

New Correlations for Predicting the Density and Viscosity of Supercritical Carbon Dioxide Under Conditions Expected in Carbon Capture and Sequestration Operations

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Abstract: Two new simple and explicit correlations have been proposed in the present paper to calculate the density and the viscosity of carbon dioxide under operational conditions anticipated for a carbon capture and sequestration (CCS) project – pressure = 1100 – 9000 psia (7 – 62 MPa) and temperature = 40 – 100 °C. The new correlations can predict carbon dioxide density and viscosity well matched to the high accuracy carbon dioxide property data available through the National Institute of Standards and Technology (NIST) web database [1]. Substantial improvement over existing correlations has also been achieved with the new correlations.

Keywords: Carbon dioxide, density, viscosity, correlation, supercritical condition, carbon capture and sequestration

1. INTRODUCTION

As one of the most popular materials used in supercritical technologies, carbon dioxide has been used in different industries including foods, beverages, pharmaceutical, energy, etc (Heidaryan *et al* [2]). More recently, CCS (Carbon Capture and Sequestration, also known as Carbon Capture and Storage) has achieved increasing popularity all over the world for mitigating the contribution of fossil fuel emissions to global warming (a.k.a. climate change). The CCS process involves capturing carbon dioxide from fossil fuel power plants, natural gas production, ambient air, and so on, and injecting it into deep geological formations. Major CCS projects with cost up to dozens of billions US dollars have been built or planned in many countries from Asia Pacific (Australia, China), to Europe (Netherlands, Norway, United Kingdom, Germany, Italy, Poland), and North America (United States, Canada). The concept of CCS process is illustrated in Fig. (1) which shows the schematics for both terrestrial and geological sequestration of carbon dioxide emissions from a coal-fired plant.

In order to appropriately design and optimally operate a CCS project, the accurate representation of carbon dioxide properties – both physical and thermal – is a must. In addition to solubility, thermal conductivity, enthalpy, entropy, Joule-Thomson coefficient, and others, density and viscosity are two critical parameters required for accurately predicting wellbore and pipeline hydraulics and well injectivity for CCS projects.

Carbon dioxide density can be calculated through a black oil model, an equation of state (EoS), or empirical correlations. Most black oil models have been developed for oil and natural gas where carbon dioxide component is

typically less than 3 percent except for sour gas where the carbon dioxide composition can reach as high as 10 – 20 percent; therefore, they may result in substantial errors when applied to pure carbon dioxide, which is also true for equations of state (EoSs). The primary EoS that have been applied to carbon dioxide includes Peng-Robinson [4], Soave-Redlich-Kwong (a.k.a. SRK) [5, 6], and Span & Wagner [7]. Span & Wagner EoS was specifically developed for carbon dioxide and has been considered as the top choice of equation of state for predicting the property of pure or high concentration carbon dioxide. Unfortunately, the Span & Wagner EoS has not been implemented in most of the commercial software packages that are routinely used for assessing the carbon dioxide flow dynamics in pipelines and wellbores. Furthermore, it could be over-complicated (i.e., computational “overkill” per Hassanzadeh *et al* [8]) and/or time-consuming to use an EoS to calculate the carbon dioxide density and viscosity under certain circumstances where accurate empirical correlations are preferred. A few correlations like Bahadori *et al* [9] have been proposed for carbon dioxide density. Unfortunately, it has been found that these correlations may not be very accurate in terms of predicting the carbon dioxide density under supercritical conditions, especially under the conditions to be anticipated for carbon capture and sequestration (CCS) applications.

Similar story exists for carbon dioxide viscosity. The viscosity can either be calculated through equation of state (EoS), or EoS based models such as Guo *et al* [10] and Fan *et al* [11], or empirical correlations including Lucas [12], Chung *et al* [13], Fenghour *et al* [14], Zabaloy *et al* [15], Bahadori & Vuthaluru [16], and Heidaryan *et al* [2]. On one hand, EoS or EoS based models require extensive and complex numerical computations and may not be a good choice for majority of engineering applications. On the other hand, some empirical correlations need density and/or other thermodynamic parameters in order to calculate the carbon dioxide viscosity. Moreover, prediction of carbon dioxide viscosity via these approaches may not be sufficiently

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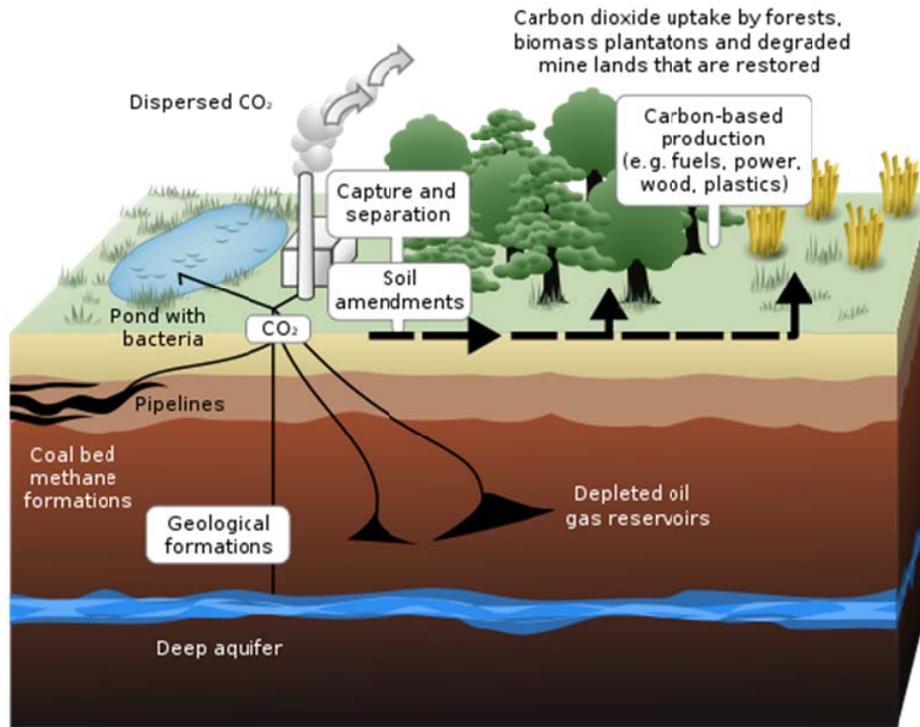


Fig. (1). Schematic showing both terrestrial and geological sequestration of carbon dioxide emissions from a coal-fired plant. Rendering by LeJean Hardin and Jamie Payne [3].

accurate when applied to pure carbon dioxide at supercritical conditions.

In the present paper, simple but accurate explicit correlations have been developed for predicting the density and viscosity of pure carbon dioxide under supercritical conditions expected in majority of carbon capture and sequestration (CCS) applications. The new correlations lead to carbon dioxide density and viscosity perfectly matched to the high accuracy carbon dioxide property data provided by the National Institute of Standards and Technology (NIST) [1].

2. METHODOLOGY

As mentioned above, the National Institute of Standards and Technology (NIST) [1] provides a high quality and high accuracy web database for carbon dioxide property. The web database is primarily based on the Span & Wagner equation of state (EoS) [7] and a number of auxiliary models such as Fenghour *et al* [14], Ely *et al* [17], Vesovic *et al* [18], etc, for physical and thermal properties and has been considered as the standard for the carbon dioxide property.

Through the NIST database, carbon dioxide properties have been generated under pressure and temperature ranges expected for CCS operations. The data was then applied to develop two simple and explicit correlations for carbon dioxide density and viscosity via a least square approach. Specifically, the correlation formulae and the associated correlation coefficients have been adjusted such that the following criteria are met:

$$\sum (\rho_{\text{pre}} - \rho_{\text{NIST}})^2 = \sum [\rho_{\text{pre}}(p, T) - \rho_{\text{NIST}}]^2 = \text{minimum} \quad (1)$$

$$\sum (\mu_{\text{pre}} - \mu_{\text{NIST}})^2 = \sum [\mu_{\text{pre}}(p, T) - \mu_{\text{NIST}}]^2 = \text{minimum} \quad (2)$$

where ρ represents carbon dioxide density in kg/m^3 , and μ represents carbon dioxide viscosity in centipoises or cp. Subscript pre refers to data calculated by the proposed correlations, whereas subscript NIST refers to data generated from the NIST web database.

3. NEW CORRELATIONS FOR CARBON DIOXIDE

Two new correlations have been proposed in the present paper, one for carbon dioxide density and the other for carbon dioxide viscosity. Details are to be provided next in this section.

3.1. New Density Correlation

The new density correlation is given below as a function of pressure in psia:

$$\rho = A_0 + A_1 p + A_2 p^2 + A_3 p^3 + A_4 p^4 \quad (3)$$

where density (ρ) is in kg/m^3 , pressure (p) in psia, and the correlation coefficients $A_0, A_1 - A_4$ are solely associated with temperature in Celsius:

$$A_i = b_{i0} + b_{i1} T + b_{i2} T^2 + b_{i3} T^3 + b_{i4} T^4 \quad (i = 0, 1, 2, 3, 4) \quad (4)$$

The values for the correlation coefficients – $b_{i0}, b_{i1}, b_{i2}, b_{i3},$ and b_{i4} ($i = 0, 1, 2, 3, 4$) – are listed in Table 1a for pressure less than 3000 psia (20.68 MPa) and in Table 1b for pressure higher than 3000 psia.

Fig. (2) shows the variation of the carbon dioxide density with pressure (1100 – 9000 psia) and temperature (40 – 100 °C) anticipated under the majority of carbon capture and sequestration (CCS) operations. It can be clearly seen that at a particular temperature, carbon dioxide density increases with pressure. The higher the pressure, the higher the carbon

Table 1a. Value of b_{ij} Coefficients in Eq. 4 for Pressure < 3000 Psia

	b_{i0}	b_{i1}	b_{i2}	b_{i3}	b_{i4}
$i = 0$	-2.148322085348E+05	1.168116599408E+04	-2.302236659392E+02	1.967428940167E+00	-6.184842764145E-03
$i = 1$	4.757146002428E+02	-2.619250287624E+01	5.215134206837E-01	-4.494511089838E-03	1.423058795982E-05
$i = 2$	-3.713900186613E-01	2.072488876536E-02	-4.169082831078E-04	3.622975674137E-06	-1.155050860329E-08
$i = 3$	1.228907393482E-04	-6.930063746226E-06	1.406317206628E-07	-1.230995287169E-09	3.948417428040E-12
$i = 4$	-1.466408011784E-08	8.338008651366E-10	-1.704242447194E-11	1.500878861807E-13	-4.838826574173E-16

Table 1b. Value of b_{ij} Coefficients in Eq. 4 for Pressure > 3000 Psia

	b_{i0}	b_{i1}	b_{i2}	b_{i3}	b_{i4}
$i = 0$	6.897382693936E+02	2.730479206931E+00	-2.254102364542E-02	-4.651196146917E-03	3.439702234956E-05
$i = 1$	2.213692462613E-01	-6.547268255814E-03	5.982258882656E-05	2.274997412526E-06	-1.888361337660E-08
$i = 2$	-5.118724890479E-05	2.019697017603E-06	-2.311332097185E-08	-4.079557404679E-10	3.893599641874E-12
$i = 3$	5.517971126745E-09	-2.415814703211E-10	3.121603486524E-12	3.171271084870E-14	-3.560785550401E-16
$i = 4$	-2.184152941323E-13	1.010703706059E-14	-1.406620681883E-16	-8.957731136447E-19	1.215810469539E-20

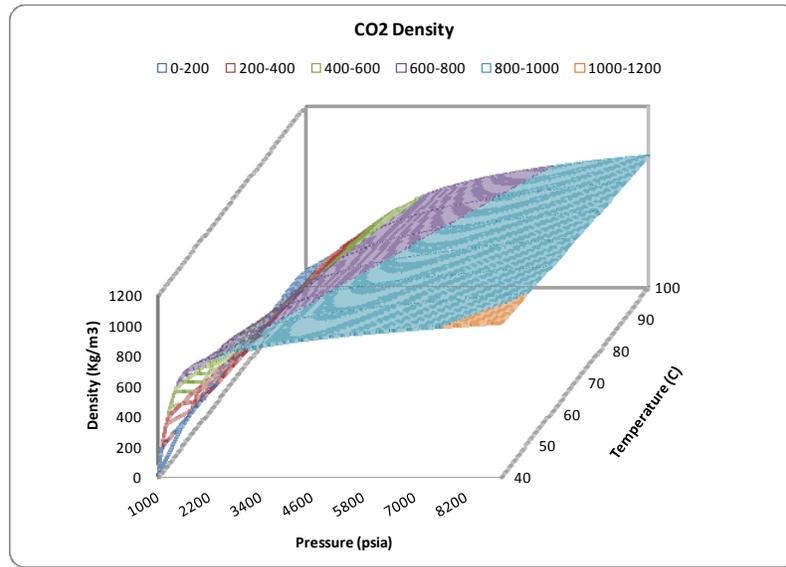


Fig. (2). Prediction of carbon dioxide density by Eq. 3 for pressure = 1100 – 9000 psia and temperature = 40 – 100 °C.

dioxide density. And the lower the pressure, the lower the carbon dioxide density would be.

3.2. New Viscosity Correlation

The new correlation for carbon dioxide viscosity takes a similar form to Eq. 3:

$$\mu = C_0 + C_1p + C_2p^2 + C_3p^3 + C_4p^4 \tag{5}$$

where the carbon dioxide viscosity (μ) is in centipoises, pressure (p) in psia, and correlation coefficients C_0 , C_1 , C_2 , C_3 and C_4 can be calculated by the following equation:

$$C_i = d_{i0} + d_{i1}T + d_{i2}T^2 + d_{i3}T^3 + d_{i4}T^4 \quad (i = 0, 1, 2, 3, 4) \tag{6}$$

The temperature (T) in Eq. 6 should be in Celsius.

The values for the correlation coefficients – d_{ij} ($i = 0, 1, 2, 3, 4; j = 0, 1, 2, 3, 4$) – required in Eq. 6 are listed in Table 2a for pressure less than 3000 psia and Table 2b for pressure larger than 3000 psia, respectively.

The carbon dioxide viscosity as predicted by the new correlation (Eq. 5) is displayed in Fig. (3), again for pressure and temperature ranges expected for carbon capture and sequestration (CCS) operations. Generally speaking, carbon dioxide viscosity increases with pressure at a specific temperature, whereas it slightly decreases with temperature for a fixed pressure. Note that under the pressure and

Table 2a. Value of d_{ij} Coefficients in Eq. 6 for Pressure < 3000 Psia

	d_{i0}	d_{i1}	d_{i2}	d_{i3}	d_{i4}
$i = 0$	-1.958098980443E+01	1.123243298270E+00	-2.320378874100E-02	2.067060943050E-04	-6.740205984528E-07
$i = 1$	4.187280585109E-02	-2.425666731623E-03	5.051177210444E-05	-4.527585394282E-07	1.483580144144E-09
$i = 2$	-3.164424775231E-05	1.853493293079E-06	-3.892243662924E-08	3.511599795831E-10	-1.156613338683E-12
$i = 3$	1.018084854204E-08	-6.013995738056E-10	1.271924622771E-11	-1.154170663233E-13	3.819260251596E-16
$i = 4$	-1.185834697489E-12	7.052301533772E-14	-1.500321307714E-15	1.368104294236E-17	-4.545472651918E-20

Table 2b. Value of d_{ij} Coefficients in Eq. 6 for Pressure > 3000 Psia

	d_{i0}	d_{i1}	d_{i2}	d_{i3}	d_{i4}
$i = 0$	1.856798626054E-02	3.083186834281E-03	-1.004022090988E-04	8.331453343531E-07	-1.824126204417E-09
$i = 1$	6.519276827948E-05	-3.174897980949E-06	7.524167185714E-08	-6.141534284471E-10	1.463896995503E-12
$i = 2$	-1.310632653461E-08	7.702474418324E-10	-1.830098887313E-11	1.530419648245E-13	-3.852361658746E-16
$i = 3$	1.335772487425E-12	-8.113168443709E-14	1.921794651400E-15	-1.632868926659E-17	4.257160059035E-20
$i = 4$	-5.047795395464E-17	3.115707980951E-18	-7.370406590957E-20	6.333570782917E-22	-1.691344581198E-24

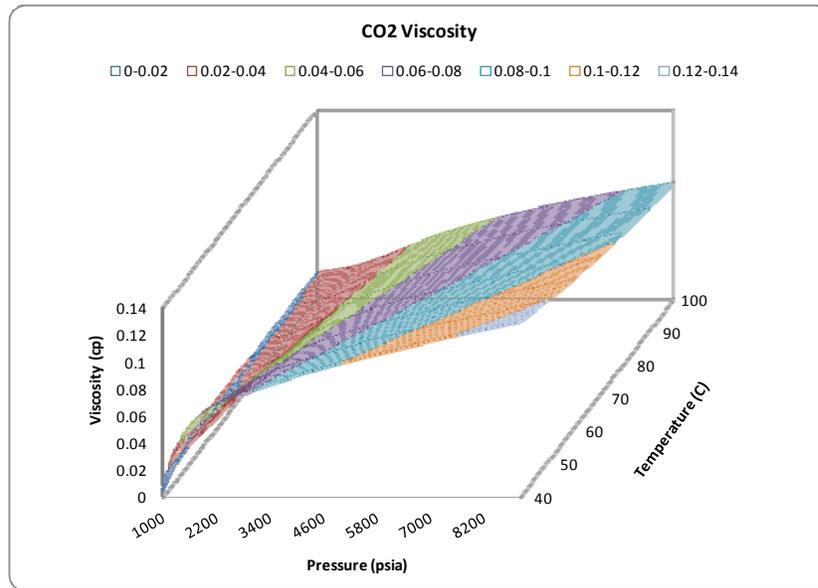


Fig. (3). Prediction of carbon dioxide viscosity by Eq. 5 for pressure = 1100 – 9000 psia and temperature = 40 – 100 °C.

temperature ranges investigated, the carbon dioxide viscosity is always lower than those of water under similar pressure and temperature conditions.

4. RESULTS AND DISCUSSIONS

The new correlations proposed in the present paper (Eq. 3 and Eq. 5) have been applied to calculate the carbon dioxide density and viscosity for pressure and temperature expected under the carbon capture and sequestration operations. Comparison has been performed with data from the NIST web database [1] and those as predicted by the

most recent and updated carbon dioxide density and viscosity correlations, i.e., the Bahadori *et al* [9] correlation for carbon dioxide density and the Heidaryan *et al* [2] correlation for carbon dioxide viscosity.

4.1. Carbon Dioxide Density

Fig. (4a-4g) show the carbon dioxide density as a function of pressure at different temperature ranging from 40 °C to 100 °C. In addition to the density data predicted by the new correlation (Eq. 3), the carbon dioxide density data based on the NIST web database [1] and those calculated by

Table 3. Carbon Dioxide Density Prediction Errors for Existing and New Correlations

Temp (C)	Average Relative Error (ARE)		Average Absolute Relative Error (AARE)	
	<i>Bahadori et al [9]</i>	<i>New (Eq. 3)</i>	<i>Bahadori et al [9]</i>	<i>New (Eq. 3)</i>
40	-1.73%	-0.04%	3.66%	0.21%
50	-0.14%	0.07%	4.35%	0.48%
60	1.13%	0.03%	4.14%	0.19%
70	2.11%	-0.02%	3.87%	0.15%
80	2.92%	-0.01%	4.12%	0.13%
90	3.67%	0.03%	4.66%	0.15%
100	4.41%	0.00%	5.25%	0.07%

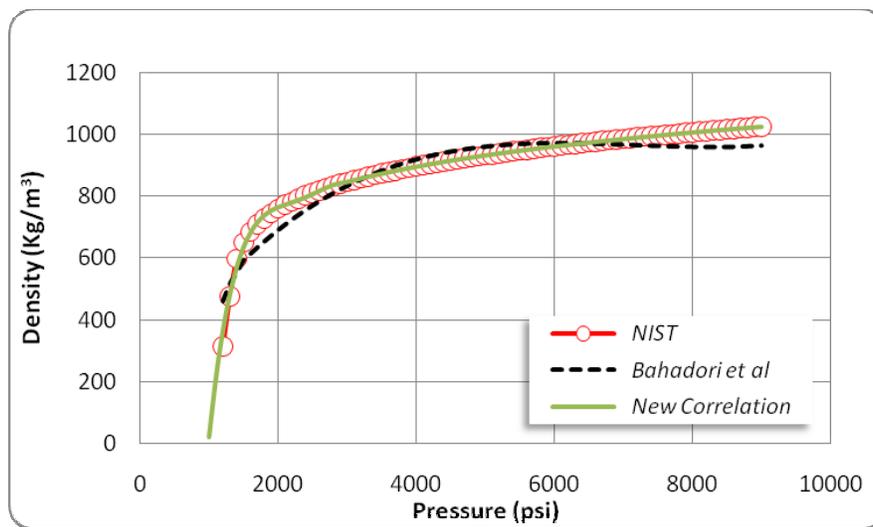


Fig. (4a). Carbon dioxide density changes with pressure at 40°C.

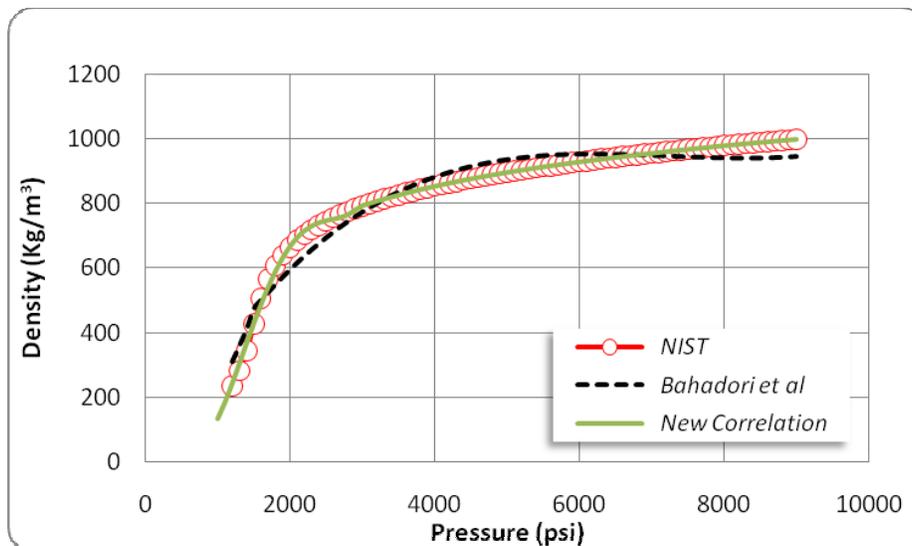


Fig. (4b). Carbon dioxide density changes with pressure at 50°C.

the Bahadori *et al* [9] correlation are also shown in the figures for comparison purpose.

It can be clearly found that a perfect match to the NIST data is present for the new correlation for all the temperatures investigated. Over the entire pressure range

studied, the new correlation prediction follows the NIST data extremely well. In contrast, even though the Bahadori *et al* [9] correlation does perform a very decent job in predicting the carbon dioxide density for the pressure and temperature ranges, non-trivial over-prediction and/or under-prediction are observed. For example, at 40 °C, the Bahadori *et al* [9] correlation under-predicts the carbon dioxide density for pressure < 3000 psia and pressure > 7000 psia, while it over-predicts density for pressure between 3000 and 7000 psia (Fig. 4a). At higher temperature such as 90 °C or 100 °C, the Bahadori *et al* [9] correlation over-predicts carbon dioxide density for pressure higher than 4000 psia (Figs. 4f and 4g).

Table 3 lists the carbon dioxide density prediction errors for the existing correlation (Bahadori *et al* [9]) and the new correlation (Eq. 3). Both the average relative error (ARE) and the average absolute relative error (AARE) are evaluated. The AREs for the new correlation are within -0.1% and +0.1% for all the temperature studied, and the AAREs are less than 0.25% for all the temperatures except 50 °C where the AARE is less than 0.5%. The AREs for the Bahadori *et al* [9] correlation ranges from -1.73% to 4.41%, whereas the AAREs are higher than 3.66% for all the temperatures and reach at 5.25% for 100 °C. Apparently, the new correlation demonstrates the substantial improvement over the existing correlation (Bahadori *et al* [9]) in predicting the carbon dioxide density.

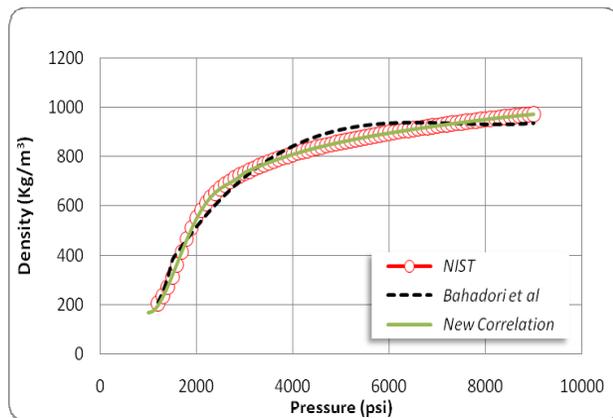


Fig. (4c). Carbon dioxide density changes with pressure at 60°C.

4.2. Carbon Dioxide Viscosity

Carbon dioxide viscosity has also been calculated by using the new correlation (Eq. 5) and the results are displayed in Fig. (5a-5g) for temperatures ranging from 40 °C to 100 °C. The prediction by the Heidaryan *et al* [2] correlation and the corresponding results from the NIST web database are also plotted in the figures. There is no doubt that the predicted carbon dioxide viscosity by the Heidaryan *et al* [2] correlation matches to the NIST data for all the pressure and temperature investigated. Nevertheless, the new correlation further improves the prediction as clearly demonstrated by the (Fig. 5a-5g) and the AREs and AAREs listed in Table 4. The AAREs for the Heidaryan *et al* [2] correlation are around 2.7% for all the temperatures studied, but the new correlation cut the AAREs further down by

around 10+ folds for all the temperatures except for 50 °C where the AARE has been reduced by about 6 times – from 2.63% to 0.41% (Table 4).

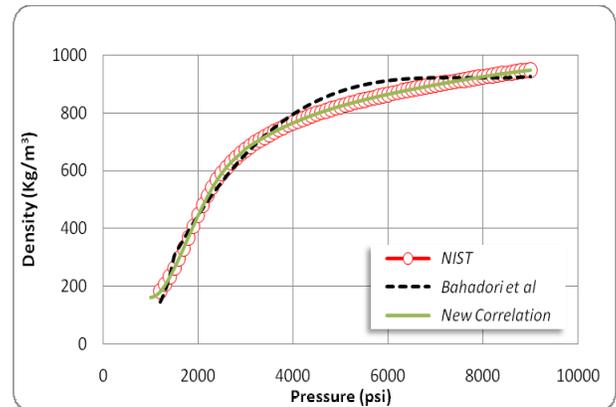


Fig. (4d). Carbon dioxide density changes with pressure at 70°C.

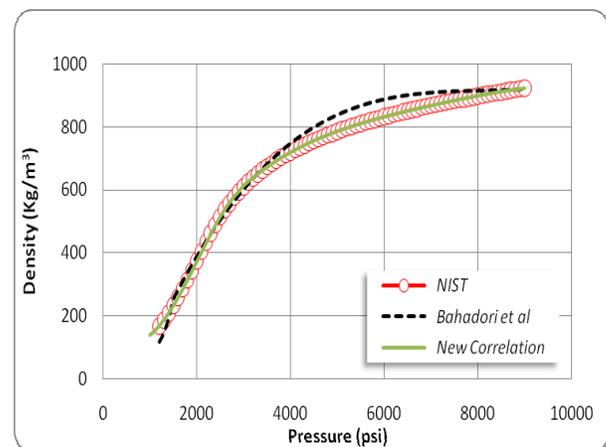


Fig. (4e). Carbon dioxide density changes with pressure at 80°C.

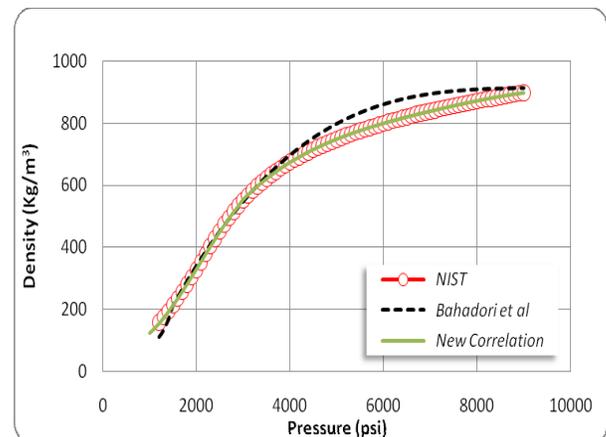


Fig. (4f). Carbon dioxide density changes with pressure at 90°C.

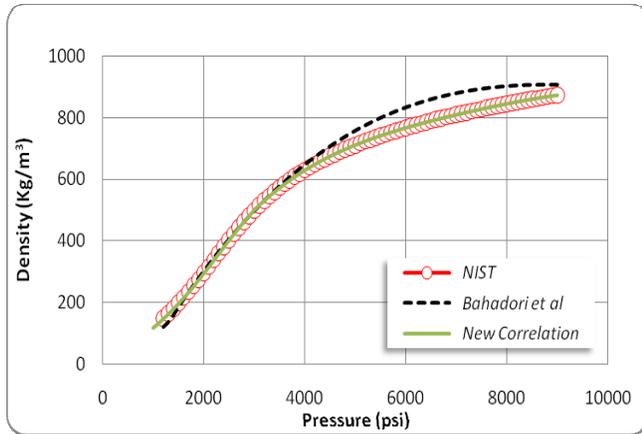


Fig. (4g). Carbon dioxide density changes with pressure at 100°C.

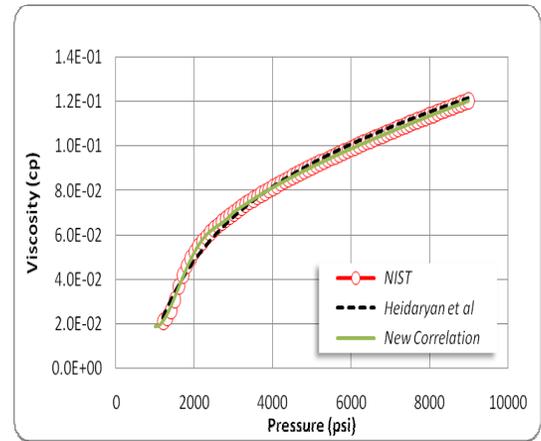


Fig. (5b). Comparison of carbon dioxide viscosity at 50°C as predicted by existing and new correlations.

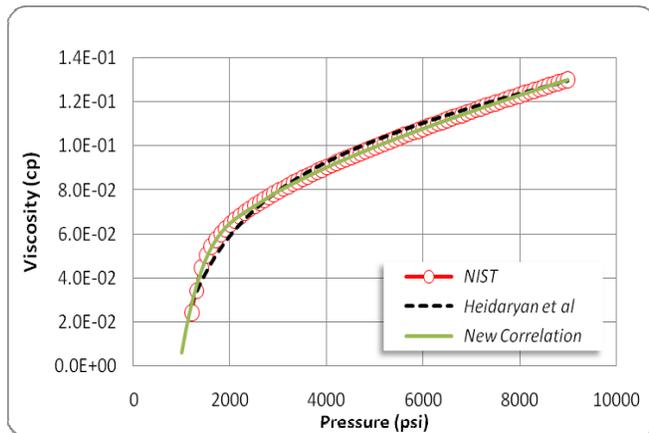


Fig. (5a). Comparison of carbon dioxide viscosity at 40°C as predicted by existing and new correlations.

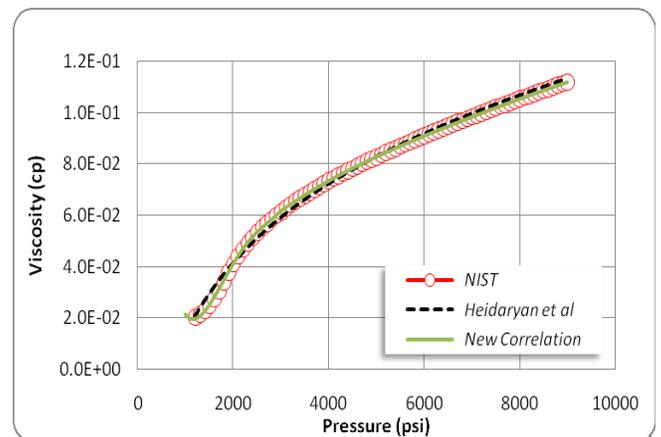


Fig. (5c). Comparison of carbon dioxide viscosity at 60°C as predicted by existing and new correlations.

Table 4. Carbon dioxide viscosity prediction errors for existing and new correlations

Temp (C)	Average Relative Error (ARE)		Average Absolute Relative Error (AARE)	
	Heidaryan et al [2]	New (Eq. 5)	Heidaryan et al [2]	New (Eq. 5)
40	-0.47%	-0.01%	2.71%	0.26%
50	0.57%	0.06%	2.63%	0.41%
60	1.10%	0.00%	2.67%	0.20%
70	1.29%	-0.01%	2.69%	0.15%
80	1.28%	0.00%	2.71%	0.13%
90	1.19%	0.01%	2.78%	0.12%
100	1.07%	0.00%	2.84%	0.03%

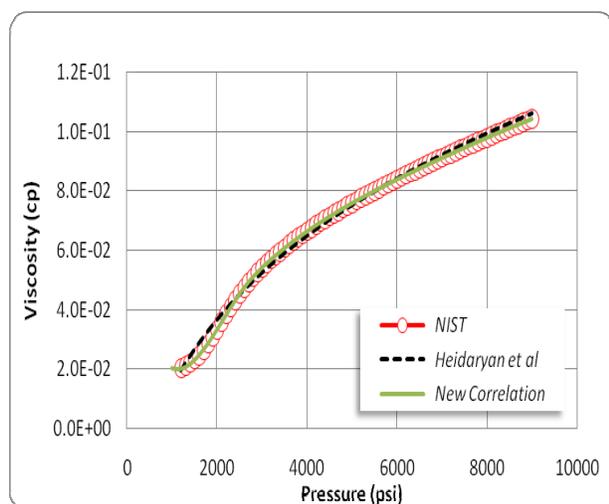


Fig. (5d). Comparison of carbon dioxide viscosity at 70°C as predicted by existing and new correlations.

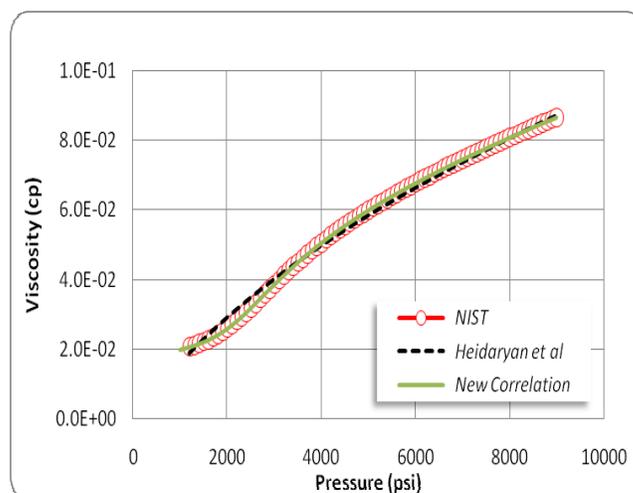


Fig. (5g). Comparison of carbon dioxide viscosity at 100°C as predicted by existing and new correlations.

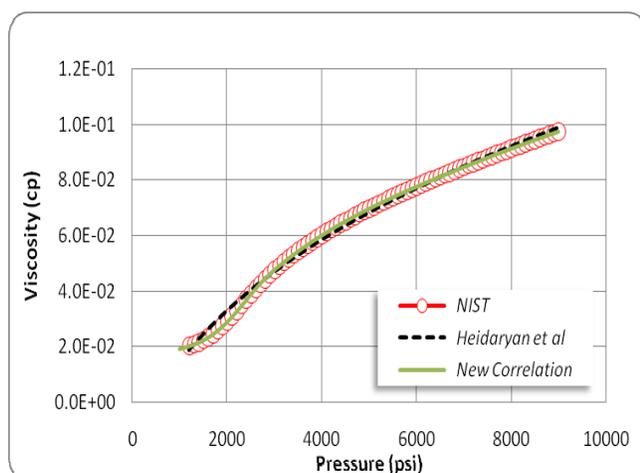


Fig. (5e). Comparison of carbon dioxide viscosity at 80°C as predicted by existing and new correlations.

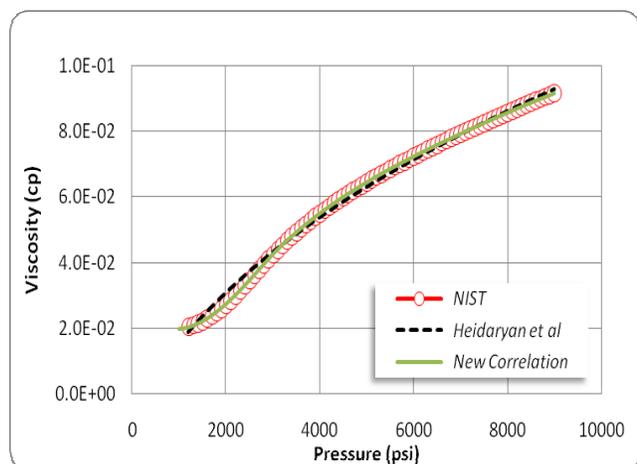


Fig. (5f). Comparison of carbon dioxide viscosity at 90°C as predicted by existing and new correlations.

5. SUMMARY

New simple yet accurate correlations have been developed for predicting both the carbon dioxide density and viscosity under carbon capture and sequestration (CCS) operating conditions. The correlations have predicted carbon density and viscosity well matched to those available in the NIST web database [1] and shown substantial improvements over existing correlations.

Note that the correlations have been specifically developed based on the assumption that they are to be applied at pressure and temperature conditions expected in a CCS process; therefore, caution should be exercised for circumstances where the correlations are to be used for pressure and temperature sitting beyond the designed ranges.

CONFLICT OF INTEREST

None Declared.

ACKNOWLEDGMENT

None Declared.

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