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Volumetric properties of supercritical carbon dioxide from volume-translated and modified Peng-Robinson equations of state

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Abstract−Following three well-established approaches, different modifications have been proposed that significantly improve the Peng-Robinson EOS's predictions of the volumetric properties of carbon dioxide in the supercritical region. By making use of 5301 experimental PVT data points of supercritical carbon dioxide (SC-CO_2), three models have been developed based on the volume-translation concept, modification of the alpha function of the attractive term of the Peng-Robinson EOS and the addition of a third translation parameter to the EOS. The experimental data considered encompass a wide temperature and pressure range of 304.35-1,273.15 K and 7.38-800.00 MPa, respectively. According to the results from several graphical and statistical analyses, the proposed models can reliably be employed for prediction and representation of the volumetric properties of SC-CO_2 with AARDs below 1.3%. Comparisons have also been made with the modified Redlich-Kwong EOS as well as the standard reference multiparameter EOS developed by Span and Wagner, demonstrating the comparable accuracy of the proposed models, while offering notably simpler mathematical formulation.

Keywords: SC-CO_2, Peng-Robinson EOS, Volume Translation, Span-Wagner EOS, PVT

INTRODUCTION

Fluid solvents, especially in the supercritical region, have been of increasing interest in a diverse range of applications. They have been widely used as a reaction or processing media with easily varied density and dielectric permittivity, low viscosity, high solvent power, essentially nonexistent surface tension, and high diffusion coefficients [1]. Particularly, the high diffusivity, coupled with the very low viscosity of supercritical fluids (SCFs), induces interesting transport phenomena in condensed phases [2]. The interesting characteristics of SCFs have prompted their extensive use in various areas of application, including, but not limited to, extraction and purification processes (supercritical fluid extraction (SFE)) [3,4], supercritical fluid chromatography (SFC) [5], hydrolytic, hydrothermal and oxidative reactions in supercritical water (SCWO) [6,7], and phase transition processes, e.g., deposition of small-sized solid particles by rapid expansion of the supercritical solutions (RESS) [8,9]. Several exhaustive reviews of the broad applications of SCFs in various industrial, near-to-industry and also food, pharmaceutical and bioanalytical processes have already been published [2,10-15]. In this regard, accurate knowledge of the physicochemical properties of SCFs at high pressures and temperatures is essential for the development and optimization of most of these clean and low-energy chemical processes [1].

SCF solvents are considered as alternative green solvents, with the unique attribute that their densities can be varied continuously and substantially from gas-like to liquid-like values by simply varying the thermodynamic conditions, i.e., temperature and pressure. Interestingly, as many of the solvating properties of fluids are strongly dependent on their density, such large changes in density can have dramatic effects on solute reactivity [16]. For instance, while at low pressures, supercritical water supports hemolytic and free radical reactions, at higher pressures, heterolytic and ionic reactions are preferred [17,18]. As such, reliable knowledge and thermodynamic control of SCF solvent densities is of great importance for having ultimate control over the reaction outcome and selectively producing the desired products, as well as selective extraction of the compounds of interest, reducing to a minimum the co-extraction of undesired compounds [19].

In fact, several compounds have been considered as working fluids in SCFs processes: for example, hydrocarbons such as hexane, pentane and butane, nitrous oxide, sulfur hexafluoride and fluorinated hydrocarbons [20]. However, amongst the various SCFs used today, supercritical carbon dioxide (SC-CO_2) is considered to be the most popular and is used extensively as a green SFE solvent [15]. This is mainly because of the non-toxicity, non-flammability, high availability and relatively low cost of SC-CO_2. In addition, critical temperature and pressure of CO_2 allow supercritical operations at relatively low pressures and near-room temperatures. Moreover, there will be no associated waste treatment of a toxic solvent, and extraction times are also moderate [4].

As explained, because of the importance of accurate knowledge of volumetric properties of CO_2 and SC-CO_2, over the years investigations have been undertaken to develop suitable models, mainly in the form of various EOSs, for correlating the volumetric properties of this component over different temperature and pressure

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ranges. A short review of available models has been given by Heidaryan and Jarrahian [21].

Despite the major advances in the available computational power which have led to the development and utilization of more advanced EOSs based on statistical thermodynamics [22], nonetheless, cubic EOSs are still considered as the mathematical models of choice for the design of various industrial processes [23]. The ongoing success and wide utilization of cubic EOSs can mainly be attributed to the simplicity in evaluating the volume roots at given values of the independent variables, pressure, and temperature. As a matter of fact, quite simple and efficient analytical and/or numerical procedures are available for evaluation of the roots of a cubic equation [23,24]. Moreover, as the fundamental theorem of algebra stipulates, the number of volume roots in cubic EOSs is strictly limited to three, and also the number of changes of sign in their volume and temperature derivatives are limited; thus, their convergence characteristics in iterative calculations are more favorable to more complicated EOSs [25]. This quick evaluation of cubic EOSs makes them suitable for highly iterative calculations such as staged unit operations; thus, the use of cubic EOSs allows the efficient design of chemical process operations in the industry.

Although cubic EOSs have proven to be reliable tools for compositional and phase behavior calculations, they nonetheless exhibit deviations in the prediction of density values [26,27]. By employing three different approaches, our main aim here was to develop accurate models for the reliable description of the volumetric properties of SC-CO_2. Towards this end, use has been made of a comprehensive dataset of experimental PVT data of SC-CO_2, covering a broad temperature-pressure range, for modifying, arguably, one of the most successful cubic EOSs, i.e., Peng-Robinson EOS [28,29], so as to make this popular EOS more accurate in the supercritical region of CO_2.

THEORETICAL BACKGROUND

Since the development of the celebrated van der Waals EOS [30], which marked the advent of a new generation of mathematical models for the representation of the volumetric, thermal, and phase equilibrium properties of fluids, many different cubic EOSs have been developed. Amongst the plethora of cubic EOSs developed so far, the Peng-Robinson EOS has widely been used in both scientific investigations and industrial applications [31]. Furthermore, to overcome the aforementioned shortcomings of cubic EOSs in the prediction and correlation of density data, several approaches have been employed. The modifications proposed have generally followed three main routes [32]: (i) modification of the volume dependence of the repulsive and attractive terms, (ii) modifications made to the alpha function of the attractive term which reflects the attractive intermolecular forces in the fluid, and (iii) use of a third substance-dependent parameter. The first approach has given rise to the volume-translation concept, first introduced by Martin [33] and later developed further by Peneloux et al. [34]. In the Peneloux et al. formulation, the predicted molar volume of any type of EOS is treated as a pseudo-volume, which is subsequently shifted mathematically by a certain value, to allow better agreement with the experimental data, as:

$$\Delta v = v_{Exp.} - v_{EOS} \tag{1}$$

where $v_{Exp.}$ and v_{EOS} are the experimental and predicted molar volumes, respectively, and also Δv represents a systematic deviation. Note that the molar volume shift, Δv, used to be taken as a constant value alongside a single isotherm: T_r=0.7 [35]. However, in its more recent formulation, the molar volume shift is usually taken as a temperature and pressure dependent parameter, to allow for a better representation of the experimental data. Short literature reviews of the several investigations carried out so far to develop volume-translated cubic EOSs have been given by Nazarzadeh and Moshfeghian [26], Baled et al. [36], and Abudour et al. [37]. Also, in most prior volume translation methods, an attempt is only made to correlate the volume correction term to saturated liquid densities [36], and as of yet this procedure has not been applied to the supercritical region.

The approach of applying modifications to the alpha function of cubic EOSs has also been examined in several case studies. These modifications have mainly been proposed to improve correlations and predictions of vapor pressure and density of pure components and mixtures [38]. The various alpha functions proposed for cubic EOSs have been reviewed by Privat et al. [39], Haghtalab et al. [38], and Valderrama [32]. Heidaryan and Jarrahian [21] proposed a modification of the Redlich-Kwong EOS by developing a simple temperature- and pressure-dependent alpha function to improve the calculation of the density of CO_2 in the supercritical region.

1. Genetic Programming

Genetic programming or, as it sometimes is called, symbolic regression, was invented in its modern, tree-based form by Cramer in 1985 [40], and further developed by Koza in 1992 [41]. It is essentially a machine learning technique inspired by evolutionary biology in nature, which is mainly used to arrive at free-form natural laws from pure experimental data with next to nothing in the way of theoretical knowledge [42]. In short, symbolic regression is a type of regression analysis that searches the space of mathematical expressions to find a closed-form correlation that best fits a given dataset, in terms of both accuracy and simplicity. The procedure of genetic programming has extensively been used in various scientific disciplines; comprehensive reviews of which have recently been given by Gandomi et al. [43], and Langdon and Gustafson [44]. We employed genetic programming to develop the intended volume-translated and modified Peng-Robinson EOSs [45].

SC-CO_2 EOSs

1. Span-Wagner EOS

Empirical multiparameter EOSs are fundamental equations explicit in either pressure or, more frequently, the reduced Helmholtz energy. They are mainly used for the representation of the thermodynamic property data of pure substances. Modern multiparameter EOSs are usually formulated in terms of the inverse reduced temperature and the reduced density as [46-48]:

$$\alpha(\tau, \delta) = \frac{a(T, \rho)}{RT} = \alpha^0(\tau, \delta) + \alpha^r(\tau, \delta) \tag{2}$$

where α is the reduced Helmholtz energy, a is the specific Helmholtz energy, $\tau=T_c/T$ is the inverse reduced temperature and $\delta=\rho/\rho_c$ is the reduced density. As can be seen, the reduced Helmholtz energy is split into two contributions, $\alpha^0(\tau, \delta)$, which describes the behavior of a hypothetical ideal gas at given values of temperature and density, and a second contribution, $\alpha^r(\tau, \delta)$, describing the residual behavior of the real fluid. Having sufficiently accurate data for the isobaric heat capacity of the ideal gas, $c_p^0(T)$, obtainable from spectroscopic data, and constructing suitable equations for their representation, development of a correlation for the Helmholtz energy of the ideal gas, $\alpha^0(\tau, \delta)$, would be straightforward [46]. In this regard, the judicious choice of the functional form of the residual contribution, $\alpha^r(\tau, \delta)$, constitutes the main challenge in setting up accurate multiparameter EOSs.

Having determined the functional form of these two contributions, the pressure explicit form of the EOS can readily be derived using the identity resulting from the fundamental thermodynamic equations:

$$P(T, \rho)=-\left(\frac{\partial a}{\partial v}\right)_T \tag{3}$$

which leads to:

$$\frac{P(\tau, \delta)}{\rho RT}=1+\delta\left(\frac{\partial \alpha^r}{\partial \delta}\right)_\tau \tag{4}$$

The most frequently used EOS for CO_2 is currently the 42-term multiparameter EOS, published by Span and Wagner in 1996 [49]. The pressure explicit form of this standard reference EOS, which includes Gaussian bell shaped as well as non-analytical terms, to improve its performance near the critical region is as represented in Eq. (5):

$$\begin{aligned}\frac{P(\tau, \delta)}{\rho RT}=1+\delta\Bigg\{&\sum_{i=1}^{7} n_i d_i \delta^{d_i-1}+\sum_{i=8}^{34} n_i \delta^{d_i-1}\tau^{t_i}\exp(-\delta^{c_i})(d_i-c_i\delta^{c_i})\\&+\sum_{i=35}^{39} n_i \delta^{d_i} t^{t_i}\exp(-\alpha_i(\delta-\varepsilon_i)^2-\beta_i(\tau-\gamma_i)^2)\left[\frac{d_i}{\delta}-2\alpha_i(\delta-\varepsilon_i)\right]\\&+\sum_{i=40}^{42} n_i\left[\Delta^{b_i}(\Psi+\delta(-2C_i(\delta-1)\Psi))+\frac{\partial \Delta^{b_i}}{\partial \delta}\delta\Psi\right]\Bigg\}\end{aligned} \tag{5}$$

where:

$$\Delta=\theta^2+B_i[(\delta-1)^2]^{a_i} \tag{6}$$

$$\theta=(1-\tau)+A_i[(\delta-1)^2]^{\frac{1}{2\beta_i}} \tag{7}$$

$$\Psi=\exp(-C_i(\delta-1)^2-D_i(\tau-1)^2) \tag{8}$$

so it follows that:

$$\frac{\partial \Delta^{b_i}}{\partial \delta}=b_i\Delta^{b_i-1}(\delta-1)\left\{A_i\theta\frac{2}{\beta_i}\left[(\delta-1)^{\frac{1}{2\beta_i}-1}\right]+2\beta_i a_i[(\delta-1)^2]^{a_i-1}\right\} \tag{9}$$

Here n_i, d_i, t_i, c_i, α_i, β_i, γ_i, ε_i, a_i, b_i, A_i, B_i, C_i, D_i are the adjusted parameters of the EOS reported by Span and Wagner [49].

2. Modified Redlich-Kwong EOS

By modification of the alpha function of the attractive term of the Redlich-Kwong EOS, Heidaryan and Jarrahian [21] developed a simple cubic EOS for representation of the volumetric properties of SC-CO_2 as reproduced in Eq. (10):

$$P=\frac{RT}{V-b}-\frac{\beta a}{V(V+b)} \tag{10}$$

The energy and co-volume parameters of the EOS are as follows:

$$a=0.42748\frac{(RT_c)}{P_c} \tag{11}$$

$$b=0.08664\frac{RT_c}{P_c} \tag{12}$$

Here, β is a function of the reduced temperature and reduced pressure as represented in Eq. (13):

$$\beta=\frac{\beta_1+\beta_2 Ln(T_r)+\beta_3 Ln(P_r)}{1+\beta_4 Ln(T_r)+\beta_5 Ln(P_r)+\beta_6 Ln^2(P_r)} \tag{13}$$

where β_1-β_6 are the estimated parameters of the EOS reported by the authors [21].

MODEL DEVELOPMENT

In its pressure-explicit form, the Peng-Robinson EOS is represented as in Eqs. (14)-(19) [28,29]:

$$P=\frac{RT}{(v_{PR}-b)}-\frac{a_c\alpha}{(v_{PR}^2+2b\,v_{PR}-b^2)} \tag{14}$$

$$a_c=0.457235\frac{(RT_c)^2}{P_c} \tag{15}$$

$$b=0.077796\frac{RT_c}{P_c} \tag{16}$$

$$\alpha=[1+m(1-\sqrt{T_r})]^2 \tag{17}$$

$$m=\begin{cases}0.37464+1.54226\omega-0.26992\omega^2 & \omega\le 0.49\\ 0.379642+1.487503\omega+0.164423\omega^2+0.016666\omega^3 & \omega>0.49\end{cases} \tag{18}$$

$$\rho_{PR}=\frac{P\cdot MW}{RTZ};\ v_{PR}=\frac{1}{\rho_{PR}} \tag{19}$$

where P, T, R, ω, MW, ρ_{PR}, Z, v_{PR} denote pressure, temperature, universal gas constant, acentric factor, molecular weight, density calculated by Peng-Robinson EOS, compressibility factor and the molar volume calculated by Peng-Robinson EOS, respectively. Also, T_c, P_c, and T_r represent critical temperature, critical pressure, and reduced temperature, respectively. By introducing the dimensionless variables, $A=a_c\alpha P/(RT)^2$ and $B=bP/RT$, the compressibility factor, Z, can more conveniently be calculated from the Peng-Robinson EOS, written as in the form of Eq. (20):

$$Z^3+(B-1)Z^2+(-3B^2-2B+A)Z+(B^3+B^2-AB)=0 \tag{20}$$

Furthermore, development of reliable new models and also modification of current models for representing the volumetric properties of SC-CO_2 requires consideration of its experimental density data over extended temperature and pressure ranges. In this regard,

CO_2 density in the supercritical region has been extensively investigated for close to a century. The experimental studies have either been solely focused on density determination or have been concurrent with viscosity and/or thermal conductivity measurements. In this study, a comprehensive dataset comprising 5301 experimental SC-CO_2 PVT data has been aggregated, the details of which are

Table 1. Overview of the experimental SC-CO_2 density data used in this study

No.	Reference	N.D.	T_{min}-T_{max} (K)	P_{min}-P_{max} (MPa)	ρ_{min}-ρ_{max} (kg/m^3)	Year
1	Zolghadr et al. [50]	145	313.15-393.15	7.58-17.24	123.10-809.80	2013
2	Kodama et al. [51]	3	313.15-313.15	8.00-10.00	276.70-627.40	2013
3	Kato et al. [52]	3	313.15-313.15	8.00-10.00	276.70-627.40	2011
4	Gil et al. [53]	48	308.15-308.15	7.38-19.93	257.63-865.10	2010
5	Kodama et al. [54]	3	313.15-313.15	8.00-10.00	276.70-627.40	2010
6	Mantilla et al. [55]	41	310.00-450.00	9.99-159.84	131.64-1186.56	2010
7	Kodama et al. [56]	3	308.15-308.15	8.00-10.00	419.30-712.40	2008
8	Pensado et al. [57]	51	313.15-353.15	10.00-60.00	429.00-1019.70	2008
9	Suárez-Iglesias et al. [58]	15	313.16-333.16	15.00-35.00	607.10-936.10	2007
10	Liu and Kiran [59]	7	320.00-369.00	13.80-34.40	682.30-912.70	2007
11	Kato et al. [60]	3	313.15-313.15	8.00-10.00	276.70-627.40	2007
12	Pečar and Doleček [61]	20	308.15-333.15	10.00-40.00	296.10-971.70	2007
13	Pečar and Doleček [62]	20	308.15-333.15	10.00-40.00	296.62-971.73	2007
14	Kato et al. [63]	3	313.15-313.15	8.00-10.00	276.70-627.30	2006
15	Škerget et al. [64]	115	313.20-353.20	7.83-30.37	160.30-911.70	2005
16	Ferri et al. [65]	24	353.20-393.20	16.00-30.00	311.20-749.80	2004
17	Eggers and Jaeger [66]	4	313.15-353.15	15.00-30.00	439.00-909.00	2004
18	Garmroodi et al. [67]	40	308.00-348.00	12.20-35.50	327.00-955.00	2004
19	Zhang et al. [68]	12	308.15-308.15	7.49-9.99	279.50-723.50	2002
20	Klimeck et al. [69]	99	313.00-523.30	7.41-30.11	85.56-910.78	2001
21	Ihmels and Gmehling [70]	70	308.28-373.29	9.98-29.99	189.27-928.26	2001
22	Shi et al. [71]	10	308.15-308.15	7.49-10.04	272.00-723.00	2000
23	Kodama et al. [72]	13	308.15-313.15	7.56-9.92	240.10-710.00	1998
24	van der Gulik [73]	41	308.15-308.15	8.61-452.50	626.75-1385.29	1997
25	Lau et al. [74]	11	350.00-350.00	8.62-34.32	183.21-796.75	1997
26	Zhang and King [75]	12	323.15-343.15	34.47-68.60	824.20-1016.40	1997
27	Yaginuma et al. [76]	4	313.15-313.15	8.00-9.80	277.50-612.00	1997
28	Nowak et al. [77]	20	313.00-313.00	8.41-12.05	339.47-720.94	1997
29	Docter [78]	3	523.15-523.15	9.41-14.74	100.16-159.97	1997
30	Seitz and Blencoe [79]	6	673.15-673.15	19.94-99.93	155.96-583.25	1996
31	Özer et al. [80]	8	313.15-333.15	8.00-11.00	198.00-688.00	1996
32	Akgerman et al. [81]	42	308.00-328.00	9.64-24.88	400.00-900.00	1996
33	Kiran et al. [82]	50	323.00-423.00	15.46-62.78	628.10-994.20	1996
34	Liu et al. [83]	2	313.15-313.15	8.00-9.40	291.00-582.00	1996
35	Roy et al. [84]	9	313.00-343.00	10.80-24.50	283.60-879.50	1996
36	Kodama et al. [85]	3	313.15-313.15	8.03-9.89	279.90-619.00	1996
37	Pöhler and Kiran [86]	51	323.00-423.00	15.46-62.78	628.10-994.20	1996
38	Gokmenoglu et al. [87]	124	314.00-425.00	13.62-66.59	738.60-944.80	1996
39	Seitz et al. [88]	25	323.15-573.15	9.94-99.93	94.52-1081.20	1996
40	Knez et al. [89]	68	333.15-373.15	10.00-30.00	221.20-829.90	1995
41	Gonenc et al. [90]	38	313.00-323.00	7.60-11.65	202.00-688.00	1995
42	Duarte-Garza et al. [91]	11	350.00-350.00	8.62-34.32	183.22-796.76	1995
43	Fenghour et al. [92]	83	330.75-697.6	7.44-34.20	83.58-298.32	1995
44	Dixon et al. [93]	12	308.15-313.15	7.96-22.47	300.00-862.00	1993
45	Levelt Sengers et al. [94]	14	306.00-313.00	7.50-13.50	316.00-755.00	1993
46	Brachthäuser et al. [95]	18	360.00-523.30	8.01-30.11	85.56-716.70	1993
47	Wells et al. [96]	16	308.15-318.15	9.67-21.05	600.00-850.00	1992

Table 1. Continued

No.	Reference	N.D.	T_{min}-T_{max} (K)	P_{min}-P_{max} (MPa)	ρ_{min}-ρ_{max} (kg/m^3)	Year
48	Langenfeld et al. [97]	30	313.15-423.15	8.21-60.90	117.00-1021.00	1992
49	Gilgen et al. [98]	153	307.00-360.00	7.46-13.51	139.74-802.65	1992
50	Giles et al. [99]	5	313.15-348.15	8.36-12.50	180.00-742.00	1992
51	Tolley et al. [100]	5	308.15-313.15	7.50-12.50	262.00-783.00	1991
52	Duschek et al. [101]	80	305.00-340.00	7.40-9.00	162.26-718.85	1990
53	Ely et al. [102]	37	305.00-330.00	7.79-34.18	218.62-960.39	1989
54	Tan and Liou [103]	8	308.00-328.00	8.83-13.10	240.00-770.00	1988
55	Magee and Ely [104]	6	310.00-330.00	8.51-20.95	517.73-759.48	1988
56	Johns et al. [105]	33	381.07-473.38	7.40-30.60	93.06-552.90	1987
57	Holste et al. [106]	24	304.58-448.15	7.44-47.71	120.88-965.01	1987
58	Scott et al. [107]	50	314.65-348.35	7.41-24.56	150.84-861.40	1983
59	Kuskova et al. [108]	39	306.60-309.60	7.75-8.54	404.00-555.40	1983
60	Iwasaki [109]	74	308.15-323.15	7.42-14.48	195.82-685.76	1981
61	Haepp [110]	30	312.20-474.25	8.50-15.00	102.44-386.31	1976
62	Shmonov and Shmulovich [111]	60	681.35-980.65	100.00-800.00	404.89-1293.89	1974
63	Tsiklis et al. [112]	10	423.15-423.15	7.60-30.40	110.3-497.85	1974
64	Tsiklis et al. [113]	8	373.15-373.15	7.60-25.33	131.57-596.34	1974
65	le Neindre et al. [114]	397	304.35-960.85	7.60-127.80	42.00-1121.00	1973
66	Besserer and Robinson [115]	32	311.04-394.26	7.59-10.34	118.83-687.63	1973
67	Tsiklis et al. [116]	50	323.15-673.15	196.13-686.47	821.08-1418.76	1971
68	Vasserman et al. [117]	16	304.35-325.27	100.50-221.50	1106.00-1230.20	1970
69	Kirillin et al. [118]	23	328.46-473.15	7.57-57.83	169.14-938.10	1970
70	Kirillin et al. [119]	79	313.27-413.16	7.46-57.99	112.71-938.10	1970
71	Kirillin et al. [120]	15	433.15-473.15	11.90-57.83	169.14-691.25	1969
72	Golovskii and Tsymarnyi [121]	5	306.18-307.37	16.63-49.69	839.30-1011.60	1969
73	Kirillin et al. [122]	12	308.15-308.15	7.69-49.23	306.54-1003.81	1969
74	Vukalovich et al. [123]	15	306.15-308.15	7.47-30.02	297.08-928.85	1968
75	Ku and Dodge [124]	5	373.15-373.15	8.19-25.12	145.84-592.48	1967
76	Sass et al. [125]	24	348.15-398.15	7.60-50.65	117.78-880.05	1967
77	Jůza et al. [126]	82	323.15-748.15	70.00-400.00	742.34-1152.34	1965
78	Kestin et al. [127]	56	305.25-323.36	7.54-11.89	246.10-575.50	1964
79	Vukalovich et al. [128]	79	313.15-423.15	7.46-59.00	104.43-924.64	1963
80	Guildner [129]	19	304.46-348.41	7.53-30.40	398.00-840.00	1962
81	Vukalovich et al. [130]	151	473.15-1023.2	7.46-59.01	47.58-640.04	1962
82	Vukalovich and Altunin [131]	102	348.41-773.15	7.55-31.72	52.36-452.16	1959
83	Kennedy [132]	1843	313.15-1273.15	7.50-140.00	30.70-1159.50	1954
84	Reamer et al. [133]	105	310.93-510.93	8.62-68.96	93.61-1051.91	1944
85	Michels et al. [134]	116	305.23-423.29	8.58-315.83	405.80-1172.30	1935
Overall:		5301	304.35-1273.15	7.38-800.00	30.70-1418.76	

reported in Table 1. This table includes the temperature, pressure, and density range, alongside the reference and the number of data points of each set.

Moreover, to depict the distribution of the experimental density data points, Fig. 1 illustrates the temperature and pressure range over which the data are spread out. As can be seen, the experimental data points have a good temperature and pressure distribution; however, more experimental investigations should be undertaken for pressures over 140 MPa.

Using the experimental PVT data reported in Table 1 and by following the procedures detailed in section 2, three models have been developed in the current study based on the Peng-Robinson EOS, for accurate representation of the volumetric properties of SC-CO_2. Note that the aggregated dataset was randomly split, so as to make use of 70% of the experimental PVT data for the development of the proposed models, and using the rest of the data for testing them. Moreover, in each of the three procedures followed, at first, the values of the unknown parameters in each model were determined for every point in the development dataset by minimizing an objective function based on the average absolute relative deviation of the density values. Subsequently, employing the *Nutonian Eureqa* [45], a recent symbolic regression software solu-

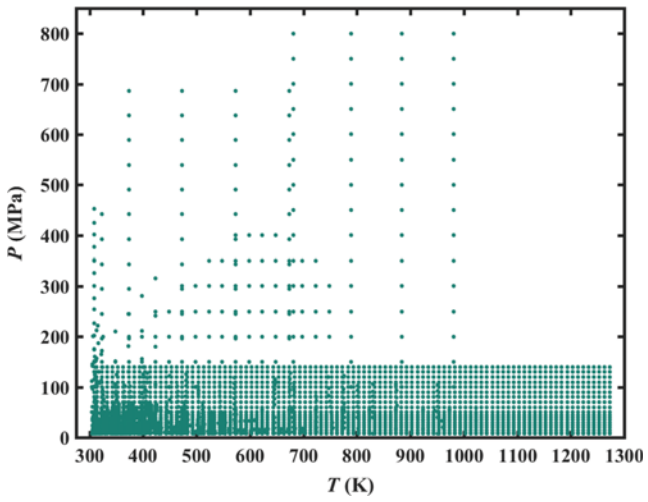

Fig. 1. Distribution of the experimental SC-CO_2 density data.

tion based on a novel principle for the identification of nontriviality [42], the final temperature and pressure dependences of the models' parameters were determined. Note that unlike traditional regression methods that are used to estimate the parameters of a mathematical model of a given form, symbolic regression seeks to determine both the form of the mathematical model and also its parameters simultaneously. In other words, the resulting free-form mathematical expressions are comprised of algebraic operators, analytical functions and state variables, alongside constants and integers. As such, the reported estimated parameters of the proposed models have been determined by the genetic programming procedure itself, rather than by using any local or global optimization algorithm.

1. Model I

Following the Peneloux et al. formulation, the volume-translation term, Δv, applicable to the original Peng-Robinson EOS is presented as follows in Eqs. (21), (22):

$$v_{Corr.} = v_{PR} + \Delta v \tag{21}$$

$$\Delta v\left(\frac{cm^3}{mol}\right) = A_1 + A_2(Ln(P_r))^{\left\{A_3 - Ln(P_r)\text{-}A_4\frac{Ln(T_r)}{Ln(P_r)}\right\}} - A_5 Ln(T_r) \tag{22}$$

where A_1=3.1145, A_2=−5.3025, A_3=−0.4542, A_4=−2.4932, A_5=0.8832. Here, $v_{Corr.}$ denotes the corrected molar volume; also, T_r and P_r represent the reduced temperature and pressure with respect to the critical values of T_c=304.1548 K and P_c=7.3814455 MPa, respectively [135].

2. Model II

After multiple symbolic regression analyses, a new improved alpha function of the attractive term of the Peng-Robinson EOS has been developed as presented in Eq. (23):

$$\alpha = B_1 + Ln(P_r)\times(B_2 + B_3\, Ln(T_r) - B_4\times Ln^2(T_r) - B_5\sin(B_6\, Ln^2(P_r))) - B_7\sin(Ln(T_r)) \tag{23}$$

where B_1=1.0010, B_2=0.0524, B_3=0.2315, B_4=0.1286, B_5=0.3258, B_6=0.0704, B_7=0.9461. It is obvious that in Models I and II, the dimensionless form of the EOS, i.e. Eq. (20), remains unchanged.

3. Model III

By introduction of a third translation parameter into the EOS and after simple arithmetic manipulations, the modified Peng-Robinson equation of state becomes as presented in Eq. (24):

$$P = \frac{RT}{(\nu + c - b)} - \frac{a_c\alpha}{(\nu + c)(\nu + c + b) + b(\nu + c - b)} \tag{24}$$

where

$$c\left(\frac{cm^3}{mol}\right) = C_1 Ln^{\beta}(P_r) - C_2 \tag{25}$$

$$\beta = (Ln(T_r))^{\left(C_3\frac{Ln(P_r)}{Ln(T_r)} - C_4\right)} - \sqrt{Ln(P_r)} \tag{26}$$

and C_1=6.36×10^{-6}, C_2=4.27×10^{-6}, C_3=0.22409133, C_4=0.77860565. Other parameters, a_c and b, are similarly defined as in the original Peng-Robinson EOS as shown in Eqs. (15), (16). Furthermore, the dimensionless form of the EOS, which facilitates finding its roots, is presented in Eqs. (27)-(30):

$$Z^3 + PZ^2 + QZ + S = 0 \tag{27}$$

$$P = B - 1 + 3C \tag{28}$$

$$Q = -3B^2 + 3C^2 + 2BC - 2B - 2C + A \tag{29}$$

$$S = B^3 + C^3 + B^2 - C^2 + BC^2 - 3CB^2 - 2BC + CA - AB \tag{30}$$

Here, $A = a_c\alpha P/(RT)^2$, B=bP/RT and C=cP/RT.

RESULTS AND DISCUSSION

To determine the relative performance and accuracy of the models proposed in this study, we made several graphical and statistical analyses. In doing so, comparisons have also been made with the modified Redlich-Kwong EOS, developed specifically for SC-CO_2 by Heidaryan and Jarrahian [21] and also the standard reference multiparameter EOS developed by Span and Wagner [49]. Moreover, as Heidaryan and Jarrahian have already demonstrated that their proposed EOS exhibits a much superior performance, in representing the volumetric properties of SC-CO_2 relative to several other EOSs, namely Redlich-Kwong EOS [136], SRK EOS [137] and van der Waals EOS [30], no attempt is made here to make similar comparisons.

Fig. 2 presents a graphical illustration of a comparison between the experimental SC-CO_2 density data and the calculated values by Peng-Robinson EOS, modified Redlich-Kwong EOS, Span-Wagner EOS and the new models developed in this study. Also, to have a quantitative estimation of the relative accuracy of the different models studied in this work, also included in the subplots of this figure are the coefficients of determination of lines fitted to the experimental versus calculated data. It is obvious that the closeness of these lines to the diagonal red line is a reliable measure of the accuracy of the studied EOSs. In Fig. 2, the three models developed in this study demonstrate appreciable improvements relative to the previous EOSs. Also, amongst the various models studied, it is clear that the model developed in the current work by modifying the alpha function of the attractive term of the Peng-Robinson EOS is particularly promising; especially, as it is accurate not only

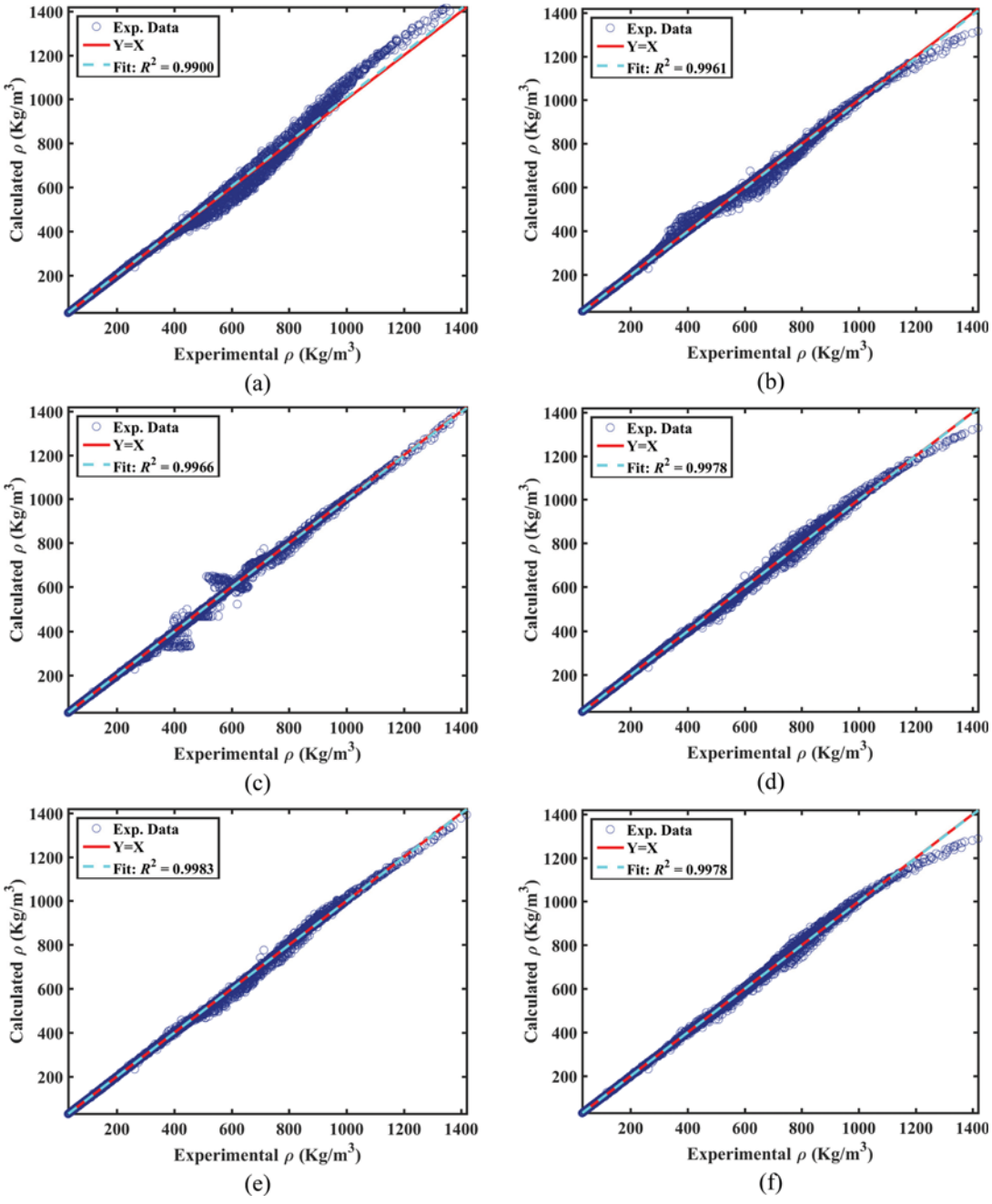

Fig. 2. Scatterplot of calculated versus experimental density data for the training dataset; (a) Peng-Robinson EOS [29], (b) modified Redlich-Kwong EOS [21], (c) Span-Wagner EOS [49], (d) Model I, (e): Model II, (f) Model III.

at low-density values but unlike other EOSs, also remains reliable at even very high densities.

Conclusions about the relative performance of the different models studied can also be drawn from the statistical criteria reported in Table 2 [138,139]. Included in this table are the values associated with the statistical parameters of average absolute relative deviation (AARD), average relative deviation (ARD), maximum absolute percentage error (MAPE), mean of absolute of residuals (MAR) and R^2 coefficient of determination, as shown in Eqs. (31)-(35), respectively, to check the closeness of the predicted values from different EOSs studied to the experimental SC-CO_2 density data.

$$\mathrm{AARD}(\%)=\frac{100}{\mathrm{N.D.}}\sum_{i=1}^{\mathrm{N.D.}}\left|\frac{\rho_i^{\mathrm{Exp.}}-\rho_i^{\mathrm{Calc.}}}{\rho_i^{\mathrm{Exp.}}}\right| \tag{31}$$

$$\mathrm{ARD}(\%)=\frac{100}{\mathrm{N.D.}}\sum_{i=1}^{\mathrm{N.D.}}\left(\frac{\rho_i^{\mathrm{Exp.}}-\rho_i^{\mathrm{Calc.}}}{\rho_i^{\mathrm{Exp.}}}\right) \tag{32}$$

$$\mathrm{MAPE}(\%)=\max\left\{\left|\frac{\rho_i^{\mathrm{Exp.}}-\rho_i^{\mathrm{Calc.}}}{\rho_i^{\mathrm{Exp.}}}\right|\right\}\times 100 \tag{33}$$

$$\mathrm{MAR}=\frac{1}{\mathrm{N.D.}}\sum_{i=1}^{\mathrm{N.D.}}\left|\rho_i^{\mathrm{Exp.}}-\rho_i^{\mathrm{Calc.}}\right| \tag{34}$$

Table 2. Statistical analysis of the performance of various EOSs studied on the training dataset

Model	AARD (%)	ARD (%)	MAPE (%)	MAR (kg/m^3)	R^2
Peng-Robinson [29]	2.929	−0.586	15.702	19.414	0.989
Modified RK [21]	1.788	0.282	22.776	9.613	0.996
Span-Wagner [49]	1.344	−0.849	36.025	6.708	0.997
Model I	1.327	−0.163	11.515	8.095	0.998
Model II	1.100	−0.194	10.882	6.509	0.998
Model III	1.136	−0.114	11.210	7.488	0.998

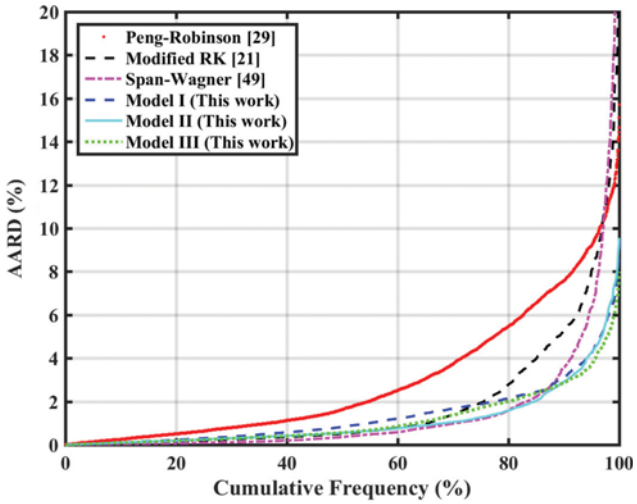

Fig. 3. Cumulative frequency plot of the AARD (%) deviations of the various EOSs in representing the experimental density data of SC-CO_2.

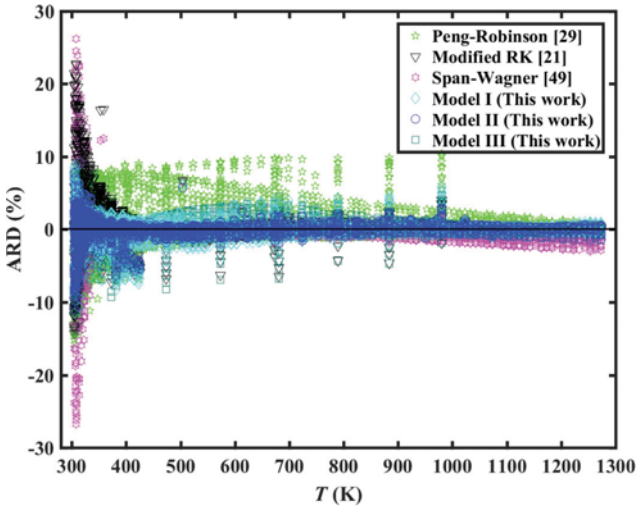

Fig. 4. Average relative deviation of the EOSs as a function of temperature for the training dataset.

$$R^2 = 1 - \frac{\sum_{i=1}^{N.D.} (\rho_i^{Exp.} - \rho_i^{Calc.})^2}{\sum_{i=1}^{N.D.} (\rho_i^{Exp.} - \text{average}(\rho^{Exp.}))^2} \quad (35)$$

As can be seen from the statistical parameters listed in Table 2, the models developed in this study present significant improvements over the original Peng-Robinson EOS, exhibiting more than a twofold increase in accuracy.

Moreover, a descriptive illustration of the relative performance of the various models studied could be obtained by plotting the cumulative frequency of the EOSs as a function of the average absolute relative deviation (AARD (%)) of each data point, as depicted in Fig. 3. This figure is especially useful for determining what percentile of the calculated data have an arbitrary maximum AARD deviation. For instance, it can be inferred from Fig. 3 that the proposed models in this study can accurately represent 80% of the data with AARDs of less than two percent. In addition, it is clear in Fig. 3 that the closer the plot of a certain model is to the down right side of the axis, the lower its overall deviation would be for a larger portion of the data.

Furthermore, to analyze the performance of the EOSs studied, we plotted their average relative deviations, as in Eq. (20), in calculating the SC-CO_2 density data as a function of temperature and pressure in Figs. 4 and 5, respectively. As can be seen, the deviations tend to decrease at higher temperatures, and to a lesser extent, pressures. Altogether, the proposed models are quite satisfactory

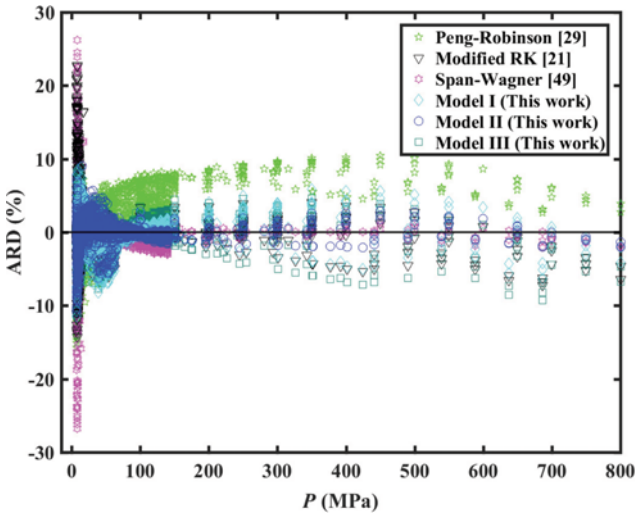

Fig. 5. Average relative deviation of the EOSs as a function of pressure for the training dataset.

for a large portion of the supercritical region of CO_2.

In addition, a plot of the residual errors of the six models studied, i.e. the difference between the experimental density data, and the calculated values from the EOSs, is illustrated in Fig. 6. As can be seen, the deviation of the equations of state studied generally increases at higher density values. Nonetheless, as stated earlier, the

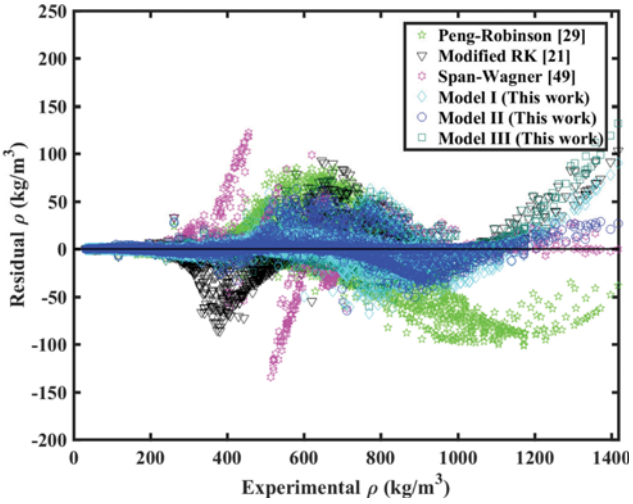

Fig. 6. Residual error of the various EOSs as a function of density for the training dataset.

model proposed in this work, by modification of the alpha function of the Peng-Robinson EOS, i.e. Model II, could reliably be employed even at high-density values.

Furthermore, to validate the developed models, it is imperative to test them on data not used in their development phase and/or optimizing their estimated coefficients. In fulfilling this requirement, use has been made of 1590 experimental SC-CO_2 data points not used in the development stage of the proposed models. A comparative study based on these data and the aforementioned statistical parameters is reported in Table 3.

As can be seen from the results of the statistical analyses tabulated in Table 3, all the three models developed in this study demonstrate a very satisfactory predictive performance on the test dataset, in comparison to the original Peng-Robinson EOS. In this regard, model II is especially promising, exhibiting close to a three-time increase in predictive capacity of SC-CO_2 density over the Peng-Robinson EOS.

The fact should also be noted that while being on par with the standard reference Span-Wagner EOS in terms of predictive performance, the proposed models offer notably simpler mathematical formulations, which in turn allows for significantly shorter evaluation times and notably simpler numerical algorithms. Even in cases where the usage of multiparameter EOSs is intended, as the highly nonlinear formulation of these EOSs necessitates the availability of suitable initial guesses [46], such close first estimates can readily be obtained using the models developed in this work.

Furthermore, considering the varying uncertainty of the reported experimental PVT data in the literature, it would be interesting to have a more detailed comparison of the performance of the different models studied for each dataset. With this objective in mind, the AARD deviations as well as the coefficients of determination of the EOSs studied, for each of the eighty-five data sources listed in Table 1, alongside their experimental uncertainties are reported in Table 4. As can be seen, the predicted values of models developed in the current work are generally in agreement with the experimental data to within their uncertainties.

CONCLUSIONS

The significance of accurate knowledge of the thermophysical data of SC-CO_2, including its volumetric properties, calls for the development of reliable predictive and correlative models. Motivated by the simplicity afforded by cubic EOSs and their widespread utilization, in this study three well-established approaches have been followed to develop three different simple models based on the venerated Peng-Robinson EOS, for precise representation of the volumetric properties of SC-CO_2. Using a comprehensive database, consisting of 5301 experimental PVT data of SC-CO_2, covering a broad temperature-pressure region, three different modifications are proposed to the Peng-Robinson EOS, which appreciably improves its performance in the supercritical region of CO_2. Subsequently, the three models proposed here based on the volume-translation concept, modification of the alpha function of the attractive term of the Peng-Robinson EOS and the addition of a third parameter to the EOS itself, and also the modified Redlich-Kwong EOS, standard reference Span-Wagner EOS and the original Peng-Robinson EOS have been compared based on several graphical and statistical analyses. As can be concluded from the results obtained, the simplicity of the cubic EOSs, coupled with the high accuracy of the developed models, makes them very reliable candidates for representation of the volumetric properties of SC-CO_2. Notably, the new proposed alpha function for the Peng-Robinson EOS exhibits a very satisfactory predictive performance, confirmed by comparisons made with 1590 SC-CO_2 experimental PVT data points. On the other hand, a large portion of the industrial applications of SC-CO_2 involve using it in heterogeneous mixtures, especially in widespread supercritical fluid extraction procedures. Moreover, the calculation of many of the derived properties of pure components and also their fugacity coefficients, used for establishing their diffusional equilibrium in multiphase heterogeneous mixtures, relies

Table 3. Statistical analysis of the predictive performance of the various EOSs studied based on a comparison with the test dataset

Model	AARD (%)	ARD (%)	MAPE (%)	MAR (kg/m^3)	R^2
Peng-Robinson [29]	2.985	−0.614	15.519	19.755	0.988
Modified RK [21]	1.939	0.338	25.413	10.279	0.995
Span-Wagner [49]	1.499	−0.969	35.313	7.261	0.996
Model I	1.364	−0.153	9.508	8.256	0.998
Model II	1.133	−0.211	11.324	6.626	0.998
Model III	1.198	−0.121	9.599	7.795	0.998

Table 4. Uncertainties alongside the AARD (%) deviations and R^2 values of the experimental datasets listed in Table 1

No.	Uncertainty (kg/m^3)	Peng-Robinson [29]		Modified RK [21]		Span-Wagner [49]		Model I		Model II		Model III	
		AARD (%)	R^2	AARD (%)	R^2	AARD (%)	R^2	AARD (%)	R^2	AARD (%)	R^2	AARD (%)	R^2
1	±1.400	6.768	0.913	4.513	0.971	3.729	0.979	2.059	0.995	2.775	0.985	0.081	1.000
2	±0.100	2.605	0.987	3.099	0.992	1.336	0.998	1.587	0.997	1.127	0.999	1.320	0.998
3	-	6.768	0.913	4.513	0.971	3.729	0.979	2.059	0.995	2.775	0.985	0.081	1.000
4	-	6.141	0.922	6.368	0.932	3.736	0.970	3.539	0.968	3.437	0.976	2.980	0.976
5	-	6.768	0.913	4.513	0.971	3.729	0.979	2.059	0.995	2.775	0.985	0.081	1.000
6	±0.100%	4.373	0.970	0.618	0.999	0.126	1.000	1.020	0.999	0.636	0.999	0.867	0.999
7	-	7.679	0.816	10.473	0.784	9.782	0.808	1.557	0.982	4.026	0.949	2.415	0.982
8	±0.200%	3.534	0.933	0.756	0.995	0.236	0.998	0.799	0.995	1.705	0.983	0.943	0.994
9	-	2.533	0.923	0.885	0.986	0.238	0.999	1.263	0.976	1.993	0.953	1.355	0.975
10	-	4.446	0.688	3.153	0.846	2.183	0.915	3.258	0.838	3.000	0.883	3.228	0.844
11	-	6.768	0.913	4.513	0.971	3.729	0.979	2.059	0.995	2.775	0.985	0.081	1.000
12	±0.300	3.865	0.962	2.211	0.985	0.789	0.997	1.866	0.988	2.394	0.984	1.953	0.989
13	±0.050	3.879	0.962	2.201	0.985	0.794	0.997	1.864	0.988	2.404	0.984	1.968	0.989
14	-	6.712	0.914	4.566	0.970	3.671	0.980	2.000	0.996	2.716	0.985	0.033	1.000
15	-	3.340	0.983	2.213	0.993	0.702	0.998	1.715	0.995	1.381	0.995	1.604	0.995
16	±7.498	4.701	0.949	0.824	0.998	1.344	0.996	2.940	0.978	1.277	0.996	3.074	0.978
17	-	3.272	0.985	1.199	0.997	1.136	0.997	2.870	0.982	2.222	0.989	3.066	0.982
18	-	2.749	0.974	1.416	0.991	0.637	0.996	1.647	0.986	1.705	0.986	1.665	0.986
19	-	7.219	0.868	8.289	0.893	6.725	0.947	3.315	0.977	4.020	0.952	2.538	0.990
20	±0.030	3.011	0.989	1.860	0.996	0.502	0.999	1.331	0.998	0.955	0.998	1.095	0.998
21	±0.200	3.044	0.987	1.803	0.995	0.469	0.999	1.677	0.996	1.163	0.996	1.519	0.996
22	-	8.348	0.849	7.930	0.878	8.526	0.849	2.753	0.987	5.421	0.945	1.971	0.994
23	-	6.090	0.913	7.787	0.913	4.841	0.961	2.128	0.992	3.337	0.976	1.304	0.996
24	-	5.728	0.921	3.102	0.971	0.572	0.998	2.708	0.977	2.196	0.989	3.268	0.960
25	±0.100%	2.790	0.991	2.249	0.996	0.204	1.000	1.419	0.998	0.485	1.000	1.311	0.998
26	-	3.879	0.415	0.250	0.998	0.067	1.000	0.235	0.997	1.619	0.916	0.379	0.993
27	-	7.863	0.860	3.912	0.973	4.311	0.948	2.686	0.987	3.437	0.972	0.674	0.999
28	±0.072	6.992	0.846	7.676	0.881	7.881	0.823	2.112	0.987	2.708	0.975	1.199	0.996
29	-	0.343	0.999	0.197	1.000	0.204	1.000	0.475	0.999	1.048	0.997	0.474	0.999
30	±1.000	1.137	0.998	0.156	1.000	0.126	1.000	0.331	1.000	0.365	1.000	0.604	0.999
31	-	7.783	0.911	4.282	0.979	5.561	0.978	3.945	0.981	5.134	0.972	4.001	0.988
32	-	4.886	0.925	3.521	0.957	1.408	0.985	2.439	0.972	2.020	0.984	2.097	0.977
33	±1.200%	2.998	0.931	2.939	0.943	2.729	0.952	3.527	0.918	2.077	0.964	3.169	0.935
34	-	7.749	0.862	3.553	0.980	8.526	0.919	4.775	0.964	5.258	0.954	4.545	0.981
35	-	3.201	0.979	3.019	0.988	0.908	0.996	1.512	0.995	1.560	0.994	1.289	0.995
36	-	7.078	0.900	4.005	0.977	4.042	0.977	2.416	0.993	3.081	0.982	0.308	1.000
37	-	3.002	0.930	2.977	0.941	2.761	0.950	3.568	0.915	2.124	0.962	3.195	0.933
38	-	3.139	0.708	3.039	0.753	2.879	0.784	3.737	0.642	3.112	0.735	3.473	0.696
39	±1.000	2.573	0.990	0.815	0.999	0.148	1.000	0.829	1.000	0.631	0.999	0.673	1.000
40	-	3.733	0.975	2.089	0.989	0.626	0.996	1.670	0.993	0.880	0.996	1.649	0.993
41	-	4.902	0.943	5.365	0.966	5.410	0.961	1.267	0.997	1.957	0.991	1.242	0.998
42	-	2.791	0.991	2.248	0.996	0.205	1.000	1.419	0.998	0.485	1.000	1.313	0.998
43	±0.300	0.698	0.999	0.499	0.998	0.058	1.000	0.478	1.000	0.678	1.000	0.227	1.000
44	-	5.017	0.961	6.762	0.960	9.445	0.870	2.890	0.986	2.619	0.988	2.025	0.991
45	±1.000%	7.851	0.849	7.329	0.889	4.679	0.960	2.841	0.982	4.095	0.956	1.722	0.992
46	±0.152	2.445	0.993	1.793	0.997	0.011	1.000	1.184	0.998	0.398	1.000	1.087	0.998
47	-	5.705	0.622	4.037	0.796	1.522	0.957	3.217	0.844	2.143	0.940	2.719	0.883
48	-	2.672	0.992	1.985	0.998	1.595	0.999	1.775	0.998	2.125	0.997	1.629	0.998

Table 4. Continued

No.	Uncertainty (kg/m^3)	Peng-Robinson [29]		Modified RK [21]		Span-Wagner [49]		Model I		Model II		Model III	
		AARD (%)	R^2	AARD (%)	R^2	AARD (%)	R^2	AARD (%)	R^2	AARD (%)	R^2	AARD (%)	R^2
49	±0.120	4.749	0.966	4.676	0.978	2.684	0.988	2.262	0.992	1.650	0.995	1.272	0.995
50	-	5.235	0.958	3.862	0.979	1.648	0.999	1.537	0.997	2.930	0.989	1.976	0.998
51	±1.000	8.751	0.908	8.295	0.933	3.111	0.993	4.851	0.979	4.976	0.978	4.386	0.985
52	±0.215	5.891	0.924	8.086	0.908	7.100	0.902	2.658	0.984	3.578	0.971	1.447	0.995
53	±1.921	4.481	0.973	5.312	0.975	3.547	0.985	2.088	0.993	1.923	0.994	1.380	0.996
54	-	5.632	0.962	5.744	0.933	5.965	0.934	6.849	0.948	4.445	0.981	5.811	0.968
55	±0.760	6.576	0.885	2.766	0.968	3.811	0.938	2.747	0.971	1.857	0.989	1.931	0.983
56	-	1.434	0.996	0.674	0.999	0.068	1.000	0.718	0.999	0.383	1.000	0.498	0.999
57	-	3.573	0.986	5.534	0.980	3.438	0.992	1.497	0.998	2.585	0.994	1.380	0.998
58	-	4.709	0.970	3.983	0.986	3.212	0.979	1.861	0.996	1.799	0.994	1.229	0.998
59	-	7.386	0.225	7.617	0.289	17.617	-7.096	2.956	0.840	3.369	0.810	2.097	0.940
60	±0.074	6.427	0.887	6.814	0.898	7.244	0.846	2.181	0.989	2.924	0.975	1.645	0.994
61	-	0.786	0.998	1.513	0.968	0.683	0.989	0.532	1.000	0.430	1.000	0.377	1.000
62	-	7.170	0.895	2.421	0.983	0.760	0.998	2.861	0.983	1.336	0.996	2.955	0.979
63	-	1.896	0.995	0.849	1.000	0.547	1.000	1.366	0.998	0.703	1.000	1.044	0.999
64	-	3.303	0.987	1.118	0.999	0.779	0.999	1.787	0.995	0.700	0.999	1.842	0.995
65	-	2.073	0.993	0.762	0.999	0.421	1.000	0.853	0.999	0.678	1.000	0.691	0.999
66	±0.690	3.245	0.975	2.249	0.984	1.214	0.993	1.500	0.998	1.306	0.993	0.704	0.999
67	-	6.175	0.730	3.059	0.883	0.743	0.993	2.337	0.935	0.908	0.990	3.867	0.820
68	-	7.489	-3.022	0.886	0.913	0.105	0.998	0.821	0.933	0.635	0.957	1.742	0.721
69	±0.200	2.185	0.993	1.225	0.998	0.537	0.998	1.081	0.999	0.563	0.999	0.543	1.000
70	-	3.011	0.990	2.222	0.995	0.893	0.997	1.378	0.998	0.776	0.999	1.082	0.999
71	±0.690	1.324	0.998	0.397	1.000	0.045	1.000	1.095	0.998	0.242	1.000	0.390	1.000
72	±1.517	3.105	0.697	0.882	0.963	0.052	1.000	2.233	0.832	2.901	0.790	2.564	0.823
73	-	5.478	0.968	4.162	0.983	4.959	0.973	2.557	0.991	3.175	0.988	2.079	0.994
74	-	6.067	0.943	6.811	0.947	3.579	0.988	3.830	0.975	3.764	0.976	3.490	0.983
75	±0.180	2.142	0.993	1.503	0.998	0.149	1.000	1.299	0.998	0.325	1.000	0.851	0.998
76	±0.440	2.089	0.996	1.268	0.999	0.168	1.000	1.291	0.999	0.471	1.000	0.877	0.999
77	±3.500	7.918	0.447	0.780	0.993	0.292	0.999	2.035	0.956	0.627	0.994	1.883	0.963
78	-	7.111	0.772	5.830	0.872	8.552	0.404	3.240	0.942	2.547	0.958	2.183	0.971
79	-	2.254	0.995	1.695	0.997	0.492	0.999	1.461	0.999	0.648	1.000	0.949	0.999
80	-	8.159	0.829	7.479	0.850	6.659	0.885	3.741	0.960	3.965	0.940	2.855	0.974
81	-	0.518	1.000	0.430	1.000	0.075	1.000	0.596	1.000	0.611	1.000	0.269	1.000
82	-	0.599	0.999	0.389	0.998	0.132	1.000	0.489	1.000	0.503	1.000	0.269	1.000
83	±2.300	1.672	0.994	0.378	1.000	0.662	1.000	0.554	1.000	0.430	1.000	0.603	0.999
84	±3.200	2.080	0.994	0.925	0.999	0.304	1.000	1.189	0.999	0.711	0.999	0.863	0.999
85	-	4.455	0.959	1.733	0.995	1.332	0.995	1.474	0.996	1.049	0.997	1.176	0.997

upon the accurate representation of their PVT data. Hence, improving the accuracy of the representation of the PVT data of SC-CO_2, coupled with utilizing appropriate mixing and combining rules, has the potential to improve the predictions of the stable multiphase equilibrium systems of interest.

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