Helmholtz Equation of State for HFO-1234yf with Comprehensive Assessment

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ABSTRACT

HFO-1234yf (2,3,3,3-tetrafluoropropene) is a recently launched refrigerant, which is proposed to substitute HFC-134a in air-conditioning and refrigeration systems. HFO-1234yf has a very low global warming index with an atmospheric lifetime 500 times lower than HFC-134a and has similar properties. It ensures minor changes in components if retrofitting is applied. Thermodynamic properties play an important role in developing thermal systems, either refrigeration or power systems. The fundamental equation of state provides the best solution to approximate thermodynamic properties in an area not covered by the experiments of HFO-1234yf. The equation of state for HFO-1234yf was developed by combining the regression method with a genetic algorithm. The most available updated experimental data were involved by considering the accuracy and distribution density. A new equation of state based on Helmholtz free energy can represent the density within an average absolute deviation of 0.20% in the liquid phase and 0.31% in the gas phase. The caloric properties can be represented within an average absolute deviation of 3.96% for the isobaric-specific heat, 1.98% for the speed of sound in the liquid phase, and 0.089% for the speed of sound in the gas phase. Consistently the second and third virial coefficients and the proper thermodynamic properties extrapolation and ideal curves are also performed.

KEYWORDS: Refrigerant, HFO-1234yf, thermodynamic properties, equation of state.

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I. INTRODUCTION

Refrigerants can cause depletion of the ozone layer and global warming if released into the air, either due to leakage in the system or being thrown away after use. The ozone depletion potential (ODP) index and global warming potential (GWP) were used to compare the effects caused by various refrigerants. Several regulations were made to ensure the appropriate use and handling of refrigerants, starting with the Montreal Protocol in 1987. In 2006, the European Parliament issued a regulation prohibiting the use of fluorine-containing refrigerants with GWP values exceeding 150 [1] [2]. This regulation applies to new types of cars produced since 2011 and to all car types since 2017.

The refrigerant that is popular in the cars today is HFC-134a. The automotive sector is in the spotlight because of its ever-increasing production, which is accompanied by innovations that attract consumers. However, the GWP value of HFC-134a is very high, beyond the regulatory limit, which is 1430. Almost the same as HFC-type refrigerants, HFO is composed of hydrogen, fluor, and carbon. HFO has at least one double bond. The use of environmentally friendly refrigerants is important to grow reality of the main issues caused, namely the depletion of the ozone layer and global warming. HFO-1234yf (2,3,3,3-tetrafluoropropane) has been applied by car manufacturers in Europe due to a small GWP of 4. In comparison, the atmospheric lifetime of HFO-1234yf is 11 days, compared to HFC-134a which is around 13 years.

Around 50 types of cars have been using HFO-1234yf since 2015 [3]. This refrigerant still needs to be researched, especially on relating safety and performance. Technical assessment of the replacement of HFC-134a with HFO-1234yf and design new air conditioning and refrigeration systems using HFO-1234yf working fluid requires accurate thermodynamic properties. Relatively few experimental data are available for thermodynamic properties. Therefore, this research aims to provide accurate data regarding the thermodynamic properties of HFO-1234yf by developing a Helmholtz equation of state.

II. THERMODYNAMIC MODELING

The experimental data used greatly affect in resulting an equation of state. The quality of experimental data can be assessed from the level of confidence, uncertainty, the purity of the sample

substance, and the measurement methods used. These parameters were generally reported in published literatures. Data needed in the development of the equation of state are pressure, density, and temperature at triple and critical points; ideal gas isobaric specific heat for developing the ideal part; saturation pressure, density of liquid and saturated vapor for developing ancillary equations; $p\rho T$, isobaric specific heat, isochoric specific heat, and speed of sound in the single phase, and second and third virial coefficients for developing the residual part.

Good quality and quantity data are a lot of the main criteria for the data to be used. Not only is it a lot in quantity, but it is also expected to have a wide range. Equation of state will be controlled more to fit data with high accuracy, which is marked by giving a greater weighting factor. The input data are used in general are divided into experimental data and artificial data. Experimental data is obtained through direct laboratory measurements, while artificial data are data from the calculation of the ancillary equations and existing theoretical equations of state.

Much of the data used in the equation provides a description of the difficulty of formulating the equation, starting from the equation of the easiest ideal part to the most complicated residual part. All data used in the ancillary equations are functions of saturated temperatures. Ideal gas isobaric specific heat equation, and second and third virial coefficients are data obtained through theoretical background virial equation.

To keep the thermodynamic consistency of the ideal gas law, the Helmholtz equation of state is separated into an ideal part (α^0) and a residual part (α^r). Mathematical modeling for the equation of state has been carried out in three steps. The first stage is modeling ancillary equations, the second stage is modeling the ideal gas isobaric-specific heat equation to get an ideal part, and the third stage is modeling multi-properties for a residual part. The ancillary equations and the isobaric specific heat equation for an ideal gas have only a function of temperature, while the residual part has a function of temperature and density according to the independent variables in the Helmholtz group equation.

The optimization method used at each stage is a combination of genetic algorithms and weighted least squares regression. This optimization method is comprehensively described in our group's previous article [4] and applied to various refrigerants such as HFC, hydrocarbon, HCFO, and HFO. Recent equations of state published by our research group are HFO-1234zf [5] and HFO-124ze(E) [6], which have the same paradigm on the development. Coefficients that have a linear relationship are optimized from regression, while nonlinear constants in the equation are generated by a genetic algorithm. The relationship between thermodynamic properties and the equation of state is presented in Table 1. Regression to minimize weighted least squares by multiplying the weighted factor by the square of the deviation between the value of the left term of the input data and the calculated value of the right term for the same point data. The sum of these weighted least squares deviations of all the traits involved in the optimization is used as a fitness in the genetic algorithm.

Property	Thermodynamic relations
Helmholtz free energy	$A = M\bar{R}T(\alpha^{0}(\delta,\tau) + \alpha^{r}(\delta,\tau))$
Ideal gas isobaric specific heat	$\frac{c_p^0}{R} = 1 - \tau^2 \alpha_{\tau\tau}^0 = 1 + \frac{c_v^0(\tau)}{R}$
Pressure	$\frac{p(\delta,\tau)}{\rho_{RT}} = 1 + \delta \alpha_{\delta}^{r}$
Vapor pressure	$\frac{p_s(\delta',\delta'',\tau_s)}{RT_s} = \frac{\rho'\rho''}{\rho'-\rho''} \left(\ln\left(\frac{\delta'}{\delta''}\right) + \alpha^{r'} - \alpha^{r''} \right)$
Third virial coefficient	$B(\tau)\rho_c = \lim_{\delta \to 0} \alpha_\delta^r$
Second virial coefficient	$C(\tau)\rho_c^2 = \lim_{\delta \to 0} \alpha_{\delta\delta}^r$
Isobaric specific heat	$\frac{c_p(\delta,\tau)}{R} = \frac{c_v(\delta,\tau)}{R} + \frac{(1+\delta\alpha_{\delta}^r - \delta\tau\alpha_{\delta\tau}^r)^2}{(1+2\delta\alpha_{\delta}^r + \delta^2\alpha_{\delta\delta}^r)}$
Isochoric specific heat	$c_v(\delta,\tau)/R = -\tau^2(\alpha_{\tau\tau}^0 + \alpha_{\tau\tau}^r)$
Speed of Sound	$\frac{w^2(\delta,\tau)M}{RT} = 1 + 2\delta\alpha^r_{\delta} + \delta^2\alpha^r_{\delta\delta} + \frac{(1+\delta\alpha^r_{\delta} - \delta\tau\alpha^r_{\delta\tau})^2}{c_v(\delta,\tau)/R}$

 Table 1: Thermodynamic property relations to Helmholtz equation of state

Property	Thermodynamic relations
Saturated liquid specific	$\frac{c_s'(\delta',\delta'',\tau_s)}{R} = \frac{c_v(\delta',\tau_s)}{R}$ $(1 + \delta' \alpha^{r'} - \delta' \tau - \alpha^{r'}) = (1 - dr - \delta' - \delta' \tau - \delta' - \delta' - \delta' - \delta' - \delta' - $
heat	$+\frac{(1+\delta'\alpha_{\delta}^{r}-\delta'\tau_{s}\alpha_{\delta\tau})}{(1+2\delta'\alpha_{\delta}^{r'}+\delta'^{2}\alpha_{\delta\delta}^{r'})}\times\left\{1+\delta'\alpha_{\delta}^{r'}-\delta'\tau_{s}\alpha_{\delta\tau}^{r'}-\frac{1}{R\rho_{c}\delta'}\frac{d\rho_{s}(\delta',\delta'',\tau_{s})}{dT}\right\}$
Saturated vapor specific heat	$\frac{c_{s}^{\prime\prime}(\delta^{\prime},\delta^{\prime\prime},\tau_{s})}{R} = \frac{c_{v}(\delta^{\prime\prime},\tau_{s})}{R} + \frac{(1+\delta^{\prime\prime}\alpha_{\delta}^{\prime\prime}-\delta^{\prime\prime}\tau_{s}\alpha_{\delta\tau}^{\prime\prime\prime})}{(1+2\delta^{\prime\prime}\alpha_{\delta}^{\prime\prime}+\delta^{\prime\prime/2}\alpha_{\delta\sigma}^{\prime\prime})} \times \left\{1 + \delta^{\prime\prime}\alpha_{\delta}^{\prime\prime\prime} - \delta^{\prime\prime}\tau_{s}\alpha_{\delta\tau}^{\prime\prime} - \frac{1}{R\rho_{c}\delta^{\prime\prime}}\frac{dp_{s}(\delta^{\prime},\delta^{\prime\prime},\tau_{s})}{dT}\right\}$
Internal energy	$\frac{u(\delta,\tau)}{RT} = \tau \left(\alpha_{\tau}^{0} + \alpha_{\tau}^{r} \right)$
Enthalpy	$\frac{h(\delta,\tau)}{RT} = \tau(\alpha_{\tau}^{0} + \alpha_{\tau}^{r}) + 1 + \delta\alpha_{\delta}^{r}$
Entropy	$\frac{s(\delta,\tau)}{R} = \tau(\alpha_{\tau}^{0} + \alpha_{\tau}^{r}) - (\alpha^{0} + \alpha^{r})$
$\alpha_{\delta} =$	$\left(\frac{\partial\alpha}{\partial\delta}\right)_{\tau}, \alpha_{\tau} = \left(\frac{\partial\alpha}{\partial\tau}\right)_{\delta}, \alpha_{\delta\delta} = \left(\frac{\partial^{2}\alpha}{\partial\delta^{2}}\right)_{\tau}, \alpha_{\tau\tau} = \left(\frac{\partial^{2}\alpha}{\partial\tau^{2}}\right)_{\delta}, \alpha_{\delta\tau} = \left(\frac{\partial^{2}\alpha}{\partial\delta\partial\tau}\right), \delta = \frac{\rho}{\rho_{c}}, \tau = \frac{T_{c}}{T}$

III.DATA PREPARATION

According to the refrigerant object in the study, experimental and theoretical studies for HFO-1234yf are very necessary and play an important role in this modeling. Critical and triple points are needed in modeling the equation of state. The ancillary equations used to produce artificial data often involve critical point because of critical temperature included inside as a dimensional reducer so that the critical and triple points is very difficult, because the phase difference at that point is difficult to distinguish. The experimental results at the critical point used in this study are the result data from Tanaka and Higashi for HFO-1234fy refrigerant [7], which are critical pressure (p_c) of 3,382 kPa, critical temperature (T_c) of 367.85 K, critical density (ρ_c) of 478 kg/m³ for the mass purity 99.96%. The triple point is obtained on the thermocouple measurement by cooling mode because it is considered more accurate than the heating mode as reported for HFO-1234yf triple point of refrigerant at with 220 K at mass purity of 99.9% [8]. Universal gas constant (\overline{R}) used in the modeling is 8.3144598 kJ/kmol K [9] and molecular mass (M) is 0.114042 kg/mol [10].

Pressure, density, and temperature $(p\rho T)$ data at saturation was used to obtain the ancillary equations and the residual part of the equation of state. To obtain accurate ancillary equations, experimental data within a triple temperature up to a critical temperature and an adequate amount of data are needed. Data of isobaric specific heat of the ideal gas is needed in developing the ideal part of the equation of state. This needing is due to the ideal part is obtained from the integral process of the ideal gas isobaric specific heat equation. The experimental data used were reported by Kano et al. [26] as many as 6 data points with temperature range of 278–353 K.

		I.		
Reference	Year	No. of Points	Purity (% w/w)	Range (K)
Vapor pressure				
Tanaka and Higashi [7]	2010	11	99.99	310–360
Nicola et al. [11]	2010	34	99.95	224.12-362.94
Richter et al. [12]	2011	30	99.96	250-366
Fedele et al. [13]	2011	40	99.5	245.65-343.15
Yang et al. [14]	2014	54	99.9	248.17-361.05
Saturated liquid				
Density				
Tanaka and Higashi [7]	2010	10	99.99	348.047-367.848
Zhao et al. [15]	2018	44	99.95	242-365
Zhao et al. [16]	2014	10	99.99	293.15-365.05
Saturated vapor				
Density				
Tanaka and Higashi [7]	2010	11	99.99	356.007-367.739
Zhao et al. [15]	2018	44	99.9	242.21-365

Table 2: Summary of available experimental saturation data for HFO-1234yf

Reference	Ŋ	ear	No. of Points	Purity (% w/w)	Range	(K)
Zhao et al. [16]	2014		10	99.99	293.15-365.05	
Table 4: Experimental data for the single-phase properties of HFO-1234yf						
Data Dafaranga	Voor	No. of	Dhaga	Purity	Ran	ge
Data Reference	Tear	Points	rnase	(%)	T (K)	p (MPa)
рρТ						
Nicola et al. [17]	2010	133	V	99.95	243.07-372.88	0.084 - 10.01
Tanaka et al. [18]	2010	23	L	99.99	310-360	1-5
Richter et al [12]	2011	39	L	99.96	232.01-365.03	1-9.6
Richter et al. [12]	2011	67	V	99.96	319.99-400.0	0.56-6.58
Klomfar et al. [19]	2016	70	L	99.5	217.44-353.15	0.9-40.03
Fedele et al. [20]	2017	280	L	99.5	283.13-353.2	0.68-35.02
Qiu et al. [21]	2013	128	L	99.99	283.50-362.96	1-100
Hu et al. [22]	2017	83	V	99.9	252.64-345.76	0.07 - 1.91
Isobaric heat capacity						
Tanaka et al. [18]	2010	22	L	99.99	310-360	2-5
Liu et al. [23]	2017	154	L	99.95	303.5-373.42	1.51-12.08
Lukawski et al. [24]	2018	33	V	99.99	373.15-413.15	3.5-10.03
Isochoric heat capacity						
Zhong et al. [25]	2018	74	L	99.9	240.93-340.26	1.67-12.84
Speed of sound						
Kano et al. [26]	2010	41	V	99.96	278.15-353.15	0.03-0.41
Lago et al. [27]	2011	22	L	99.95	259.98-360.03	1.99-6.06

The second and third virial coefficient data were used in the process of developing the residual part of the Helmholtz equation. In the unavailable of second and third virial coefficient data, the equation developed by Pitzer et al. [28] for the second virial and equations developed by Obey et al. [29] for the third virial. The equation developed by both is a function of temperature. In this study a temperature range of 220–1000 K was used for the second virial coefficient data, while in the third virial coefficient data a range of 205–1000 K was used.

IV.MODELING RESULT

Two groups of equations are resulted from thermodynamic modeling. The first group is ancillary equations to calculate vapor pressure, saturated liquid, and saturated vapor densities. The second group is the Helmholtz equation of state which consists of the ideal and the residual parts. The modeling procedure used in this study can refer to our newly previous article [30].

4.1 Ancillary Equation

The ancillary equations consist of equations for vapor pressure (p_s) , saturated liquid density (ρ') , and saturated vapor density (ρ'') written in Equations (1)–(3), which each is a function of temperature (*T*). The critical parameters used to reduce the properties to non-dimension are critical pressure (p_c) , critical density (ρ_c) , and critical temperature (T_c) . These equations were used to complete input data at saturation and provide Maxwell criteria in developing of the Helmholtz equation of state. These equations accurately represent $p\rho T$ at saturation state.

$$\ln\left(\frac{p_s}{p_c}\right) = \sum_{i=1}^{4} E_i \left(\frac{T_c}{T}\right) \left(1 - \frac{T}{T_c}\right)^{ti} \tag{1}$$

$$\left(\frac{\rho'}{\rho_c} - 1\right) = \sum_{i=1}^{5} F_i \left(1 - \frac{T}{T_c}\right)^{r_i} \tag{2}$$

$$\ln\left(\frac{\rho^{*}}{\rho_{c}}\right) = \sum_{i=1}^{5} G_{i} \left(1 - \frac{T}{T_{c}}\right)^{s_{i}}$$
(3)

					-	
i	t _i	E _i	r _i	F _i	s _i	G _i
1	1	-8.2692	0.125	-0.47216	0.3499	-1.70146
2	1.25	1.80762	0.25	3.04747	0.40	-0.99318
3	3.25	-1.88471	0.375	-3.67878	1.20	-7.26045
4	6.25	-8.50827	0.5	3.73649	3.25	-19.04828
5	-	-	5.125	4.26799	6.40	-44.65044

Table 3: Numerical coefficients and constants of Equations (1)–(3)

4.2 Helmholtz Equation of State

The Helmholtz equation of state consists of the ideal and the residual parts. The ideal part was obtained first through an optimization process using the genetic algorithm and the least squares regression in the ideal-gas isobaric heat equation. The ideal-gas isobaric gas heat equation was then integrated to get the ideal part. The development of ideal-gas isobaric heat equations used the experimental data of Kano et al. [26] with a total of 6 points in the temperature range of 278–353 K. With a very minimal amount of data, the equation was developed by Kano et al. and the data of Akasaka [31] with a wider temperature range. The ideal part consists of the polynomial and Einstein-Planck terms, and integral constants following a reference state. The relation can be written in Equation (4). The numerical coefficients and constants of the equation are represented in Table 4.

$$\alpha^{0}(\delta,\tau) = \ln \delta - \ln \tau + \sum_{i=1}^{2} N_{i}^{0} \tau^{\eta_{i}^{0}} + \sum_{i=3}^{6} N_{i}^{0} \ln \left(1 - e^{-\eta_{i}^{0} \tau}\right)$$
(4)

 Table 4: Numerical coefficients and constants of the ideal part

i	η_i^0	N_i^0
1	0	-6.6557489
2	1	8.8592372
3	12.6358	1.38667
4	4.9895	7.26031
5	2.2936	7.90416
6	0.4697	7.60888

The residual part is a product that resulted from the multi-property regression and the genetic algorithm optimization. The final residual part can be written in Equation (5) with numerical coefficients and constants given in Table 5. It consists of 17 terms, which have 6 polynomial terms and 11 exponential terms.

$$\boldsymbol{\alpha}^{r}(\boldsymbol{\delta},\boldsymbol{\tau}) = \sum_{i=1}^{6} N_{i} \boldsymbol{\delta}^{d_{i}} \boldsymbol{\tau}^{t_{i}} + \sum_{i=7}^{12} N_{i} \boldsymbol{\delta}^{d_{i}} \boldsymbol{\tau}^{t_{i}} \mathbf{e}^{-\boldsymbol{\delta}} + \sum_{i=13}^{17} N_{i} \boldsymbol{\delta}^{d_{i}} \boldsymbol{\tau}^{t_{i}} \mathbf{e}^{-\boldsymbol{\delta}^{2}}$$
(5)

Table 5: Numerical coefficients and constants of the residual part

i	d _i	t _i	N _i
1	1	0.156	0.99789817
2	1	1.375	3.46550277
3	1	1.938	1.45758065
4	3	0.594	0.14103108
5	5	0.688	0.00183853
6	5	1.094	0.00294111
7	1	2.75	-0.31118458
8	1	3.75	-0.35840466
9	6	0.5	-0.02395599
10	6	2.5	-0.16233408
11	6	2.875	0.13023551
12	6	3.5	-0.01970155
13	1	2.25	0.27681232
14	2	2.125	0.14962603
15	2	7.25	-0.20770116
16	4	3.125	0.08184228
17	4	8.625	0.0106312

V. MODEL ASSESSMENTS

Assessment of the new equation of state was conducted as long its development to find the best one as a proposed equation of state in this study. Assessment includes its accuracies in producing thermodynamic values compared to the experimental data and values calculated from other existing equations of state. The values derived from the new equation of state were used as a reference basis to represent visualization assessments of each property. All deviations of the assessments are represented in relative deviations with respect to the values calculated from the equation of state.

The deviation of the ideal gas isobaric equation in this study is shown in Figure 1. Some deviations are revealed for some data used in the development. The average absolute deviation (AAD) is 0.17% and the maximum absolute deviation (MAD) is 0.25% regarding the experimental data of Kano et al.[26]. The deviation for the experimental data of Kano et al. is in a narrow temperature range. This assessment shows that the equation obtained is correct. In this case, the uncertainty of the isobaric specific heat data of Kano et al. is 0.10%.



Figure 1. Deviation of ideal gas specific heat from the new equation of state

The vapor pressure equation consists of 4 terms and the saturated liquid and saturated vapor density equation consists of 5 terms as indicated in Equations (1)–(3). The number of terms is chosen as a minimum as possible without reducing the accuracy of the equation in the range of existing data. The vapor pressure equation has a deviation from the experimental data as the graph shown in Figure 2. With the limited availability of experimental results, artificial data is obtained from the Wagner correlation [7] to compare in this assessment.



Figure 2. Deviation of vapor pressure from the Equation (1) and the new equation of state

The vapor pressure equation has the smallest average absolute deviation (AAD) value from the experimental data of Tanaka and Higashi [7] within a temperature range of 310–360 K. The assessment result of these data has an average absolute deviation (AAD) of 0.007% and a MAD of 0.24%. An AAD of 0.007% of the experimental results of Tanaka and Higashi is better than the results of the equation by Akasaka [31] which amounted to 0.08%. Deviation of the vapor pressure equation in the area near the critical point with a small value is necessary, it is intended that the vapor pressure equation can calculate the thermodynamic properties with good accuracy.

The vapor pressure equation to represent the data of Richter et al. [12] with a temperature range of 250–366 K has an AAD of 0.052% and a MAD of 0.44%. The result of this equation performs better than the equation by Akasaka [31], which is equal to 0.07%. In the temperature range of 224.12–362.94 K, the experimental data from Nicola et al. [11] has an AAD of 0.10% and a MAD of 0.31%. Compared with the results of the equation by Akasaka [4], which is equal to 0.09% of the experimental data from Nicola et al. [11], this vapor pressure equation is less inferior. In a wider temperature range of 224–363 K for the vapor pressure, the experimental data of Yang et al. [14] is represented within an AAD of 0.076% and a MAD of 0.44%. For a temperature range of 245–344 K, the experimental data was used by Fedele et al. [13] within an AAD of 0.14% and the MAD of 2.3%. The MAD occurs in the experimental data of Fedela et al. These visually presented results also show that the ancillary equation can present the pressure with higher accuracy than the equation of state of this study.

The saturated liquid density can be calculated from Equation (2) and it can also be derived from the equation of state i.e. directly using Equation (5). Figure 3 shows the assessment result of their deviations. The ancillary equation for the saturated liquid density consists of 5 terms as written in Equation (2). From the assessment results of the saturated liquid density equation, the experimental data of Tanaka and Higashi [7] having a temperature range of 348–368 K can be represented within an AAD of 0.69% and a MAD of 2.62%. The experimental data from Zhao et al. [16] in the range of 242–365 K has an AAD of 0.10% and a MAD of 0.31%, on the other hand, other data of Zhao et al. [15] having a temperature range of 293–365 K has an AAD of 0.13% and a MAD of 0.28%. Compared to the values derived from the equation of state, the ancillary equation can represent the saturated liquid density near the critical point, but both their representation with higher deviation. At lower temperatures, the equation of state can be represented more accurately than the ancillary equation.



Figure 3. Deviation of saturated liquid density from the Equation (2) and the new equation of state

The same way to get value of the saturated vapor density is by deriving from the equation of state and the ancillary equation for the saturated vapor density. The assessment results are shown in Figure 4. This ancillary equation consists of 5 terms as written in Equation (3). Assessment of the ancillary equation shows that the saturated vapor density can represent the experimental data of Zhao et al. [15] having a temperature range of 242–365 K within an AAD of 0.08% and a MAD of 0.80%, the data of Zhao et al. [16] in the temperature range of 293–365 K within an AAD of 0.28% and a MAD of 0.81%. While in the temperature range of 356–368 K using the experimental data of Tanaka and Higashi [7] is represented within an AAD of 1.24% and a MAD of 2.49%. Similar ability to represent the densities near the critical point with large deviations. Generally, the values of the saturated vapor density derived from the equation of state give larger deviation compared to the value derived from the equation of state.

The following assessment focuses on the ability of the equation of state to represent the density and caloric properties in a single phase. The discussion is grouped into the liquid and gas phases because the magnitude of the deviations is very different in each phase. The very different properties due to this phase difference have caused the capabilities and uncertainties of the measuring instruments to differ between the two. This tendency occurs in measurements of density, specific heat, and the speed of sound.



Figure 4. Deviations of the saturated vapor density from the Equation (3) and the new equation of state

The calculation of the thermodynamic equation of state for densities in the single phase can be divided into liquid and gaseous phases. Therefore, evaluation is divided into two cases in assessments of the equation obtained. Deviations of the liquid phase density from the equation of state are shown in Figure 5. Experimental data for the thermodynamic properties of pressure, temperature, and density in the liquid phase used in developing the equations of the state come from five sources of experimental data. Each experimental data represents different temperature and pressure points. The deviations of the data are represented for a temperature range of 217–363 K and a pressure range of 0.971–100 MPa as shown in the figure.



Figure 5. Deviations of the liquid density from the new equation of state

The liquid density of the experimental data by Klomfar et al. [19] in the temperature range of 217–353 K was represented with an AAD of 0.05% and a MAD of 0.22%. For a temperature range of 232–365 K liquid density data of the Richter et al. [12] can be represented with an AAD of 0.088% and a MAD of 0.41%. The figure shows a large increase in the temperature range of 360–365 K. The deviation of saturated liquid density at

low temperatures has a relatively lower deviation and will be higher if the temperature approaches the critical temperature. Experimental data from Fedele et al. [7] with a temperature range of 283–354 K can be reproduced within an AAD of 0.064% and a MAD of 0.40%. Experimental data from Fedele et al. [7] used 280 data, with the largest amount of data used in this equation. The maximum deviation occurs at the highest temperature of 353,2 K.

The liquid phase density data in the temperature range of 283–363 K reported by Qiu et al. [21] can be represented within an AAD of 0.14% and a MAD of 1.66%. Experimental data with a temperature range of 310–360 K of Tanaka et al. [18] can be produced within an AAD of 0.15% and a MAD of 0.97%. The equation of state for HFO-1234yf proposed by Akasaka [31] with respect the data of Richter et al. [12] and Tanaka et al. [18] has an AAD in the liquid phase density of 0.04% and 0.10%, respectively. Compared with the development of liquid phase produced by this study for the same experimental data having an AAD of 0.08% and 0.15%, respectively. It is not enough to present the behavior of its thermodynamic properties in accordance with the data uncertainties. Experimental data from Klomfar et al. [19], Fedele et al. [20], and Qiu et al. [21] does not used the HFO-1234yf by Akasaka [4] since the three experimental data were reported after Akasaka [31] published the equation of state. The experimental data of Klomfar et al. [19], Fedele et al. [20], and Qiu et al. [21] were compared to the liquid density derived from the equation by Akasaka [31] and they have an AAD of 0.054%, 0.13%, and 0.38%, respectively.

The equation of state of this study for to experimental data of Klomfar et al. [19], Fedele et al. [20], and Qiu et al. [21] have an AAD of 0.047%, 0.064%, and 0.14%, respectively. These assessments confirm that a lower AAD resulted from this study than Akasaka [31]. The deviation pattern from this study equation of state for liquid phase density of the three experimental data indicates a more accurate representation of the thermodynamic properties.

Deviations of gaseous density from the equation of state are shown in Figure 6. In this development, the properties of pressure, temperature, and density of the gas phase used experimental data that came from three sources, namely Richter et al. [12], Hu et al. [22], and Nicola et al. [11]. At high temperatures in the range of 320–400 K experimental data of Richter et al [12] are represented within an AAD and a MAD of 0.73% and 2.33% for the values calculated from the equation of state. As shown in the figure, it can be seen that for a temperature range of 350–400 K, the deviations tend higher values. Among these ranges, there is also a critical temperature point, which is difficult to fit.



Figure 6. Deviations of the gaseous density from the new equation of state

The equation of state of this study for representing density in the gaseous phase for the experimental data of Hu et al. [22] in a range of 252–346 K performs an AAD of 0.39% and a MAD of 0.96%. In a temperature range that is not too wide, the experimental data of Hu et al. [22] is representative of density in the gaseous phase. In the wide temperature range of 243–373 K, the experimental data from Nicola et al. [17] can be represented within an AAD and a MAD of 0.35% and 2.99%. When compared with other data in the gaseous phase, the experimental data of Nicola et al. [17] have the smallest AAD. This result was obtained because the accuracy of the density data of Nicola et al. [17] is higher than the others. The data density can be seen from the

amount of data and temperature range. The data of Nicola et al. [17] has 133 points. The tightness of the data had a positive influence on the accuracy of the fitting result.

With the limited distribution and amount of available caloric data, the equation of state was assessed for its ability to represent these properties. The assessment begins with the specific heat and then continues with the speed of sound. Figure 7 presents the deviation of the isochoric specific heat between the experimental data and the calculation results from the equation of this study. The experimental data of Zhong et al. [25] can be estimated with an ADD of 1.71% and a MAD of 3.13%.



Figure 7. Deviations of isochoric specific heat from the new equation of state

Figure 8 presents the isobaric specific heat deviation between the experimental data for the pressure range of 1-12 MPa and the calculation results from the equation of this study. The experimental data of Tanaka et al. [18] is estimated with an ADD of 1.96% and a MAD of 4.31%, while the experimental data of Liu et al. [23] can be estimated with an ADD of 2.16% and a MAD of 5.00%. The deviation is more spread out and does not appear to have a high bias, although the deviation is still large.



Figure 8. Deviations of the isobaric specific heat from the new equation of state

The speed of sound is an interesting caloric property from a measurement aspect because the accuracy and uncertainty of the measurement results are generally better than those of specific heat. However, the available experimental data are very limited in point number and measurement range of pressure and temperature. The results of a visual assessment of the speed of sound are shown in Figure 9. The only comparable data are those from Kano et al. [26] for the gas phase and Lago et al. [27] for the liquid phase. The Kano et al. experimental data can be presented within an AAD of 0.09% and a MAD of 0.28%, while the Lago et al. data can be represented within an AAD of 1.98% and a MAD of 5.82%. The Kano et al. data have a pressure range of 0.03–0.41 MPa in the gas phase, and the Lago et al. data have a pressure range of 1.99–6.06 MPa in the liquid phase.



Figure 9. Deviations of the speed of sound from the new equation of state

Extrapolation curves derived from the equation of state play an important role in revealing its consistency trend to represent thermodynamic properties in a region where the experimental data is unavailable. By the fact that experiments on thermodynamic properties are not easily conducted on a wide range of thermodynamic surfaces. The equation of state developed must be able to reliably predict properties outside the range of experimental data. A highly accurate equation of state for representing the experimental data does not assure reliable extrapolation can be achieved. Therefore, this assessment is very essential to be conducted. Figure 9 shows the result of extrapolating the thermodynamic properties of temperatures, pressures, and specific volume derived from the equation of state of this study. The extrapolation was conducted from the triple point up to a temperature of 1000 K and a pressure of 100 MPa. Experimental data used in this study are the lowest temperature of 217 K and the highest temperature of 400 K. The points at a saturation state form a dome-like pattern of lines with peaks at specific critical pressures and volumes. In the liquid phase, the curve formed has a very steep slope. Pressure, specific volume, and temperature relation are shown in Figure 10. This illustration shows that with the increase or decrease in pressure in the liquid phase, changes in specific volume will not be much different. Inversely proportional to the gaseous phase, the increase or decrease in pressure in the gaseous phase will have a considerable influence on specific volumes. Large specific volume changes in the gas phase are clearly illustrated with slower lines than the liquid phase lines.



Figure 10. Extrapolate of the *pvT* property

The isochoric-specific heat experimental data for the available HFO-1234yf fluid is in a temperature range of 241–340 K and a pressure range of 1.673–12.837 MPa. The isochoric-specific heat extrapolation was conducted in a temperature range of 200–600 K and a pressure of 0.01–100 MPa. The extrapolation results are shown in Figure 11. The isochoric-specific heat c_v is directly proportional to the pressure and temperature. The higher the pressure and temperature values, the higher the isochoric-specific heat value obtained. For the same temperature at lower than critical pressure, the isochoric-specific heats in the liquid phase have higher values than the gas phase and higher pressures will give higher values. The isochoric-specific heat c_v value jumps up as it approaches the critical temperature region. The isochoric-specific heat value will be highest at the critical point.



Figure 11. Extrapolation of isochoric specific heat from new equation of state

The isobaric specific heat extrapolation derived from the equation of state from this study is shown in Figure 12. The extrapolation was conducted for a temperature range of 200–600 K and a pressure of 0.01–100 MPa. The isobaric specific heat extrapolation result shows a similar pattern with isochoric-specific heat extrapolation, but the change value near has more increased steeply.



Figure 12. Extrapolation of isobaric specific heat from new equation of state

Extrapolation of the speed of sound derived from the equation of state from this study was shown in Figure 13. Extrapolation was conducted for a temperature range of 200–600 K and a pressure range of 0.01–100 MPa. The extrapolation result performs a proper behavior and trend. The speed of sound values is higher at saturated-liquid than saturated-vapor states. The curve shows that the speed of sound will decrease in the liquid phase as the temperature increases, but in the gas phase, the speed of sound will increase if the temperature increases. The lowest value of the speed of sound is at the critical point.



Figure 13. Exploration of speed of sound from new equation of state

The structural form of the equation of state has a great influence on the tendency of the reasonableness of thermodynamic properties outside the state range of measurement that can be done. Assessment of the characteristic curves is one method that can be done. The characteristic curves consist of the ideal gas curve, the Boyle curve, the Joule-Thomson inversion curve, and the Joule inversion curve. Figure 14 shows the behaviors of each curve. Definitions of each curve can be found in this reference [32]. The ideal gas curve has a sloping shape at low temperatures and steeply at high temperatures to form an asymptote on the Boyle curve. The ideal-gas curve and Boyle have the same characteristics, but the difference between the Boyle curve starts from the critical temperature. The Joule-Thomson inversion curve and the Joule inversion also have the same behavior as the Boyle curve only differ at the starting point and asymptotes at high temperatures. The saturation curve meets the starting point on the Boyle curve. The smooth and smooth curve shape shows the shape of the equation of

state developed in this study, which has a good extrapolation ability and follows an existing pattern previously developed by Akasaka [31].



Figure 14. Characteristic curves of the new equation of state

A comparison of the second and third virial coefficients for several equations of state is shown in Figures 15 and 16, respectively. The second virial coefficient curves derived from the equation of state of Richter et al. [12], Akasaka [31], and Pitzer et al. [28] and this study have a similar tendency where the curve will form negative asymptotes at low temperatures and coefficient values close to zero for very high temperatures. Therefore, the presentation of the second virial coefficient derived from the equation of state of this study is consistent and proper such as the others.



Figure 15. Comparison of second virial coefficient from the new equation of state

The difference occurs in the calculation results of the third virial coefficient. The results of this study are consistent with Orbey et al. [29], but not the other two equations of state. The equation of state of Akasaka [31] in the temperature range below 310 K does not meet the equation of Orbey et al. [29]. The third virial coefficient derived from Akasaka's equation of state forms an infinitely positive asymptote at temperatures below 290 K. The result of the Richter et al [12] equation performs infinitely negative asymptotes like the Orbey et al. [17] equation, but both results have different slopes. From Figure 16 it can be seen that the Richter et al. having a non-negative asymptote is gentler than the Orbey et al. equation under 260 K.



Figure 16. Comparison of third virial coefficient from the new equation of state

VI.CONCLUSION

The ancillary equations and Helmholtz equation of the state of thermodynamic properties for 2,3,3,3-Tetrafluoropropena refrigerants which also known as HFO-1234yf was developed in this study. The equation of state consists of two parts, i.e., the ideal part and the residual part. In addition to the equation, three ancillary equations for saturation properties were also developed. The ideal part has an AAD of 0.17% and a standard deviation of 0.21%.

The liquid density derived from the equation of the state of the study for all experimental data has an AAD of 0.20% and a standard deviation of 0.41%. The vapor density derived from the equation of state for the entire experimental data has an AAD of 0.31% and a standard deviation of 0.64%. The results of the calculation of the vapor pressure of the equation of state for all experimental data have an AAD of 0.08% and a standard deviation of 0.23%. The calculation result of the saturated liquid density for all experimental data has AAD of 0.09% and the standard deviation is 0.16%. The calculation of the saturated vapor density derived from the equation of state for all experimental data has an AAD of 0.45% and a standard deviation of 0.69%.

The isochoric-specific heat calculation of the equation of state on all experimental data has an AAD of 1.71% and a standard deviation of 0.74%. The calculation of the isobaric specific heat of the equation of state for all experimental data has an AAD of 3.96% and a standard deviation of 11.02%. The calculation result of the liquid phase speed of sound from the equation of state for all experimental data has an AAD of 1.98% and a standard deviation of 1.34%. The calculation of the gas phase speed of sound of the equation of state for all experimental data has an AAD of 0.089% and a standard deviation of 0.075%.

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