Equations of State (EoS) Modelling Framework for Full-Chain Carbon Capture & Storage (CCS) Systems

Dhanaraj TURUNAWARASU[a,b], Bing Shen HOW[b], Viknesh ANDIAPPAN[b,]*

a Pace CCS Ltd, 10 Lower Thames Street, London EC3R 6AF, United Kingdom
b Research Center for Sustainable Technologies, Faculty of Engineering, Computing and Science, Swinburne University of Technology, Jalan Simpang Tiga, 93350, Kuching, Sarawak, Malaysia
* Corresponding Author Email: vmurugappan@swinburne.edu.my

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Extended Abstract

Accurately predicting the thermo-physical properties of CO_2-rich mixtures is essential for the safe, efficient and cost-effective design of full-chain Carbon Capture and Storage (CCS) systems. A full-chain CCS systems encompasses the end-to-end process of capturing carbon dioxide from industrial or energy-related sources, transporting it, often over long distances and injecting it into deep geological formations for permanent storage. Each segment of the CCS value chain imposes unique thermodynamic requirements, necessitating models that can handle wide variations in temperature, pressure and composition. The properties of interest such as density, viscosity, water solubility, phase equilibria and heat capacity directly affect material compatibility, flow assurance, safety margins and equipment sizing.

From the initial capture phase, where CO_2 is separated using techniques such as post-combustion, pre-combustion or oxy-fuel combustion, to the intermediate transport phase via pipelines or shipping and finally to underground storage, each step demands specific and accurate thermodynamic predictions. For example, oxy-fuel combustion produces high-temperature, high-pressure flue gas streams containing complex impurities, posing challenges in modelling phase behaviour and fluid properties. Similarly, cryogenic shipping introduces low-temperature operating conditions that are highly sensitive to phase transitions, which are influenced by minor and trace impurities.

In response to the growing need for accurate EoS models, the Energy Institute (EI) conducted a comprehensive technical review evaluating existing EoS approaches for CO_2-rich mixtures, particularly those exceeding 95 mol% CO_2 (EI, 2022). This evaluation compared the performance of widely-used cubic models (e.g., Peng-Robinson (PR), Redlich-Kwong-Soave (RKS)), Helmholtz energy-based models (e.g., GERG-2008, EoS-CG) and Statistical Associating Fluid Theory (SAFT)-based models such as PC-SAFT. The report assessed each model's accuracy, software compatibility, computational cost and impurity-handling capabilities including common and trace impurities like hydrogen, nitrogen, water, mercury and amines.

Key findings revealed that while cubic EoS models are versatile and supported by most commercial simulation platforms, they require tuning using binary interaction parameters (BIPs) and volume shift corrections. In contrast, EoS-CG provide improved accuracy for polar components and water-containing mixtures compared to GERG-2008 but are computationally demanding. SAFT-based models like PC-SAFT offer improved handling of associating compounds but suffer from limited availability of parameters for less common impurities. A critical barrier remains: the lack of reliable experimental data for minor and trace impurities reduces model reliability in multi-component systems.

Importantly, the EI report focuses primarily on gas and dense-phase CO_2 applications and does not address thermodynamic modelling challenges specific to cryogenic CO_2 separation or shipping. This represents a critical research gap, particularly as CO_2 shipping is becoming a viable transport mode for CCS deployment in regions without pipeline infrastructure.

In parallel, the development of supercritical CO_2 power cycles especially in oxy-fuel combustion systems has garnered attention for its potential to improve energy efficiency and reduce emissions. While most studies have concentrated on process optimisation and economic assessments, the role of accurate thermodynamic models in sizing equipment and simulating process dynamics remains underexplored. Although the Span-Wagner EoS is well-validated for pure CO_2 up to 826 °C (Span & Wagner, 1996), modelling of impure CO_2 mixtures in the supercritical region remains uncertain and is an area ripe for further research (Zhao et al., 2017).

Given these limitations, there is growing interest in developing a unified EoS selection framework that spans the entire CCS value chain. This paper proposes a structured thermodynamic modelling framework for EoS selection, aimed at supporting end-to-end CCS applications including capture, transport (pipeline and shipping), cryogenic handling and oxy-combustion systems. Figure 1 illustrates this framework currently still under development, which evaluates models across three main domains: (i) CO_2 capture and pipeline transport, (ii) cryogenic shipping and (iii) oxy-fuel combustion and power cycles.

Each domain is characterised by distinct operating conditions from ambient pressures during capture to sub-zero conditions in shipping and supercritical states in oxy-fuel systems necessitating tailored EoS capabilities. The evaluated models include

PR, RKS, CPA, GERG-2008, EoS-CG and PC-SAFT. These are benchmarked against key thermodynamic properties such as phase behaviour, density, water solubility, viscosity and surface tension. Additional properties such as heat capacity, enthalpy and speed of sound are identified as areas requiring further model development.

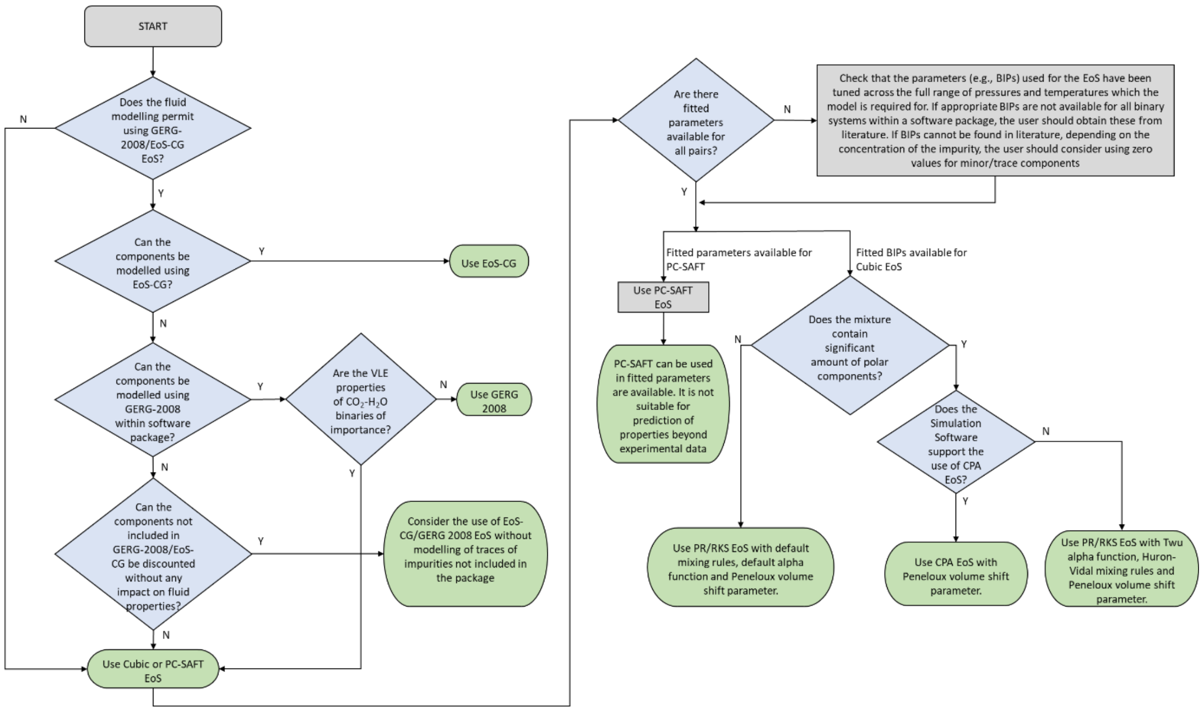

Figure 1: EoS Model Selection Framework

Moreover, the framework addresses the challenge of consistency across simulation platforms. Variability in EoS implementation can lead to discrepancies in thermodynamic predictions across different stages of CCS projects. This is particularly problematic during phase transitions in cryogenic shipping or when integrating design and flow assurance tools.

A major contribution of this work is the introduction of a scenario-based EoS guidance for the full-chain systems with CO_2 shipping as the mode of transportation. Table 1 presents recommendations for EoS model selection under low, medium and high-pressure shipping conditions, considering impurity levels, model availability, computational constraints and software compatibility. Findings show no single EoS is universally applicable; model selection must be context-specific, factoring in impurity composition, operational pressure-temperature envelopes and data availability (Turunawarasu et al., 2024).

In summary, this paper presents a comprehensive, unified approach to EoS model selection for full-chain CCS applications, addressing existing gaps in modelling impure CO_2 mixtures, particularly in cryogenic and oxy-fuel combustion regimes. The proposed framework offers practical guidance for engineers and researchers developing CCS systems that demand high-fidelity thermodynamic predictions.

Table 1: Recommended EoS Models for Full-Chain Systems with CO_2 Shipping (Turunawarasu et al., 2024)

Shipping System Condition	**Disposal[b]**	**CO_2 Content (mol %)**	**Recommended EoS Model (Full Chain)**	**Remarks**
LP (7 bar, -49°C) & MP (15 bar, -30°C)	Wellhead conditions: >75 bar & >0°C	≥ 99.97 (≤ 0.03 mol. % H_2 + CO + N_2 + O_2 + Ar+others)[a]	EoS-CG or Span and Wagner	• If there are impurities present which cannot be modelled using EoS-CG, the user should consider removing these in the list of components if there is no significant effect on the overall fluid properties. Alternatively, pure CO_2 can be considered using Span and Wagner.

Shipping System Condition	Disposal[b]	CO_2 Content (mol %)	Recommended EoS Model (Full Chain)	Remarks
	Bottomhole Conditions: >10 bar & >0°C	< 99 .97 (> 0.03 mol. % H_2 + CO + N_2 + O_2 + Ar + others)[a]	CPA with Peneloux Volume Shift Parameter	• If simulation software does not support CPA EoS, use PR/RKS EoS with Twu alpha function, Huron-Vidal mixing rules and Peneloux volume shift parameter. • Check that the parameters (e.g., BIPs) used for the PR/RKS have been tuned across the full range of pressures and temperatures which the model is required for. If appropriate BIPs are not available for all binary systems within a software package, the user should obtain these from literature e.g., from (Fandino et al., 2015). If BIPs cannot be found in literature, depending on the concentration of the impurity, the user should consider using zero values for minor/trace components.
HP (75 bar, 10°C)		≥ 96	CPA with Peneloux Volume Shift Parameter	

[a]Any light impurities that can substantially increase the saturation pressure of the CO_2 liquid making carrier transport infeasible due to the elevated bubble-point pressures at refrigerated temperatures. These impurities widen the two-phase envelope in the stream, thus increasing the risk of operational issues throughout the CO_2 shipping system.
[b]Assumed conditions.

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