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Modelling CO_2 –Water Thermodynamics Using SPUNG Equation of State (EoS) concept with Various Reference Fluids

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Abstract

Due to the continuous increase of CO_2 emission to environment, the Carbon Capture and Storage (CCS) processes gained a very high importance in the last decades. One common CO_2 impurity during various CCS processes is water. Therefore, the calculation of CO–water thermodynamic properties is a vital issue. This work preliminary investigates the accuracy of the extended corresponding states equation of state SPUNG using various reference fluids for the density and vapour liquid equilibrium (VLE) calculations of the CO_2 - water system. The evaluation is done by comparing the numerical prediction with experimental data. The study is conducted at different mixture concentrations, and covering a broad range of conditions. The study is conducted using N_2, O_2, C1, C2, C3, and C4 as reference fluids. The results show an impact on density prediction. On the other hand, the VLE calculations exhibited very low sensitivity to varying reference fluids.

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Keywords: Coressponding States, Extended Corresponding States, Reference Equation of State, MBWR, CCS, VLE

Nomenclature

Symbols

C	Arbitrary variable [-]
N	Total number of points
P	Pressure [Pa]

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T	Temperature [K]
V	Volume [m^3]
x	Mole fraction [-]
Z	Compressibility factor [-]
θ	Shape factor [-]
φ	Shape factor [-]
ω	Acentric factor [-]

Subscripts/Superscripts

c	Critical state
exp	Experimental
i	Component i
R	Reduced variable
r	Point index
Ref	Reference fluid co-ordinate
s	Simulation

1. Introduction

One important aspect for the analysis and simulations of Carbon Capture and Storage (CCS) processes is the modeling of the thermodynamic properties for pure CO_2 and CO_2 mixtures. Indeed, the choice of model may have a great impact on efficiency, economy and safety. One such model is the SPUNG EoS. It is an extended corresponding state model that uses one reference fluid to calculate the behavior for mixtures of interest. The SPUNG EoS is a consistent approach that was developed for hydrocarbons systems and it showed a good compromise in accuracy and computational efficiency [1]. A later work [2] showed the same results for non-polar binary and ternary CO_2-rich mixtures. In an on-going research, this approach also shows a superiority in density predictions of the CO_2-water system at low pressures compared to the cubic equation Soave-Redlich-Kwong (SRK) [3], and SRK with Huron Vidal mixing rules (SRK-HV) [4]. The value of the error using the standard SPUNG equation was still high compared to experimental data, reaching above 20% at extreme conditions. Furthermore, the work by Ibrahim et al. [5] showed that the VLE predictions of SPUNG and SRK were poor. The standard SPUNG model, used in the previous studies, uses propane (C3) as the reference fluid. Therefore, this work will preliminarily investigate the impact of using various reference fluids on the predictions of CO_2–water thermodynamics. The aim was to get guidance or criterions of how to select the reference fluid and what are the limitations and constraints in order to improve the density and VLE prediction using the SPUNG EoS or similar concepts.

Here, an evaluation is done by comparing the behavior of the SPUNG EoS using alternative reference fluids like N_2, methane (C1), and ethane (C2). The first investigations suggested the use of heavier hydrocarbons. Therefore, the normal-butane (NC4) was implemented for comparisons as well.

2. Theory

2.1. Equations of state

An EoS is a model that calculates for both the liquid and gas phases using the same expression, which enhances the continuity near the critical point. An EoS for a mixture with a given number of components is an expression for pressure as a function of the mole fraction x_i, the temperature T, and the volume V;

$$P = P(x_i, T, V) \qquad (1)$$

Given this expression, it can be manipulated to calculate the fugacity of each component. In the following subsection, a brief description of the EoS used in the work will be given together with references for further reading.

There is a variety of EoS that have different structure complexity. One of the simplest structure set of EoS is the cubic EoS, examples are SRK[2], SRK-HV[3], and Peng—Robinson (PR) [6]. A more complicated structure is the set of multi-parameter approaches like GERG [7] and Span—Wagner [8] EoS. The Extended Corresponding States (ECS) is also one of the advanced modelling concepts and will be discussed in the following subsection as the base theory for the SPUNG EoS investigated. The most sophisticated concept is the SAFT approach [9].

2.2. The corresponding states principle

The principle of corresponding states assumes that all substances exhibit the same behavior at reduced states, (V/V_c and T/T_c). A corresponding states EoS typically has one or more reference components described very accurately by a reference EoS. Therefore, the compressibility of the investigated fluids or mixtures can be evaluated as

$$Z = Z(V_{\mathrm{Ref}}, T_{\mathrm{Ref}}, \omega, \dots.)_{\mathrm{Ref}} \qquad (2)$$

In the corresponding states approach the reference fluid V_{Ref} and T_{Ref} are the reduced volume and temperature V_{R} and T_{R} of the fluid or the mixture investigated.

2.3. The extended corresponding states principle (ECS)

In the ECS concept, the mapping between the investigated fluid or mixture T and V and the reference fluid V_{Ref} T_{Ref} is done via the shape factors φ, θ. These shape factors take into account how the fluids or the mixture in consideration differs from the reference fluid.

$$T_{\mathrm{Ref}} = \frac{T}{\theta} \qquad (3)$$

$$V_{\mathrm{Ref}} = \frac{V}{\varphi} \qquad (4)$$

The shape factors φ and θ can be computed analytically, using an accurate EoS, or using simpler forms of EoS.

2.4. The SPUNG EoS

SPUNG EoS is an ECS type of EoS that uses propane as a reference fluid, the modified Benedict-Webb-Rubin (MBWR) [10] as a reference EoS, and SRK EoS to evaluate the shape factors. The SPUNG EoS was developed by Jørstad in 1993[1] as part of his doctoral work. Propane was chosen as reference fluid to guarantee that the reduced triple point of the reference fluid is always below the reduced triple point temperature of any hydrocarbon mixture since propane has the lowest reduced triple point among all hydrocarbons.

3. Methodology

3.1. Numerical Tools

For the numerical prediction of the density and VLE properties, the NTNU-SINTEF in-house thermodynamic library TP_Lib was used for the study presented.

3.2. Setup

3.2.1. Single phase density

In addition to the standard SPUNG equation using C3 as the reference fluid, the four additions reference fluids N2, C1, C2 and NC4 were used for density prediction. For this preliminary study data at elevated pressures (from 10 up to 100 MPa) and at a temperature of 400 °C were used. Four concentrations of 20, 40, 60 and 80% of CO_2 were investigated. The pressures, temperature and mole fractions were chosen to allow a comparison with the set of experimental data of Seitz and Blencoe [11]. A more detailed study are on-going to cover a wider range of CCS applications.

3.2.2. Vapour Liquid Equilibrium

The ECS concept using N2, C1, C2, C3, and NC4 was used for the prediction of the mutual solubilities of CO_2 and H_2O. A set of experimental data by Bamberger et al. [12] was used in the comparison that provided data over moderate pressures that ranged between 4 and 14 MPa at a temperature of 50 °C.

3.3. Error definition

The prediction error compared with experimental data sets is described by the Relative Error (RE) and the Average of Absolute Deviation (AAD) defined for an arbitrary variable C as:

$$RE(C,r) = \frac{|C_{s,r} - C_{\mathrm{exp,r}}|}{C_{\mathrm{exp},r}} \qquad (5)$$

$$\boldsymbol{AAD(C)} = \sum_{\boldsymbol{r=1}}^{\boldsymbol{N}} \frac{|\boldsymbol{C_{s,r}} - \boldsymbol{C_{\mathrm{exp,r}}}|}{\boldsymbol{C_{\mathrm{exp},r}}} \qquad (\boldsymbol{6})$$

4. Results and discussion

4.1. Single phase density prediction

The single phase density predictions using SPUNG and the similar ECS-based EoS that only differ in using N_2, C1, C2 as a reference fluid are plotted in Fig. 1. The predications were compared with experimental data by Seitz and Blencoe [11] over moderate to elevated pressures that varied from approximately 10 to 100 MPa. The REs of the predictions compared with experimental data are plotted in Fig. 2. The comparison was done over a broad band of concentrations from 20 to 80% of CO_2. The results showed that the error of all the used reference fluids grew as the pressure and H_2O mole fraction increased. The error using propane, which is the reference fluid used by SPUNG EoS was the lowest out of all the tested reference fluids. Nevertheless, Figs. 1 and 2 show a clear trend that within the hydrocarbons, the heavier the reference fluid is the better it predicts the heavy phase density. The comparison with O_2 showed an overlap with C1 results, and was omitted for clarity of the figure. In order to confirm this observation, NC4 set of coefficients by Younglove et al. [10] was implemented. The new results

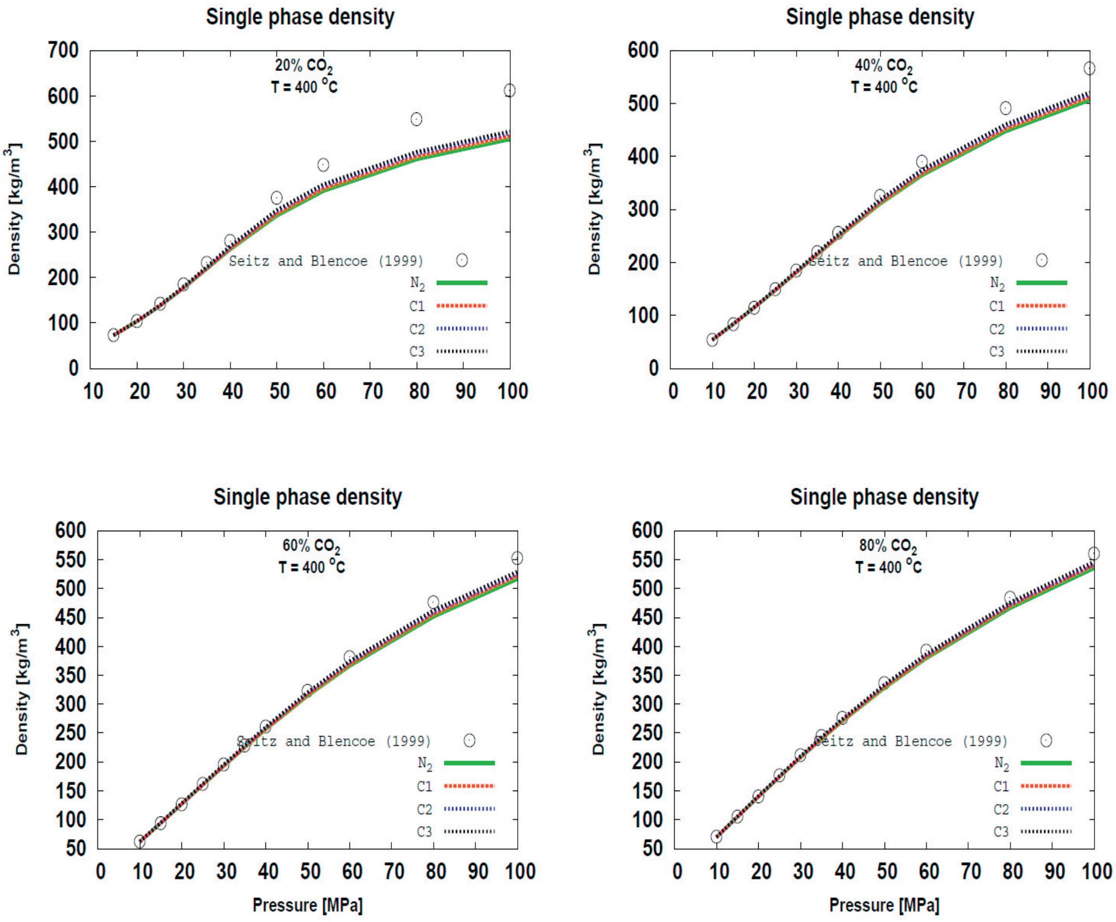

Figure 1: Density predictions using N_2, C1, C2, and C3 in comparison with experimental data set of Seitz and Blencoe (1999) [10] over pressure, at mole fractions of 20, 40, 60, and 80% of CO_2, and a temperature of 400 °C.

together with C3, the heaviest among the initially tested reference fluids, are shown in Fig. 3 in comparison with the experimental data. The REs of propane and normal butane are compared in Fig. 4. Except for the case of 80% CO_2, the results show the same behavior, where that normal butane as a heavier reference fluid predicted the density of the CO_2 mixture better than propane did. However, the improvement was very small, which did not suggest butane as an ultimate alternative to propane in solving the investigated problem. Therefore, a more comprehensive study in the guidance of the trend observed from the results need to be conducted to find the optimal reference fluid for modeling CO_2-water using ECS.

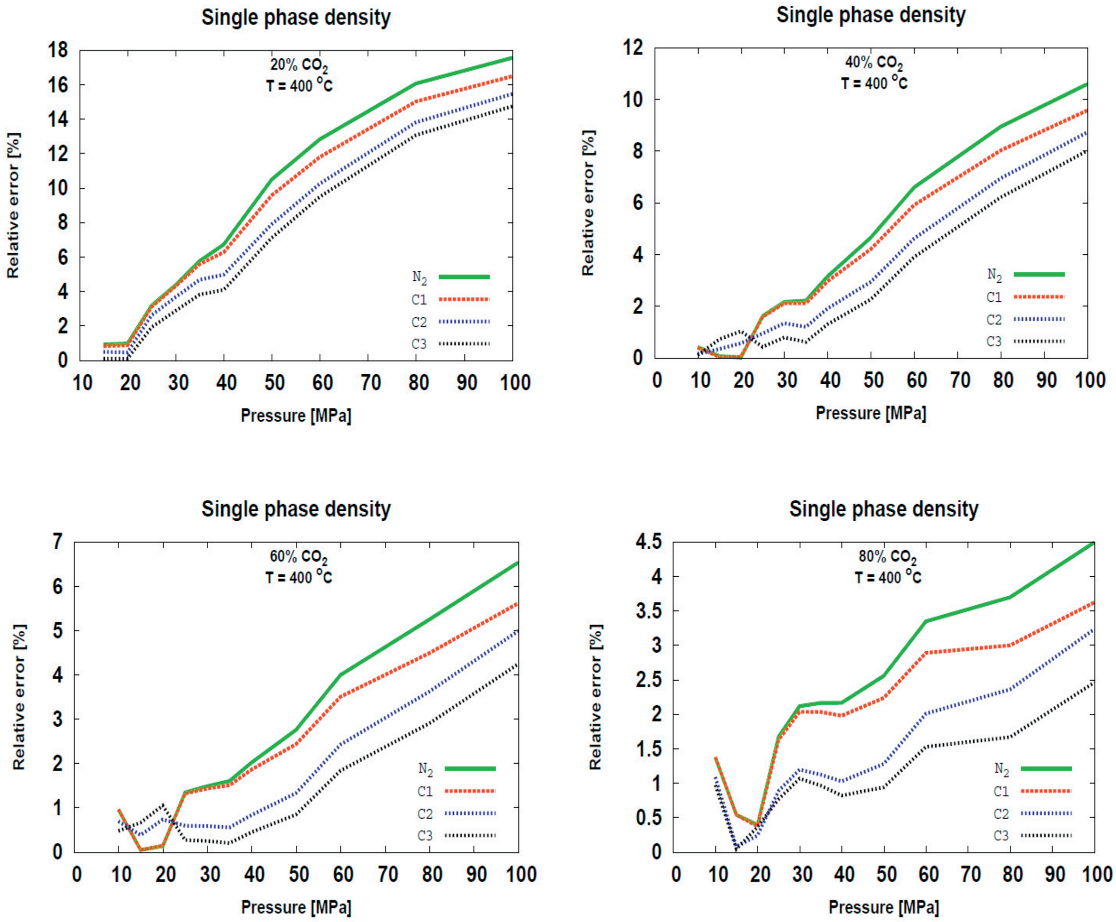

Figure 2: The relative error in density predictions using N_2, C1, C2, and C3 over pressure, at mole fractions of 20, 40, 60 and 80% of CO_2, and a temperature of 400 °C.

4.1.1. Vapour Liquid Equilibrium predictions

The predictions of the CO_2-water mutual solubility at moderate pressures were computed using N_2, C1, C2, C3 and NC4 as reference fluid. The solubility predictions compared with experimental data of Bamberger et al. [12] are plotted in Fig. 5. Top right and left are the H_2O and CO_2 solubilities, respectively. Below each solubility plot, the corresponding REs are plotted in the same Fig. 5.

From the results in Fig. 5 it was observed that there was no certain trend according to how heavy the reference fluids is in similarity to the density calculations. The improvement and deterioration between a reference fluid and the other might have come from the accuracy of the reference equation with respect to each of them. Besides the non-trendy behavior, the errors were extremely high which imply that the overcome of this VLE inaccuracy problem will require a different type of solution. Nevertheless, these results imply the need for parameter regression of binary interaction coefficients specifically for the choice of reference fluid. As the impact of the reference fluid is excluded, the VLE error is thought to be mainly due to the use of the SRK geometric averaging mixing rule for the shape

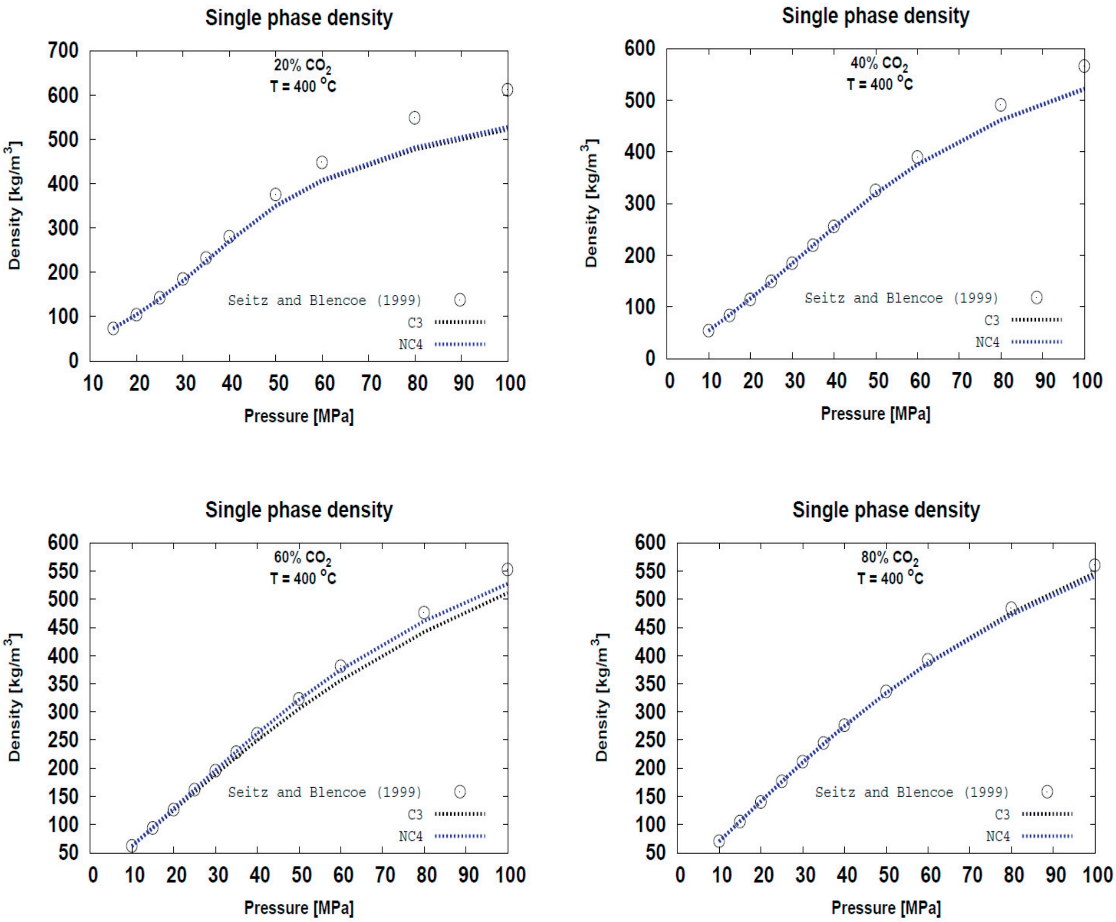

Figure 3: Density predictions using C3, and NC4 in comparison with experimental data set of Seitz and Blencoe (1999) [11] over pressure, at mole fractions of 20, 40, 60 and 80% of CO_2, and a temperature of 400 °C.

factors computations. Therefore doing the shape factor scaling with a mixing rule more adequate of dealing with polar mixtures could improve the VLE predictions.

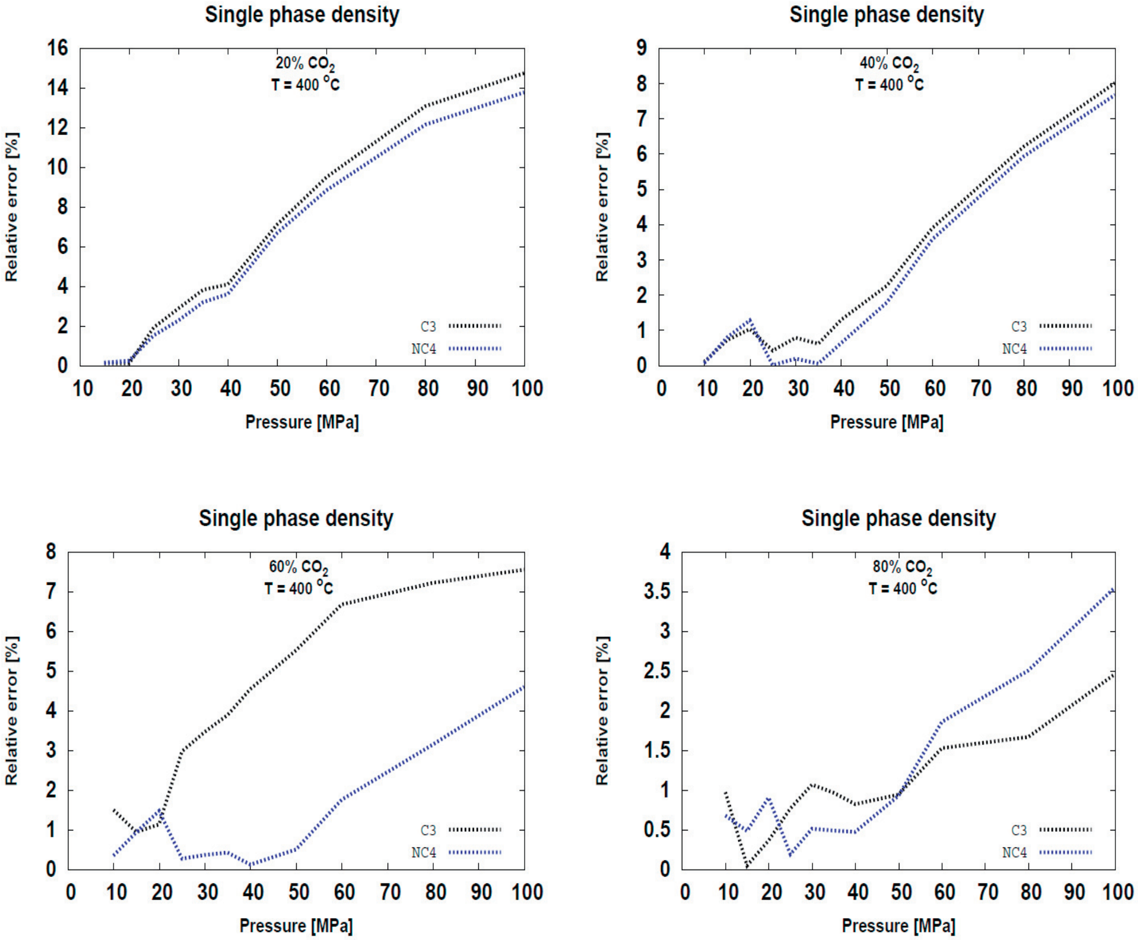

Figure 4: The relative error in density predictions using C3, and NC4 over pressure, at mole fractions of 20, 40, 60 and 80% of CO_2, and a temperature of 400 ºC

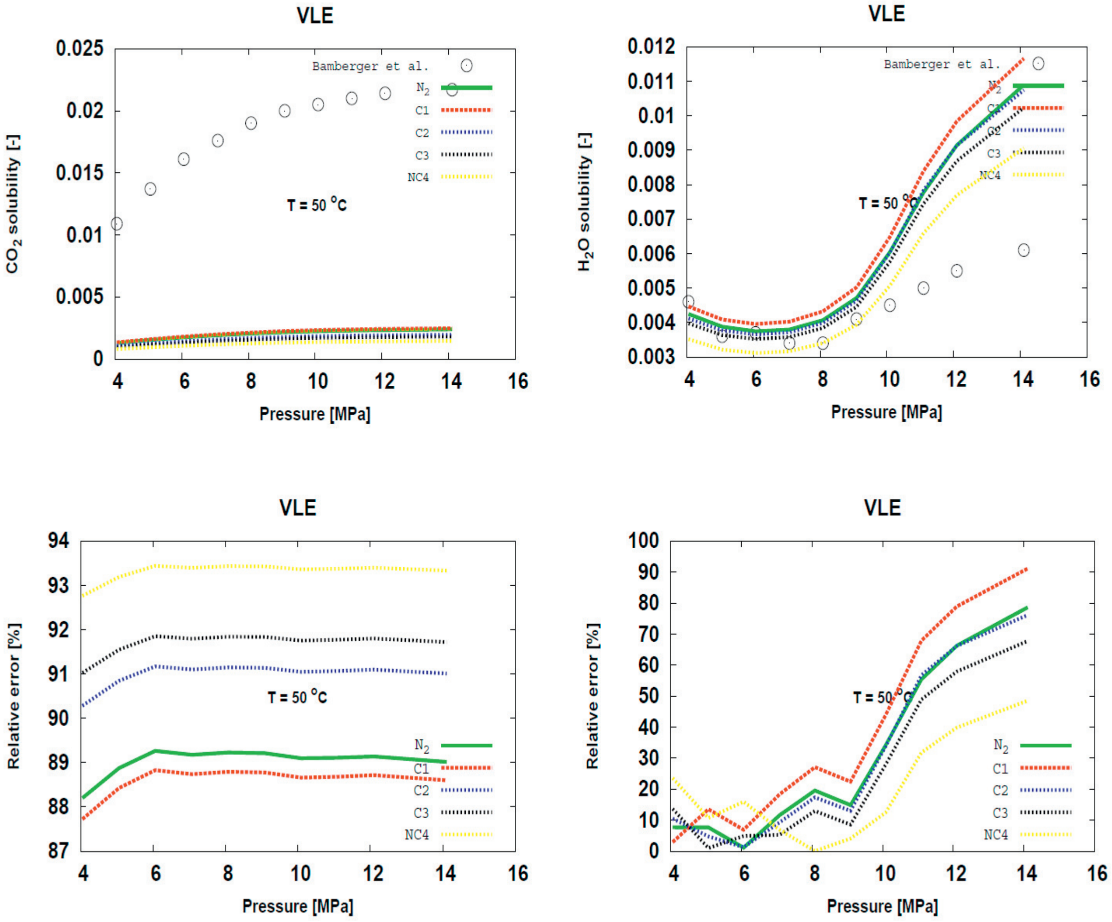

Figure 5: The solubility predictions and relative errors using N_2, C1, C2, C3 and NC4 over pressure, at a temperature of 50 ºC. Top left and right are the CO_2 and H_2O solubility respectively, in comparison with the experimental data of Bamberger et al. [12]. Bottom is the corresponding relative errors.

5. Conclusions

In this work the sensitivity of the density and VLE predictions to the choice of reference fluid used for modelling CO_2/H_2O systems using the SPUNG EoS was studied.

The results showed that the heavier the reference fluid was, the larger the range of densities the EoS can represent. In this case, within the set of hydrocarbons, the heavier the reference fluid was, the better the method predicted the densities. This implies that the SPUNG Eos has a potential for improving the density predictions by using other reference fluids than propane. Further work is undergoing investigating the best reference fluid and reference equation for this system.

The results also showed that the choice of reference fluid had small impact on the predictions of the VLE solubilities. For VLE, how the interaction between CO_2 and water is described (mixing rules) plays a more significant rule that the choice of reference fluid. Further development of SPUNG mixing rules for this system is required.

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