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Introducing Thermodynamics-informed Neural Network: A Smart Equation of State for CCUS Application

E. Rostaminikoo[1], E. Joonaki[2], H.R. Nasriani[1], L. Khajenoori[1], E. Asimakopoulou[1]

[1] University Of Central Lancashire; [2] TÜV SÜD NEL

Summary

Accurate prediction of thermophysical properties of fluids is crucial for optimising processes involving CO_2-rich mixtures, particularly in CCUS. The Soave-Redlich-Kwong equation of state exhibits deviations when modeling non-ideal CO2-rich mixtures in the supercritical phase, necessitating advanced optimisation techniques. In this study, a novel hybrid SRK-neural network model was developed through integrating a vectorised SRK model with deep learning to enhance the accuracy of physical properties predictions, consists of a preprocessing scaling layer, a vectorised SRK EoS layer, and one or four hidden layers, trained using the MAPE loss function.The SRK-NN model was validated against some experimental datasets for CO_2-N_2 mixtures with CO2 mole fraction ranging from 0.50365 to 0.9585, and pressure and temperature ranges of 8 – 99.93 MPa and 245 – 673.15 K, respectively. The results show reduction in the average absolute relative deviation (AARD%), from 1.25 to 0.49% at high CO2 concentrations. The one-hidden-layer SRK-NN variant provides more accurate predictions at various pressures compared to deeper architect.These new findings highlight the innovative application of integrating data-driven optimisation with classical EoS for accurate estimation of CO2-rich streams physical properties. This work offers a promising direction for future thermodynamic modelling of CCUS fluids with introducing a new and reliable technique.

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Introduction

A recommended methodology for reducing the continued risen of atmospheric carbon dioxide (CO_2) level is to capture and transport it to a geological storage site, resulted in isolating a huge amount of CO_2 for an extended period of time. The CO_2-rich stream may contain a wide range of components known as impurities such as non-condensable gases (e.g., N_2, O_2, Ar, and H_2), solvents (e.g., amines), light hydrocarbons (e.g., methane and ethane) [Chinello et al., 2024]. Non-condensable components or light hydrocarbons may significantly impact the density of CO_2-rich mixtures compared to pure CO_2. Therefore, Understanding the thermophysical properties of CCUS mixtures is critical, especially for designers and operators of pipeline transportation networks [Hoopanah et al., 2024]. Soave Redlich Kwong (SRK) EoSs as a cubic equation of state is widely used to calculate density due to its simplicity and availability in commercial software packages within the oil & gas industry [Péneloux et al., 1982; Soave, 1972].

In recent decades some researchers attempted to investigate the accuracy and applicability of various types of equations of state (EoSs) for modelling of thermophysical properties of binary CO_2-mixtures. As an example, Nazeri et al. employed two cubic EoSs of SRK and PR with modified binary interaction parameters as well as the GERG-2008 EoS for modelling of density and phase equilibria of various CO_2-rich binary mixtures. They found that the predictions by SRK in the gas phase were slightly more accurate than PR, while in the dense liquid/supercritical phase, predictions by PR were better than SRK.

There are ongoing research studies on assessment of different EoSs in terms of applicability and optimisation of binary interaction parameters (BIPs) for cubic EoSs. Mantovani et al. measured experimental data for supercritical CO_2 binary systems of nitrogen, oxygen and argon. Subsequently, the data were utilised for the calibration of the BIPs using PR, SRK-Peneloux and Benedict-Webb-Rubin-Starling (BWRS) EoSs. The maximum likelihood algorithm was used to calculate the optimal value of BIP for each mixture.

In this work, for the first time we are proposing the integration of artificial neural networks into a classical cubic EoS in order to improve the reliability and accuracy of the thermodynamic modelling. Firstly, a detailed review was carried out on the available experimental data of the density of CO_2 binary mixtures in presence of nitrogen as impurity under variety of pressures and temperatures. Then, a new framework has been developed for calculation of density in the supercritical phase based on the SRK EoS. This novel framework was built based on the deep learning framework PyTorch [Paszke et al., 2019] and consists in the vectorised SRK equation of state, one or four fully connected hidden layer(s). The neural networks (NNs) within the newly developed model are to fine-tune the SRK predictions by adjusting the parameters in the equation of state. This paper demonstrates how effective modifications of the attractive/repulsive forces between molecules using neural networks will improve the accuracy of the modelling outputs on thermophysical properties of complex fluids.

Method and/or Theory

The newly proposed SRK-NN model integrates the SRK EoS with a NN architecture to improve density predictions for CO_2-N_2 mixtures. The model pipeline begins with pre-processing of the experimental data. The specifications of the density experimental datasets for the binary mixtures of CO_2 with N_2 at supercritical phase have been shown in Table 1.

We considered three categories involving a specific range of CO_2 concentration. The first category of study focuses on a 96 datapoints system with a range of concentration below 0.6 mole fraction, the second one involves concentrations in the range of $0.6 < xCO_2 < 0.8$ with 84 datapoints, and the third one as more representative of CO_2-rich mixtures, which covers compositional space of $xCO_2 \geq 0.8$,

consisted 190 datapoints. In total, there are 369 datapoints under the pressure and temperature ranges of 8 – 99.93 MPa and 245 – 673.15 K, respectively.

Table 1. *Density experimental data for the binary mixtures of CO_2 -N_2 at different compositional mole fraction and operating conditions within the supercritical phase*

Reference	CO_2 Concentration	Operating condition
[Mantovani et al., 2012]	0.9021, 0.9585	8 MPa - 20 MPa 303.22 K - 383.14 K
[Jeffery C. Seitz and James G. Blencoe, 1996]	0.6 – 0.9	19.94 MPa - 99.93 MPa 673.15 K
[Seitz et al., 1996]	0.6 – 0.9	9.94 MPa – 99.93 MPa 323.15 K – 573.15 K
[Brugge et al., 1997]	0.50365 – 0.90921	8 MPa – 70 MPa 245 K – 450 K

To continue the model pipeline, we manually vectorised the solution of the SRK EoS, thus, it took as inputs $\boldsymbol{P} = (P_1, \ldots, P_n)$, $\boldsymbol{T} = (T_1, \ldots, T_n)$, $\mathbf{z} = (\boldsymbol{z}_1, \ldots, \boldsymbol{z}_n)$, T_c, P_c, and Ω where pressure and temperature are vectors, mole fraction is a matrix, n denotes the number of samples processed concurrently and is often referred to the batch dimension, critical temperature, critical pressure, and acentric factor are scalars. In this way, the vectorised function can process a batch of inputs simultaneously rather than processing them one by one in a loop which result in accelerating modelling computation. Therefore, the input of the model includes P, T, z, T_c, P_c, and Ω, undergo pre-processing via a scaling layer and post-processing transforming inverse scaling layer, and its output is modelled density (Figure 1).

To train and test the model, the gathered data points were divided into the training 70%, validation 15% and test 15% sets. The SRK-NN model has one or four fully connected hidden layer with different neurons. All hidden layers use the LeakyRelu activation function to consider nonlinearity with negative slope 0.01. Output layer has 8 neurones without activation function. The connection from the SRK layer to the output layer through NN layers enables direct learning of fundamental physical trends while refining predictions through deep network layers and optimising BIPs. The training process minimises the mean absolute percentage error (MAPE) loss to optimise model weights and biases.

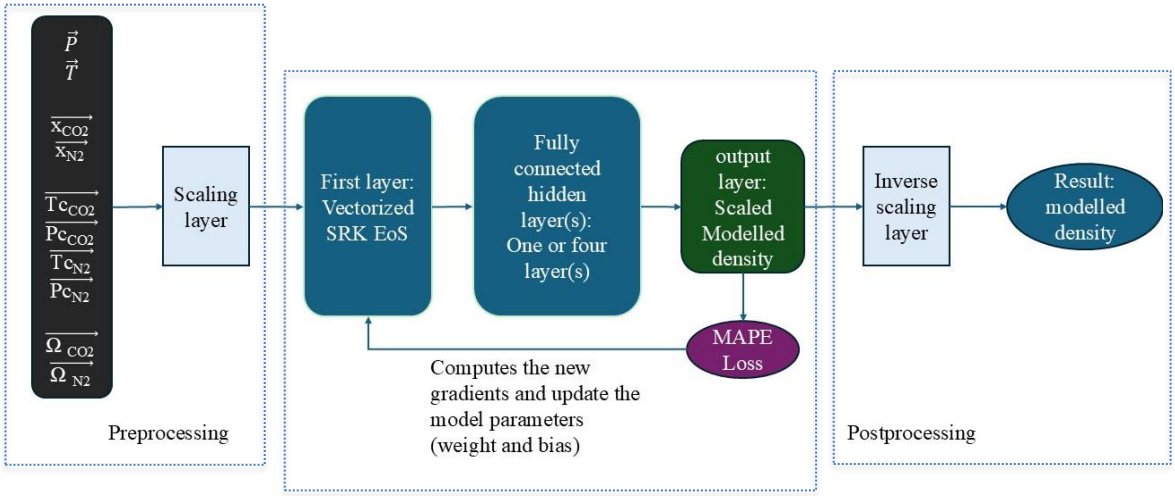

Figure 1. *The first layer of the network is a vectorised SRK EoS, ensuring a physics-informed foundation before deep learning-based corrections. The model architecture consists of one or four fully connected hidden layers with Leaky ReLU activation, capturing complex thermodynamic interactions. The output layer provides a scaled density prediction, which is then adjusted by an inverse scaling layer to recover the physical density value. The model is trained using the Mean Absolute Percentage Error (MAPE) loss, and backpropagation updates the weights and biases accordingly.*

Results and Discussion

The comparative analysis of the SRK-NN model against the standalone SRK EoS reveals a substantial reduction in absolute relative deviation (ARD%) across varying pressures and compositions. In both cases, the SRK-NN model with one or four hidden layers consistently outperforms the SRK EoS, particularly in regions of high non-ideality (near critical point e.g., low pressures). Notably, the SRK EoS demonstrates large deviations at specific pressure ranges (e.g., ≤ 10 MPa), whereas the SRK-NN models effectively smooth these discrepancies (Figure 2).

The model with four hidden layers exhibits slightly higher deviations at select points compared to the one-hidden-layer model, indicating a possible trade-off between network depth and overfitting. Nevertheless, both SRK-NN models achieve better agreement with expected trends, confirming their ability to refine the density predictions (Figure 3).

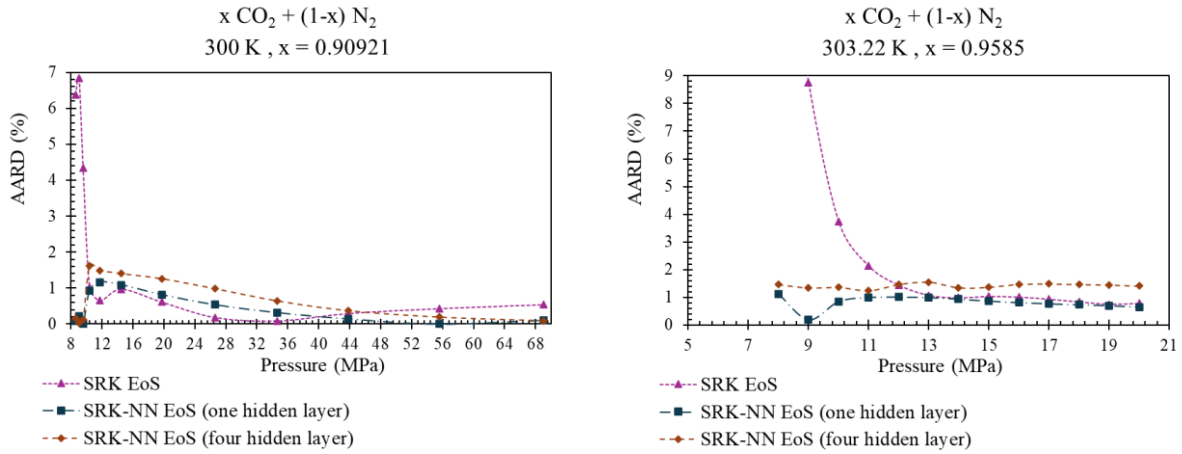

***Figure 2**. Comparison of the absolute relative deviation (ARD%) of density predictions using the SRK EoS and SRK-NN EoS models for a CO_2-N_2 mixture at (I) 300 K with xCO_2 = 0.90921, where the SRK-NN models (both one-hidden-layer and four-hidden-layer variants) exhibit lower deviations across the pressure range, demonstrating improved accuracy over the conventional SRK EoS. (II) 303.22 K with xCO_2 = 0.9585. where the SRK EoS shows significant deviations at lower pressures (up to 10 MPa), while the SRK-NN models substantially reduce errors. The one-hidden-layer SRK-NN model provides a more accurate prediction compared to more complex NN structure(e.g., four hidden layer).*

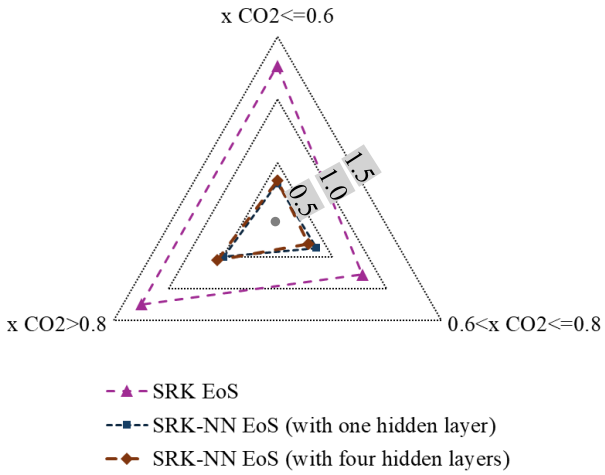

***Figure 3.** Comparison of the absolute relative deviation (ARD%) of density predictions using the SRK EoS and SRK-NN EoS models for a CO_2-N_2 mixture at three categories where (I) xCO_2 ≤0.6, (II) 0.6*

< xCO_2 < 0.8, and (III) $xCO_2 \geq 0.8$. The SRK-NN model with one and four hidden layers both consistently outperforms the SRK EoS.

Conclusions

This work, for the first time, presented a novel fast and reliable methodology through efficient vectorisation of SRK EoS using PyTorch for modelling of the density of two binary CO_2-rich mixtures at supercritical phase. This integration successfully improves the accuracy of density predictions for CO_2-N_2 mixtures, particularly in complex pressure-dependent regimes (near to the critical point). The results demonstrate the importance of network architecture selection, with a balance required between model depth and generalisation. As the continuation of this research work, we will extend our work to vectorise more advanced equation of the state with a focus on optimising the network structure and extending this methodology to other gas mixtures relevant for both CCUS and hydrogen applications.

Acknowledgements

Special thanks to the TÜV SÜD National Engineering Laboratory (NEL) at Scotland for their sponsorship and technical support as part of the PhD research project.

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