidence was found for degradation of either the refrigerant or lubricant with any of these materials. Several of the elastomers, however, were found to be incompatible with HFC-245fa. Figures 2-4 present the elastomer results graphically. Thiokol results are not shown for the volume and linear swell measurements due to the brittleness of the aged material which made it difficult to obtain data.

Figure 2: Average Percent Volume Change of Elastomers

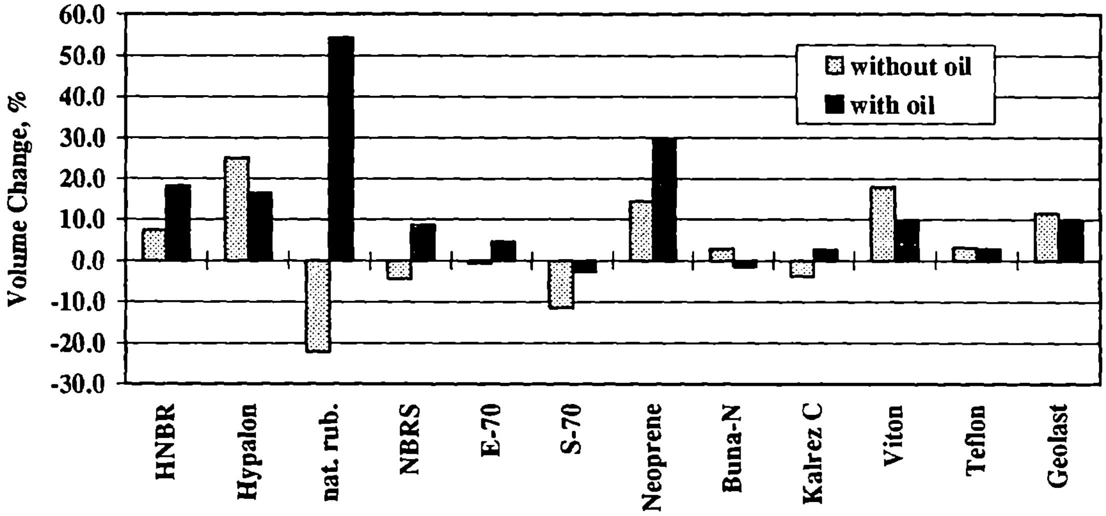


Figure 3: Average Percent Linear Swell of Elastomers

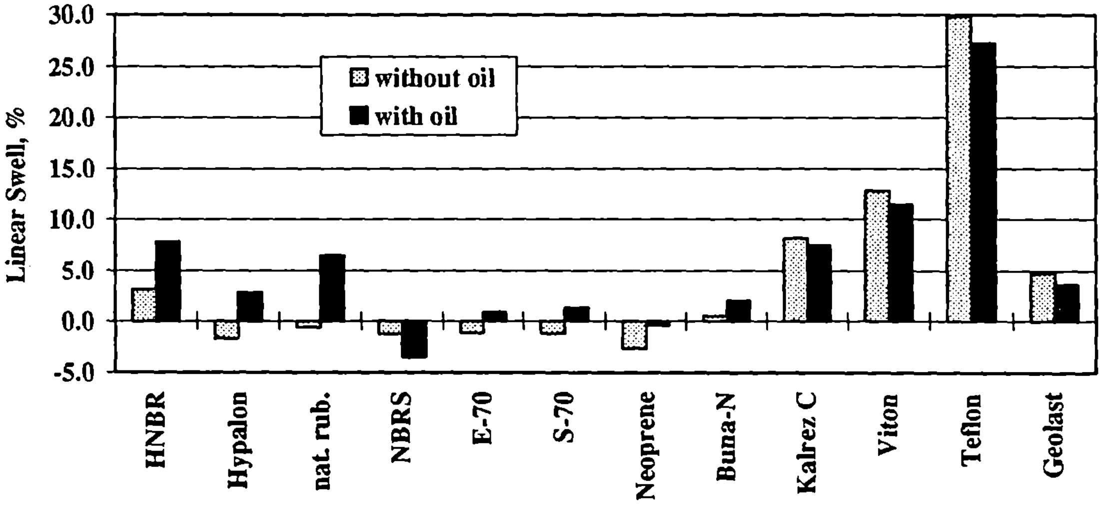
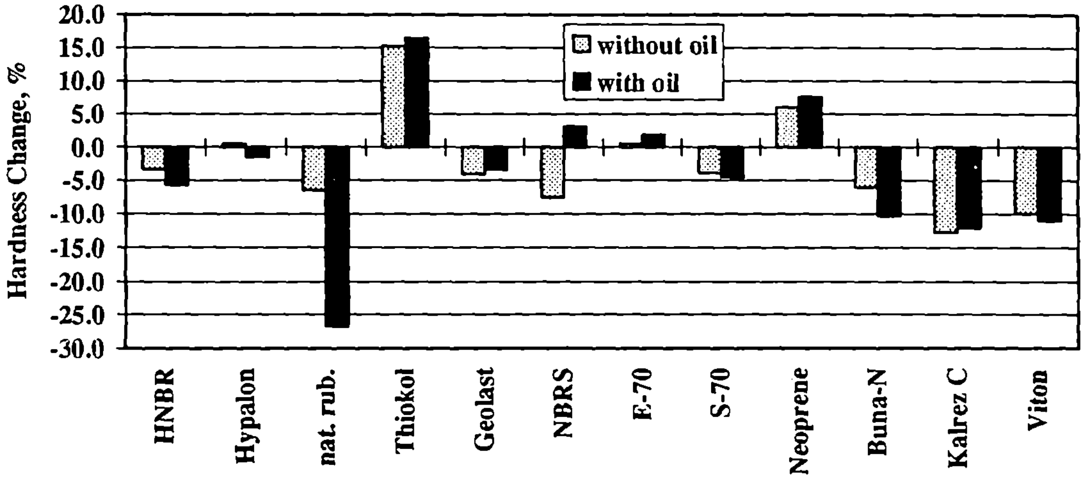


Figure 4: Average Percent Hardness Change of Elastomers



Based on acceptable criteria being a volume increase of not greater than 20 percent, a linear swell of not greater than 5 percent, no shrinkage, and a change in hardness of not more than ±10 percent, only a few elastomers were judged to be compatible. Table 4 summarizes the compatibility test results.

Table 4. Compatibility Summary of Elastomers Exposed to HFC-245fa and Lubricant

	Linear Swell		Volume Change		Hardness Change	
	without oil	with oil	without oil	with oil	without oil	with oil
HNBR	pass	fail	pass	pass	pass	pass
Hypalon	fail	pass	fail	pass	pass	pass
Nat. rubber	fail	fail	fail	fail	pass	fail
Thiokol	fail	fail	fail	fail	fail	fail
NBRS	fail	fail	fail	pass	pass	pass
E-70	fail	pass	fail	pass	pass	pass
S-70	fail	pass	fail	fail	pass	pass
Neoprene	fail	fail	pass	fail	pass	pass
Buna-N	pass	pass	pass	fail	pass	fail
Kalrez C	fail	fail	fail	pass	fail	fail
Viton	fail	fail	pass	pass	pass	fail
Teflon	fail	fail	pass	pass	n/a	n/a
Geolast	pass	pass	pass	pass	pass	pass

n/a = not applicable

Geolast passed the volume, linear swell, and hardness tests in the presence of refrigerant alone and in the presence of combined refrigerant/lubricant. HNBR and Buna-N passed all three compatibility criteria in the presence of refrigerant alone but failed at least one test in the presence of lubricant. Hypalon and E-70 passed all three compatibility criteria in the presence of combined refrigerant/lubricant but failed at least one test in the presence of refrigerant alone. Pass/fail criteria used here are somewhat arbitrary; therefore, some elastomers which may have failed one or more of the criteria used here may in fact be suitable for a specific application. Note, for example, that elastomer E-70 exceeded the volume change criterion only in the absence of the lubricant and then by exhibiting a volume decrease of only 0.61 percent.

Based on visual observations, there was no indication of any deterioration of the desiccants or copper plating on the metals.

Atmospheric Stability and Global Warming Potential

Although HFC-245fa has zero ozone depletion potential, it was of interest to estimate its atmospheric lifetime as an indication of the global warming potential of the refrigerant. To this end, the reaction rate constant was determined for the reaction of HFC-245fa with hydroxyl (OH) radical. This work was performed by NIST under the sponsorship of AEERL. The measured OH rate constant was determined to be 5.3×10^{-15} cm^3 $molecule^{-1}$ sec^{-1} at 277 K. Comparing this rate constant to that of methyl chloroform (6.5×10^{-15} cm^3 $molecule^{-1}$ sec^{-1}), whose tropospheric lifetime due solely to OH removal is known to be 7.0 years, gives an estimated tropospheric lifetime for HFC-245fa of 8.6 years. This is slightly longer than the 6.3 year lifetime of HFC-245ca previously determined by NIST.[5] Both HFC-245ca and HFC-245fa have tropospheric lifetimes which compare favorably with that of HFC-134a (15.5 years) and suggest a halocarbon global warming potential (HGWP) for both HFC-245 isomers, roughly 50 percent that of HFC-134a.

Summary and Conclusions

HFC-245fa has been shown in laboratory testing and modeling performed to date to be a good potential long-term replacement refrigerant for CFC-11 or HCFC-123 in low pressure chillers. Computer modeling of chiller systems using HFC-245fa indicates that reduced energy efficiencies on the order of 4 to 5 percent may occur relative to CFC-11.

On the basis of testing with a single polyolester lubricant, such lubricants appear to afford excellent compatibility and miscibility with HFC-245fa. Of the 13 different elastomeric materials tested, 3 gave acceptable compatibility in the presence of combined refrigerant/lubricant and 3 gave acceptable compatibility in the presence of the refrigerant alone. HFC-245fa was found to be thermally and hydrolytically stable under all test conditions.

Flammability testing of HFC-245fa showed the refrigerant to be weakly flammable at room temperature and then only at relative humidities above approximately 50 percent. Upper and lower flammability limits at room temperature and 50 percent relative humidity were found to be 8.9 and 11.2 volume percent HFC-245fa in air, respectively, using a spark as the ignition source.

HFC-245fa has zero potential to deplete stratospheric ozone. Its atmospheric lifetime, estimated from its measured reaction rate with OH radical, is 8.6 years. This lifetime corresponds to a halocarbon global warming potential roughly 50 percent that of refrigerant HFC-134a.

Due to limited supplies of HFC-245fa available for testing, essentially no toxicological information is known for the refrigerant. However, based on its molecular structure and on toxicity information known for isomers of other HFCs, it is believed that HFC-245fa will exhibit lower toxicities than HFC-245ca. The latter refrigerant was previously tested for acute inhalation toxicity on rats using a 4-hour exposure at 993 ppm and was found to yield no ill effects.

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16. ABSTRACT

The paper reports results of an evaluation of HFC-245fa as a potential alternative for CFC-11 in low pressure chillers. (NOTE: It was reported previously that HFC-245ca (1,1,2,2,3-pentafluoropropane) has many attributes that make it an attractive candidate alternative for CFC-11 and HCFC-123.) This paper gives results of an initial evaluation of HFC-245fa (1,1,1,3,3-pentafluoropropane) and updated results of HFC-245ca testing. HCFC-123 (1,1-dichloro-2,2,2-trifluoroethane) is currently the only alternative refrigerant for low pressure CFC chillers. This chlorine-containing alternative is scheduled for a production cap beginning in 1996, followed by a production phase-down through the year 2030, at the end of which production must cease. This phaseout timeframe is expected to allow new equipment designed for use with HCFC-123 and placed into service in the next few years to be utilized over the useful lifetime of the equipment. Meanwhile, the search for a long-term alternative continues.

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