

Evaluation of HFO-1234yf as a Potential Replacement for R-134a in Refrigeration Applications

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ABSTRACT

In response to concerns about the contribution of fluorocarbon refrigerants to global climate change, a new, more environmentally sustainable, refrigerant molecule has been developed and is being evaluated. This new molecule is the hydrofluoroolefin 2,3,3,3-tetrafluoroprop-1-ene, or HFO-1234yf. The molecule has been shown to be stable inside refrigeration equipment, but to quickly decompose if accidentally released into the atmosphere. (Nielsen, 2007) This paper presents results of work to develop a Martin Hou equation of state model for calculation of thermophysical properties of this new molecule. Thermodynamic cycle calculations have been performed to compare this new gas with R-134a in a refrigeration system. Results of work to evaluate the stability and compatibility of this gas with refrigeration system lubricants and materials, and evaluations of the performance of this gas as a working fluid in refrigeration applications are described.

1. INTRODUCTION

Concerns about the potential impacts of industrial refrigerant gases on the earth's atmosphere have resulted in the phasing out of the use of chlorine and bromine containing refrigerant gases due to their contribution to depletion of the ozone in the stratosphere. Now concerns about possible global climate change have led to legislative action in Europe to phase down the use of the hydrofluorocarbon R-134a in automobile air conditioning systems, beginning in the year 2011. The search for possible replacement gases which are suitable for use in private automobiles has yielded the fluoroolefin 2,3,3,3-tetrafluoropropene. This molecule has been evaluated and its properties reported with respect to its use in automobile air conditioning systems. (Minor and Spatz, 2008)

This paper describes some of the work which has been performed within the DuPont Company laboratories, to evaluate HFO-1234yf for use in more types of refrigeration applications. Refrigeration, as opposed to auto air conditioning, involves the use of hermetically sealed motor/compressor systems, many of which operate 24 hours a day for many years. A wider variety of materials of construction are employed, and different compressor lubricants used. System design and engineering of multiple possible system configurations requires the use of modeling tools for calculation of thermophysical properties and theoretical system performance. A useful approach, a Martin-Hou Equation of State has been developed for this, and is described to aid the necessary calculation and modeling work. Some results from the model will be presented. Additionally some results of laboratory tests to show how HFO-1234yf compares with R-134a in terms of compatibility with polyolester lubricants and with polymers commonly used in stationary HVAC&R equipment will be described.

2. DEVELOPMENT OF MARTIN-HOU EOS COEFFICIENTS

The Martin-Hou equation of state (MH EoS) is a highly usable equation of state to generate property information with sufficient accuracy for refrigeration and air conditioning modeling and design, using only a limited amount of available data. This tool is capable of generating tables of thermodynamic properties and generating accurate Pressure-Enthalpy (*PH*) diagrams. The *PH* plot is particularly useful for graphical or digital estimation of refrigeration cycle parameters and therefore is one of the desired products in evaluation of refrigerant thermophysical properties. The MH EoS can be used within modeling programs for evaluation of refrigeration cycles under a variety of input scenarios of operating temperatures, conditions, and system design variations. Further, it can be refined as more accurate measurement data for the HFO-1234yf becomes available.

For much practical air conditioning and refrigeration work it is not necessary that the phase space of liquid phase properties to the left side of the *PH* dome be fully defined. However, it is important to know the limits and shape of the Pressure-Enthalpy dome. This can be determined using fundamental principles and a limited amount of measured property data. The two-phase region within the dome and the gas phase region to the right side of the *PH* dome need to be accurately defined, and can be mapped with the MH EoS.

Measured thermophysical property data on HFO-1234yf have been very limited, and up until now only a small amount of published data has been available.

The large-scale equations of state required to support a fully robust modeling program like REFPROP (NIST, 2007) require a more extensive amount of precise data measurement and fitting to develop. The MH EoS described, is an alternative method for developing modeling equations with smaller amounts of data and application of fundamental principles of thermodynamics.

The general form of the MH EOS is well known, and is shown as Equation (1) below. Presented here are the developed Martin-Hou equation coefficients and thus a model which is quite sufficient for use to evaluate a developmental gas without the need for spending large amounts of money for large volume sample synthesis and purification, or for extensive property measurement.

The Martin-Hou equation and approach has long been used to generate thermodynamic property data and pressure-enthalpy relationships. (Martin, 1959 and Downing, 1988) It has been shown to be well suited to describe halocarbons, having been used to generate data for CFC refrigerants, for HCFCs, then for HFCs, and now this approach is being used to develop data for other developmental molecules, including hydrofluoroolefins (HFOs).

Briefly, this method requires vapor pressure, critical point properties, saturated liquid density data, vapor phase *PVT* data and heat capacity. We do not in this method model the liquid properties. Those are not necessary for modeling and comparison of air conditioning and refrigeration thermodynamic properties.

2.1 Data Used for Model Development

Saturation vapor pressures were determined by conventional means, in a thermostatted static equilibrium cell, to develop points which would define the saturated vapor line. Saturated liquid density is determined in the same apparatus. Within the *PH* dome, the width ΔH is calculated at constant pressure levels using the Clausius-Clapeyron equation, using measured vapor pressure and saturated vapor density and liquid density. The enthalpy along the saturated liquid line is determined by subtracting ΔH from the saturated vapor line. Properties near the critical point must be measured in a very precisely controlled high pressure equilibrium cell. While our model was initially developed using critical property data determined within our own apparatus, we found that data could be better fit to physical measurements by adopting the more precise critical property measurements reported by Higashi (Tanaka and Higashi, 2008). The MH coefficients were determined from a few measured *PVT* data points, density data, and the

critical property measurements. ***** Ideal gas heat capacity data was calculated using *ab-initio* molecular orbital methods using the “Gaussian-03” software. (CyberChem, Inc.) The results are correlated in the polynomial forms shown below. Measured liquid phase properties would be plotted to the left of the *PH* dome and below the critical pressure and will take the form of straight and perpendicular lines. As pressures approach the critical point these lines do begin to curve, so more detailed physical measurements would be necessary, but as these data are not as important for calculation of refrigeration system performance, this is not included in this model. When plotted, the liquid density data would be extrapolated from the liquid curve of the *PH* dome. The lines representing the gas phase region of the *PH* diagram is determined with the Martin-Hou equation of state. Some liquid density data are being collected to be made available for future model development. Typical use of this method is illustrated in Downing (1988) as it is used within our laboratory for general screening of candidate refrigerant gas candidates, for comparison and modeling work. Readers are referred to (Downing,1989) or similar reference texts for listing of equations derived from the MH EoS which are useful for refrigeration system modeling and for calculation of other thermodynamic properties. Shown here MH EOS, Equation (1), and a sampling of the related equations (2) to (5) which are used to develop coefficients from measured data or are useful for modeling:

$$P = \frac{RT}{V-b} + \sum_{i=2}^5 \frac{A_i + B_i T + C_i e^{-kT/T_c}}{(V-b)^i} \quad (1)$$

Vapor pressure relationships used are shown in Equations (2) and (3) below:

$$\ln P = A + \frac{B}{T} + C \ln T + DT + E \left(\frac{F-T}{T} \right) \ln(F-T) \quad (2)$$

$$\frac{dP}{dT} = P \left[-\frac{B}{T^2} + \frac{C}{T} + D - E \left(\frac{F}{T^2} \ln(F-T) + \frac{1}{T} \right) \right] \quad (3)$$

Saturated Liquid Density

$$\rho_L / \rho_C = \sum_{i=0}^4 d_i X^i \quad \text{where} \quad X = (1 - T / T_C)^{1/3} - d_5 \quad (4)$$

Saturated liquid density data were measured at range of temperatures from -10 °C to 70 °C and pressures from 1030.8 kPa to 4957 kPa , and the resulting data fit to determine the coefficients in Table 2.

Ideal Gas Heat Capacity

$$C_p^0 = \sum_{i=0}^5 c_i T^i \quad (5)$$

A more complete set of related and derived equations based on the Martin Hou EoS for other thermophysical property modeling can be found in textbooks and reference works, such as Downing (1989)

The coefficients which have been determined for use with the EOS for HFO-1234yf are shown in Table 1 and following:

Table 1. Properties and EOS Constants for Coefficients

[EOS units: P in kPa, T in K, and V in $\text{m}^3 \text{kg}^{-1}$]

M_w (molecular weight) / g mol^{-1}	114.04
T_c / K	367.85
P_c / kPa	3374.87
Z_c	0.2633
T_b (normal boiling point) / K	243.80
ω (acentric factor)	0.27803
R (gas constant) / $\text{kJ kg}^{-1} \text{K}^{-1}$	7.290839×10^{-2}
J (unit conversion factor)	1.0
A_2	-0.1398755
B_2	1.677524×10^{-4}
C_2	-1.518125
A_3	4.031561×10^{-4}
B_3	-6.739375×10^{-7}
C_3	5.521381×10^{-5}
A_4	-1.508838×10^{-7}
B_4	0
C_4	0
A_5	-2.736082×10^{-9}
B_5	6.760000×10^{-12}
C_5	4.773515×10^{-8}
α	0
C'	0
κ	5.033
b	3.973395×10^{-4}

Constants for the remaining equations are shown in Table 2:

Table 2. Constants for Eq. (2) and (3) [P in kPa, T in K]

A	B	C	D	E	F
48.70134	-4054.888	-5.353373	5.632772×10^{-3}	0.2423738	368.7851

Table 3. Constants for Eq. (4) [Density, ρ_L , in kg m^{-3} and T in K]

ρ_c	d_0	d_1	d_2	d_3	d_4
478.0	1.667131	2.314933	1.032959	0.09413147	-0.8200684

$$d_5=0.3315471 \text{ and } T_c = 367.85 \text{ K}$$

Table 4. Constants for Eq. (5) [C_p^0 in $\text{kJ kg}^{-1} \text{K}^{-1}$ and T in K]

c_0	c_1	c_2	c_3	c_4	c_5
0.233399	1.82451×10^{-3}	3.51596×10^{-6}	-1.12489×10^{-8}	1.06071×10^{-11}	-3.48283×10^{-15}

2.2 Some Modeling Results, Comparing R-134a with HFO-1234yf.

Table 5 is an abbreviated table of saturation properties of HFO-1234yf which was generated from the M-H model. Comparison of the data in Table 5 with similar data for R-134a calculated using its MH EoS or RERPROP shows that the vapor pressure of HFO-1234yf is very similar to that of R-134a. The vapor pressures are essentially the same at about 40 °C. At lower temperatures the vapor pressure of HFO-1234yf is higher than that of R-134a, and above 40 °C the HFO-1234yf drops to less than that of R-134a. If plotted, the two vapor pressure curves nearly overlay one another, except at the higher temperatures. Some of the data for HFO-1234yf are plotted along with the same properties for R-134a in Figure 1 and Figure 2.

As a check of the accuracy of the MH EOS for HFO-1234yf the saturation temperature was measured independently in another equilibrium cell, and the MH EoS was found to under predict the measured temperature by 0.388 C at 393.69 kPa, and under predict the temperature by 0.500 C at 888.73 kPa. Additional work is under way to refine the coefficients to allow a more accurate fit of the calculated results.

Table 6 is a summary of refrigeration cycle model calculations made using this MH EOS model and the corresponding MH EOS for R-134a. Note the relationship of performances of HFO-1234yf and R-134a. R-134a was also calculated using a MH equation, but the R-134a results have been compared and shown to agree well with thermophysical data and cycle models generated from REFPROP (NIST, 2007).

2.3 Laboratory Evaluation of HFO-1234yf with Refrigeration Materials

Key features of a new refrigerant candidate include its compatibility with typical materials of construction that are used in the manufacture of refrigeration and air conditioning equipment, and its thermal stability in the presence of those materials. We have made extensive use of the ASHRAE/ANSI Standard 97 sealed glass tube protocols for evaluation of the stability of HFO-1234yf with copper, steel, and aluminum and polyolester refrigeration compressor lubricants. At the standard test conditions of 175 °C for 14 days we saw no evidence of breakdown or reaction of the refrigerant with the metals or the lubricants. In addition we have evaluated numerous polymers samples and lubricants that are used in stationary refrigeration systems and have shown them to be similarly compatible with HFO-1234yf as they are with R-134a. Typical results are shown in Tables 7 (lubricants) and 8 (polymers). The data show that HFO-1234yf behaves very similarly to R-134a with refrigeration system materials.

A Martin-Hou Equation of State has been developed is being used to calculate thermophysical properties of the developmental refrigerant candidate HFO-1234yf. The measured and calculated properties show that this new molecule should behave similarly to R-134a in refrigeration and air conditioning systems, and this is being borne out in system testing. Laboratory measurements are showing that HFO-1234yf will be compatible with lubricants, plastics, elastomers, and metals currently used in construction of hermetic as well as open drive refrigeration systems.

Table 5. Properties of R-1234yf at Saturated Conditions

T C	P kPa	D_{liq} kg m ⁻³	D_{vap} kg m ⁻³	H_{liq} kJ kg ⁻¹	H_{latent} kJ kg ⁻¹	H_{vap} kJ kg ⁻¹	S_{liq} kJ kg ⁻¹ K ⁻¹	S_{vap} kJ kg ⁻¹ K ⁻¹
-40	62.197	1288.461	3.791	153.432	183.658	337.090	0.81686	1.60458
-30	98.501	1262.799	5.837	164.374	179.299	343.673	0.86268	1.60008
-20	149.908	1235.889	8.679	175.775	174.428	350.202	0.90846	1.59749
-10	220.324	1207.573	12.532	187.647	168.989	356.636	0.95423	1.59640
0	314.033	1177.653	17.648	200.000	162.925	362.925	1.00000	1.59647
10	435.640	1145.875	24.340	212.842	156.175	369.018	1.04579	1.59736
20	590.023	1111.908	32.998	226.183	148.666	374.850	1.09162	1.59875
30	782.304	1075.299	44.132	240.036	140.307	380.343	1.13749	1.60032
40	1017.859	1035.404	58.441	254.426	130.974	385.399	1.18346	1.60171
50	1302.344	991.258	76.930	269.399	120.481	389.880	1.22964	1.60248
60	1641.907	941.281	101.182	285.055	108.527	393.582	1.27628	1.60204
70	2043.480	882.550	133.992	301.615	94.541	396.156	1.32394	1.59945
80	2515.779	808.383	181.513	319.653	77.166	396.819	1.37414	1.59265
90	3072.852	693.348	266.498	341.261	51.039	392.300	1.43238	1.57292

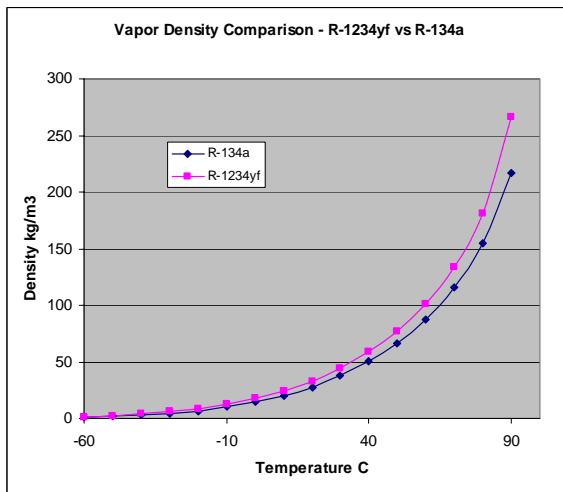


Figure 1: Vapor Density Comparison

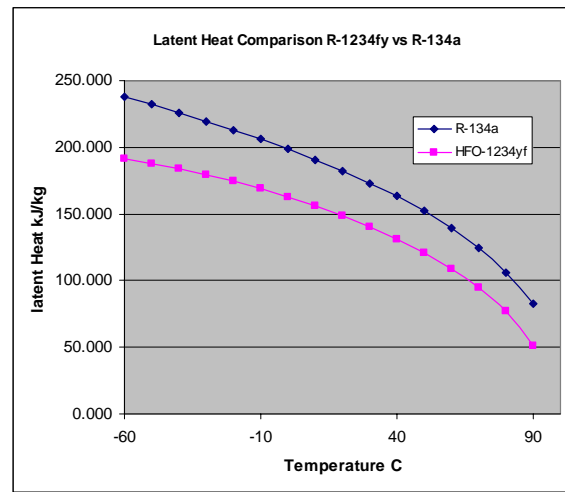


Figure 2: Latent Heat Comparison

Table 6. Calculated Theoretical Cycle Performance Comparison for HFO-1234yf Refrigeration

Comparison of Modeled Cycle Performance for refrigeration

T Evap = -2 °C (28.4 °F) T Cond = 30 °C to 56 C ° as noted
 Return Gas Temp = 15 °C (59 °F) Compressor Efficiency = 70 %
 performance model includes suction line heat exchanger
 Subcool = 47.8 °K (86 °F)

Refrig.	T °C	T °C	Suction kPa	Disch kPa	Comp. ratio	Disch T °C	Cap kJ/m3	Cap w/r R134a	COP	COP w/r R134a
R134a	-2	30	272.1	769.6	2.83	60.8	2114.7		5.088	
1234yf	-2	30	293.4	780.8	2.66	52.4	2073.5	98.05%	5.004	98.35%
R134a	-2	35	272.1	886.6	3.26	67.4	2023.4		4.275	
1234yf	-2	35	293.4	892.45	3.04	57.8	1964.5	97.09%	4.173	97.61%
R134a	-2	47	272.1	1222	4.49	82.5	1795.4		2.97	
1234yf	-2	47	293.4	1209	4.12	70.5	1691.4	94.21%	2.831	95.32%
R134a	-2	56	272.1	1530.7	5.63	93.6	1614.1		2.318	
1234yf	-2	56	293.4	1496.5	5.10	79.9	1473.4	91.28%	2.151	92.80%

Table 7. Miscibility Characteristics of HFO-1234yf in selected Lubricants

Lubricant	Composition - % lubricant in HFO-1234yf	Lower Phase Separation Temperature °C	Upper Phase Separation Temperature °C
Solest 32 cSt POE	60 % to 95 %	< - 50 °C	> 90 °C
Solest 68 cSt POE	60 % to 95 %	< - 50 °C	> 90 °C
POE RL32-3MAF	5 % to 70 %	UCST -45 °C at 20% POE	LCST 65 °C at 20 % POE
POE ND-11	1 % to 90 %	UCST -50 °C at 25 % POE Cloudy -5 °C to - 30C at 1 % Oil; 2 phase below -30 °C	LCST 70 °C at 25 % POE
Suniso 3GS Mineral Oil	1 % to 90 %		LCST 0 °C at 1 % lubricant

Table 8. Comparison of HFO-1234yf and R-134a with Selected Plastics
 Refrigerant Absorption or Extraction after 14 days exposure at 100 °C

Polymer	HFO-1234yf		R-134a	
	0 Hours	24 Hours	0 Hours	24 Hours
	% weight change		% weight change	
Polyester resin (Hytreil 5526)	4.2	2.3	7.6	2.2
Nylon resin (Zytel 330)	-0.2	-0.4	0.3	-0.5

Epoxy Resin	-0.1	-0.1	0.1	-0.3
Polyester PET (Bexloy 550)	5.3	3.8	9.3	5.8
Polyester PBT (Crastin SK605)	1.1	1.1	12.5	12.3
Polycarbonate	0.9	0.8	4.2	3.9
Polyimide (VespeI)	3.4	3.2	3.7	3.2
polyethylene (Alathon)	1.7	1.3	1.3	1.1
Teflon PTFE	3.0	2.4	2.7	2.3
Teflon FEP	3.8	3.2	3.1	2.7
Tefzel ETFE	4.9	4.2	6.0	4.8
Phenolic	-0.8	-0.8	-0.8	-1.0
Acetal (Derlin)	0.7	0.6	2.7	2.1
Mylar PET Film	-1.0	-2.1	0.8	-1.3

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NOMENCLATURE

p	pressure (kPa)	R	molar gas constant (8.314 472 J·mol ⁻¹ ·K ⁻¹)
T	temperature (K, unless specified as °C)	V	molar volume (mol·L ⁻¹)
c	subscript for a quantity at the critical point	ρ	density, kg m ⁻³
Z_c	compressibility factor, $P_c V_c / RT_c$, at the critical point		
A_i, B_i, C_i	constants used in the Equation of State		
A, B, C, D, E, F	constants used in vapor pressure equations 2 and 3\		
d_1, d_2, d_3, d_4, d_5	constants used in density equation		

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